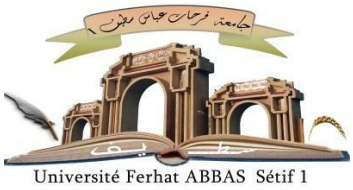
الجمهورية الجزائرية الديمقراطية الشعبية

République Algérienne Démocratique et Populaire

Ministère de L'Enseignement Supérieur et de la Recherche Scientifique



UNIVERSITÉ FERHAT ABBAS - SETIF1

FACULTÉ DE TECHNOLOGIE

THÈSE

Présentée au Département de Génie des Procèdes

Pour l'obtention du diplôme de

DOCTORAT

Domaine: Sciences et Technologie

Filière: Génie des Procédés **Option: Matériaux Polymères**

Par

TABLIT Sarra

THÈME

Recherche d'un nouveau produit à partir de la valorisation des déchets polymériques « Effet de charge végétale sur les propriétés finales »

Soutenue le 04/ 07/2024 devant le Jury :

BENACHOUR Djaafer	**Professeur**	**Univ. Ferhat Abbas Sétif 1**	**Président**
KRACHE Rachida	**Professeur**	**Univ. Ferhat Abbas Sétif 1**	**Directrice de thèse**
BENANIBA Mohamed Tahar	**Professeur**	**Univ. Ferhat Abbas Sétif 1**	**Examinateur**
HELLATI Abdelhak	**Professeur**	**Univ. Bordj Bou Arreridj**	**Examinateur**

الجمهورية الجزائرية الديمقراطية الشعبية

Democratic and Popular Republic of Algeria

Ministry of Higher Education and Scientific Research

University of Ferhat ABBAS- Setif-1

FACULTY OF TECHNOLOGY

THESE

Presented to the Process Engineering Department

For obtaining of the diploma of

DOCTORAT

Domain: Science and technology

Sector: Process Engineering **Option: Polymer Materials**

By

TABLIT Sarra

THEME

Search for a new product from the recycling of polymeric waste

"effect of natural fibres on the final properties"

Defended on 04/07/2024 Front of the Jury:

BENACHOUR Djaafer	**Professor**	**Univ. Ferhat Abbas Sétif 1**	**President**
KRACHE Rachida	**Professor**	**Univ. Ferhat Abbas Sétif 1**	**Supervisor**
BENANIBA Mohamed Tahar	**Professor**	**Univ. Ferhat Abbas Sétif 1**	**Examiner**
HELLATI Abdelhak	**Professor**	**Univ. Bordj Bou Arreridj**	**Examiner**

DEDICATION

To my dearest parents, whose unwavering support, love, and encouragement have been the foundation of my journey. Your sacrifices and guidance have shaped me into the person I am today. This thesis is a testament to the values and strength you instilled in me.

To my beloved sisters and brother, your constant belief in my abilities and the countless moments of shared joy and challenges have been a source of inspiration. Your presence has been my greatest motivation, and this achievement is as much yours as it is mine.

This work is dedicated to my dearest friends' pillars of my life and my family, whose presence has illuminated every step of this academic endeavor. Thank you for being my source of strength, my sounding board, and my greatest cheerleader. This achievement is a reflection of the collective love, support, and unity that define our family bonds.

TABLIT SARRA

AACKNOWLEDGMENTS

First, I would like to express my praises to **GOD**, the most generous and compassionate, for his guidance and blessing in allowing me to discover and ingest novel knowledge. Without his **ALMIGHTY**, I would not be able to obtain the strength and patience needed to accomplish my investigation.

I would like to thank my supervisor, Prof. **KRACHE RACHIDA**, for her insightful and helpful ideas and advice during the conception and implementation of this research project.

I would also like to express my gratitude to **Prof. MOHAMMAD JAWAID** for providing the necessary advice and support for me to complete my thesis. His generosity in volunteering his time and experience has been much appreciated. I would also like to thank everyone at the Biocomposite Technology Laboratory, Institute of Tropical Forestry and Forest Products (INTROP), University Putra Malaysia for their assistance throughout the Mobility exchange program.

I would like to express my gratitude to my committee members, Prof. Benachour Djaafer, Prof. Hellati Abdelhak, and Prof. Benaniba Mohamed Tahar, for their valuable time, constructive criticisms, and suggestions. Thank you for the opportunity to revise my thesis, I really appreciate your careful review.

I also wish to express my appreciation to the technical members of our department and the laboratory of LMPMP.

All the gratitude and best wishes to my Ph.D. colleagues and friends. Throughout the research's advancement, they provided several ideas and guidance that were required to ensure the research's success and completion.

Finally, yet importantly I want to express my heartfelt thanks to my father, my mother, and my family for their encouragement and support, which has given me the strength to persevere till the finish of this research project.

Tablit Sarra

Table of Contents

List of Figures

List of Tables

GENERAL INTRODUCTION

1. Background

Recycling plastic is essential to tackling the growing environmental issues that plastic waste is causing. Plastics are widely used in modern culture due to their durability and diverse properties, yet their continued presence in the environment has negative effects. Single-use plastics in particular may build up in rivers, seas, and terrestrial settings, endangering ecosystems, animals, and marine life[1], [2]. Over time, plastics degrade slowly, releasing dangerous chemicals and contaminating land and water habitats. By keeping plastic waste out of landfills and incinerators, mechanical recycling reduces the need to produce virgin plastic, conserves resources, and offers a sustainable alternative[3].

Polypropylene PP is known for its high tensile strength, chemical resistance, and lightweight nature, making it an ideal material for packaging, textiles, automotive components, and various consumer goods[4].Over time, there has been a significant increase in the use of plastics worldwide, particularly polypropylene, demonstrating its indispensable existence across several sectors[5].However, the accumulation of plastic waste is a serious environmental problem imposed by the increasing demand. To deal with this problem and promote sustainability, it is essential to create effective methods for reusing or recycling polypropylene waste[6].To reduce environmental effects and transition to a circular economy, it is imperative to investigate novel and environmentally friendly recycling solutions[7] and ensure that the valuable properties of polypropylene are reused without causing long-term damage to the planet.

One effective method of recycling polypropylene is to combine it with other polymers. This process, known as polymer blending, aims to minimize the environmental impact of polypropylene waste while simultaneously utilizing its unique properties or hopefully, obtaining novel material [8]. When polypropylene is combined with other suitable polymers, the resulting mixture may exhibit enhanced mechanical, thermal, or chemical characteristics, depending on the particular requirements of the intended use[9].

Polylactic acid (PLA) is a biodegradable and bio-thermoplastic derived from renewable resources such as corn starch or sugarcane. Given its excellent stiffness, transparency and biocompatibility, PLA is becoming increasingly popular for use in various sectors, including 3D

printing, packaging, and biomedical applications[10]. However, the brittleness limitations of PLA restrict its usage to high-impact resistance applications. PLA presents difficulties in high temperatures as it tends to distort, indicating limited heat resistance[10], [11]. Combining PLA with polypropylene (PP) is an effective way to improve PLA's overall properties[12], [13], [14].Polypropylene, known for its toughness, impact resistance, and versatility, acts as a reinforcing agent in the PLA/PP blend. The incorporation of PP helps address the brittleness of PLA, resulting in a composite material that combines the eco-friendly attributes of PLA with the enhanced mechanical performance of PP[15].

Arundo donax L., commonly known as giant reed, stands as a prominent natural source of fibers, in the Mediterranean region[16]. Arundo donax L., a giant reed species of the Poaceae family, is a perennial grass that grows naturally and prolifically across Algeria, exhibiting rapid growth and a notable capacity for high yield. Previous studies on gigantic reeds have highlighted their significant productive potential in a variety of Mediterranean areas[17]. These agricultural leftovers offer an important resource that may be used to create ecologically friendly goods at a reasonable cost[18].

3D printing, particularly Fused deposition modeling (FDM), provides a new approach to expanding and promoting composite materials based on natural fibers[19]. The incorporation of natural fiber reinforcement in PLA polymer filaments for additive manufacturing presents environmental and sustainability advantages. These include the renewability of natural fibers, helping sustainable sourcing, and minimizing the lack of non-renewable resources[20]. In addition, compared to synthetic fibers made from petrochemicals, natural fibers have a less carbon footprint[21]. Furthermore, because natural fibers are compostable and biodegradable, utilizing them in PLA filaments may help minimize the amount of plastic waste generated by 3D printing[22]. In the end, this strategy may encourage the creation of more environmentally friendly and sustainable goods and procedures, which would support the additive manufacturing sector's long-term viability.

A lack of research exists, with minimal prior investigations reported on PLA/PP waste-reinforced Arundo fiber composites. This study addresses this gap by focusing on the treatment of fibers extracted from Arundo donax L. stems through chemical modification. The treated fibers undergo alkali and silane treatment, serving as a reinforcing material for a PLA/PP waste blend intended for 3D printing applications.

2. Problem statement

Polypropylene (PP) is widely used due to its various desirable properties. Its cheap cost, resilience to chemicals, fatigue, and moisture combined with its lightweight make it the perfect material for a wide range of applications, from packaging and textiles to automotive components[23]. However, the widespread use of polypropylene has resulted in a serious environmental problem as a large amount of it ends up in landfills, contributing to pollution and long-lasting ecological impacts. Unfortunately, there have been significant environmental concerns raised by the widespread utilization of polypropylene since a significant portion of it ends up in landfills, where it causes contamination and long-term ecological effects. Global polypropylene post-consumer recycling rates are estimated by the Gulf Petrochemicals and Chemicals Association (GPCA) to be about 1%[4]. The positive characteristic of polypropylene is that it can be recycled quite well. The polymer is easily recovered and processed, and even after several recycling cycles, it retains its valuable properties and performance[24]. This exceptional recycled quality not only reduces the environmental impact of disposal but also encourages the use of materials in a more sustainable and circular manner [25].

The challenge is to develop a new sustainable material using waste polypropylene (PP) and local natural fiber, called Arundo Donax L. The selected waste polypropylene (PP) and Arundo fibers are meant to function as reinforcing agents in polylactic acid (PLA), most especially in Fused Deposition Modeling (FDM). Additionally, a study will be conducted to investigate the effects of various chemical treatments applied to Arundo fibers.

3. Research objectives

This research encompasses two primary aims:

i)The integration of PP waste into PLA biocomposites, enabling the production of sustainable and cost-effective feedstock for Fused Deposition Modeling (FDM).

ii) Unraveling the underlying mechanisms of Chemical modification of the filler (specifically Arundo donax L. fibers) impact on the properties of PLA/PP waste biocomposite feedstock.

4. Thesis Layout:

This thesis comprises general introduction, five chapters and a conclusion. The introduction provides a brief overview of the research background, emphasizing concerns related to plastic waste (PP waste), and discussing the advantages of incorporating it into PLA/biomass biocomposites for Fused Deposition Modeling (FDM) applications. The introduction also outlines the research objectives and the structure of the thesis.

chapter 1 focuses on an assessment of the current literature on the natural fiber Arundo donax L. and the influence of chemical alteration on it, while chapter 2 delves into 3D printing methods, notably FDM and feedstock. It investigates the effect of chemical modification of biomass on the characteristics of PLA biocomposites and the use of PP biocomposites in FDM. Chapter 3 delineates the research workflow and identifies methodology.

Chapters 4 through 5 delve into the results, providing discussions and presenting key research findings. The conclusion is presented, summarizing the significant findings of this research and proposing recommendations for the future development of PLA/biomass feedstock.

References:

[1] D. Jubinville, E. Esmizadeh, S. Saikrishnan, C. Tzoganakis, and T. Mekonnen, “A comprehensive review of global production and recycling methods of polyolefin (PO) based products and their post-recycling applications,” *Sustain. Mater. Technol.*, vol. 25, p. e00188, Sep. 2020, doi: 10.1016/j.susmat.2020.e00188.

[2] F. Burgada , “Upgrading Recycled Polypropylene from Textile Wastes in Wood Plastic Composites with Short Hemp Fiber,” *Polymers*, vol. 13, no. 8, Art. no. 8, Jan. 2021, doi: 10.3390/polym13081248.

[3] J. D. Badia and A. Ribes-Greus, “Mechanical recycling of polylactide, upgrading trends and combination of valorization techniques,” *Eur. Polym. J.*, vol. 84, pp. 22–39, Nov. 2016, doi: 10.1016/j.eurpolymj.2016.09.005.

[4] A. Alsabri, F. Tahir, and S. G. Al-Ghamdi, “Environmental impacts of polypropylene (PP) production and prospects of its recycling in the GCC region,” *Mater. Today Proc.*, vol. 56, pp. 2245–2251, Jan. 2022, doi: 10.1016/j.matpr.2021.11.574.

[5] RANJAN, Ved Prakash , GOEL, Sudha," Recyclability of polypropylene after exposure to four different environmental conditions," *Resources, Conservation and Recycling*, 2021, vol. 169, p. 105494. doi: 10.1016/j.resconrec.2021.105494.

[6] A. L. Andrady, *Plastics and the Environment*. John Wiley & Sons, 2003.

[7] A. R. Shafqat, M. Hussain, Y. Nawab, M. Ashraf, S. Ahmad, and G. Batool, “Circularity in Materials: A Review on Polymer Composites Made from Agriculture and Textile Waste,” *Int. J. Polym. Sci.*, vol. 2023, p. e5872605, Sep. 2023, doi: 10.1155/2023/5872605.

[8] C. Fang, L. Nie, S. Liu, R. Yu, N. An, and S. Li, “Characterization of polypropylene–polyethylene blends made of waste materials with compatibilizer and nano-filler,” *Compos. Part B Eng.*, vol. 55, pp. 498–505, Dec. 2013, doi: 10.1016/j.compositesb.2013.06.046.

[9] D. C. Licea Saucedo, R. G. Nuñez, M. O. Vázquez Lepe, and D. Rodrigue, “Polymer Processing Technology to Recycle Polymer Blends,” *Recycled Polymer Blends and Composites: Processing, Properties, and Applications*, pp. 111–132,2023, doi: 10.1007/978-3-031-37046-5_7.

[10] A. Joseph Arockiam, Karthikeyan Subramanian, R. G. Padmanabhan, Rajeshkumar Selvaraj, Dilip Kumar Bagal, and S. Rajesh, “A review on PLA with different fillers used as a filament in 3D printing,” *Mater. Today Proc.*, vol. 50, pp. 2057–2064, Jan. 2022, doi: 10.1016/j.matpr.2021.09.413.

[11] S. Choe , “Biodegradation of 3D-Printed Biodegradable/Non-biodegradable Plastic Blends,” *ACS Appl. Polym. Mater.*, vol. 4, no. 7, pp. 5077–5090, Jul. 2022, doi: 10.1021/acsapm.2c00600.

[12] S. Pivsa-Art , “Effect of Compatibilizer on PLA/PP Blend for Injection Molding,” *Energy Procedia*, vol. 89, pp. 353–360, Jun. 2016, doi: 10.1016/j.egypro.2016.05.046.

[13] H.-S. Kim and H.-J. Kim, “Miscibility and performance evaluation of natural-flour-filled PP/PBS and PP/PLA bio-composites,” *Fibers Polym.*, vol. 14, no. 5, pp. 793–803, May 2013, doi: 10.1007/s12221-013-0793-0.

[14] RAJAN, K. Prasad, THOMAS, P. Selvin, GOPANNA, Aravinthan, " Rheology, mechanical properties and thermal degradation kinetics of polypropylene (PP) and polylactic acid (PLA) blends," *Materials Research Express*, 2018, vol. 5, no 8, p. 085304.doi: 10.1088/2053-1591/aad1d3.

[15] N. Tripathi, M. Misra, and A. K. Mohanty, “Durable Polylactic Acid (PLA)-Based Sustainable Engineered Blends and Biocomposites: Recent Developments, Challenges, and Opportunities,” *ACS Eng. Au*, vol. 1, no. 1, pp. 7–38, Oct. 2021, doi: 10.1021/acsengineeringau.1c00011.

[16] Ana M. L. Seca, José A. S. Cavaleiro, Fernando M. J. Domingues, Armando J. D. Silvestre, and Dmitry Evtuguin, and C. P. Neto, “Structural Characterization of the Lignin from the Nodes and Internodes of Arundo donax Reed,” ACS Publications. Accessed: Oct. 12, 2021. [Online]. Available: https://pubs.acs.org/doi/abs/10.1021/jf9910988

[17] L. G. Angelini, L. Ceccarini, and E. Bonari, “Biomass yield and energy balance of giant reed (Arundo donax L.) cropped in central Italy as related to different management practices,” *Eur. J. Agron.*, vol. 22, no. 4, pp. 375–389, May 2005, doi: 10.1016/j.eja.2004.05.004.

[18] H. P. S. Abdul Khalil, A. M. Issam, M. T. Ahmad Shakri, R. Suriani, and A. Y. Awang, “Conventional agro-composites from chemically modified fibres,” *Ind. Crops Prod.*, vol. 26, no. 3, pp. 315–323, Oct. 2007, doi: 10.1016/j.indcrop.2007.03.010.

[19] A. Le Duigou, D. Correa, M. Ueda, R. Matsuzaki, and M. Castro, “A review of 3D and 4D printing of natural fibre biocomposites,” *Mater. Des.*, vol. 194, p. 108911, Sep. 2020, doi: 10.1016/j.matdes.2020.108911.

[20] C. H. Lee, F. N. B. M. Padzil, S. H. Lee, Z. M. A. Ainun, and L. C. Abdullah, “Potential for Natural Fiber Reinforcement in PLA Polymer Filaments for Fused Deposition Modeling (FDM) Additive Manufacturing: A Review,” *Polymers*, vol. 13, no. 9, Art. no. 9, Jan. 2021, doi: 10.3390/polym13091407.

[21] H. J. Aida, R. Nadlene, M. T. Mastura, L. Yusriah, D. Sivakumar, and R. A. Ilyas, “Natural fibre filament for Fused Deposition Modelling (FDM): a review,” *Int. J. Sustain. Eng.*, vol. 14, no. 6, pp. 1988–2008, Nov. 2021, doi: 10.1080/19397038.2021.1962426.

[22] W. Ahmed, F. Alnajjar, E. Zaneldin, A. H. Al-Marzouqi, M. Gochoo, and S. Khalid, “Implementing FDM 3D Printing Strategies Using Natural Fibers to Produce Biomass Composite,” *Materials*, vol. 13, no. 18, p. 4065, Sep. 2020, doi: 10.3390/ma13184065.

[23] SHUBHRA, Q. TH, ALAM, A. Moshiul, QUAIYYUM, M. Adul," Mechanical properties of polypropylene composites: A review," *Journal of thermoplastic composite materials*, vol. 26, no 3, p. 362-391, 2013. doi:10.1177/089270571142869.

[24] J. E. Galve, D. Elduque, C. Pina, and C. Javierre, “Life Cycle Assessment of a Plastic Part Injected with Recycled Polypropylene: A Comparison with Alternative Virgin Materials,” *Int. J. Precis. Eng. Manuf.-Green Technol.*, vol. 9, no. 3, pp. 919–932, May 2022, doi: 10.1007/s40684-021-00363-2.doi: 10.1177/0892705711428659.

[25] M. Z. Shiferaw and H. S. Gebremedhen, “Recycled Polymer for FDM 3D Printing Filament Material: Circular Economy for Sustainability of Additive Manufacturing,” *Advances of Science and Technology*, 2022, pp. 243–261. doi: 10.1007/978-3-030-93712-6_17.

CHAPTER 1: ARUNDO DONAX L.

A COMPREHENSIVE REVIEW

1.1 Natural fibre

Using natural fibres as fillers in composite materials presents a promising substitute for synthetic fibres, owing to their versatility, eco-friendliness, cost-effectiveness, renewable nature, and global availability [1], [2], [3]. Although the plants that provide these fibres are renewable and sustainable, it's possible that the fibres don't naturally have these attributes[4], [5]. Research efforts to maximize the use of plant-based natural fibres including hemp, jute, bamboo, kenaf, ramie, and pineapple leaf fibres have significantly increased recently in response to rising environmental and sustainability concerns [6], [7].

The main factor influencing the selection of natural fibres is mostly based on the intended uses, which are customized to fulfill different requirements[8], [9]. These applications cover a broad spectrum of requirements, ranging from building [10]to textiles [4] and beyond. The fibres' mechanical characteristics are linked to a number of variables, such as microfibril angle[11]**,** elongation, and Young's modulus[12], all of which affect how these fibres behave under stress and strain. Furthermore, the amount of cellulose in the fibres is significant since it determines how strong and stiff the fibres become by creating hydrogen bonds [13]. Therefore, to achieve maximum performance across various applications, it is crucial to carefully analyze both the intended use and the unique characteristics of natural fibres[14].

Furthermore, the selection process is seriously affected by the sources and costs of natural fibres[15], [16]. The potential for biomass production in a variety of perennial species was highlighted by Pulighe et al.[17], with a focus on Arundo donax L., popularly known as giant reed (**Figure 1.1**), in marginal and polluted regions of Italy. remarkably, gigantic reeds demonstrated exceptional performance in terms of crop output, irrigation requirements, water efficiency, and fertilizer usage even under less-than-ideal agronomic circumstances. Given its adaptability and output in a variety of climatic conditions, this emphasizes Arundo donax L.'s favorable applicability as a natural fibre alternative.

Fig. 1.1 Arundo donax L. plant.

1.1.1 Arundo donax L.

Arundo donax L. belongs to the family Grammineae and is a perennial grass [18]. **Figure 1.1** shows the entire plant, including the culms or stems, leaves, and flowers. Hollow, 2-3 cm in diameter, and up to 6 m tall, culms feature stem-clasping leaves all the way up the stem. Its seeds are often not viable, at least outside of Asia. This plant reproduces either by the rhizome or by growing roots on the nodes, which accounts for its quick dispersal and little genetic diversity [19].

This species' fast growth and ability to quickly adapt to a variety of climatic circumstances have greatly aided in its naturalization and widespread distribution, particularly in Mediterranean nations[20]. A. donax is now regarded as an invasive species mostly in nations with a subtropical or Mediterranean environment, although having been introduced in a number of warm countries around the world (**Figure 1.2**)[21].

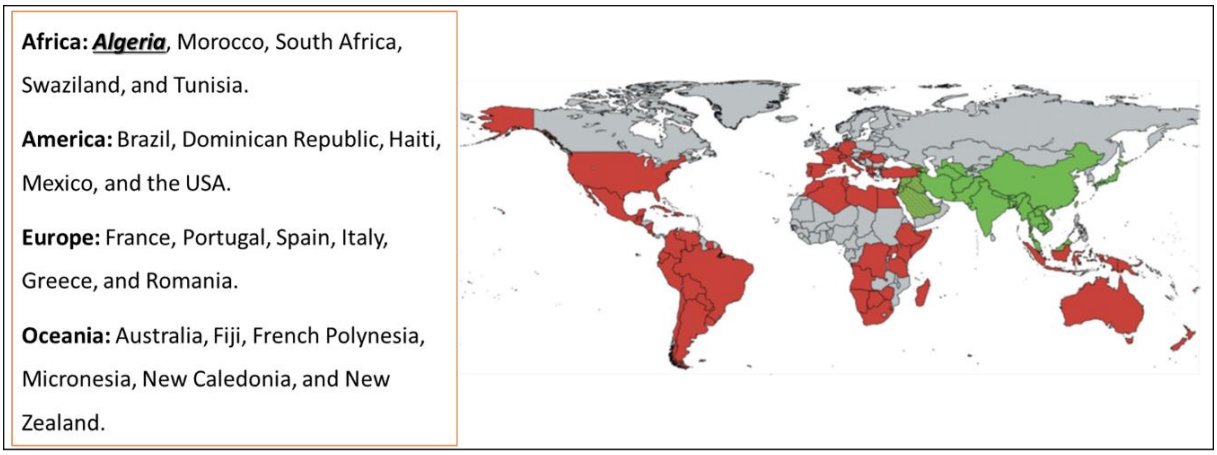


Fig. 1.2 Arundo donax's range distribution: native (green) and introduced (red). Countries for whom this status is contested or questioned in the literature are shown by hatching on the map.

In Mediterranean regions, Arundo donax may produce around 74 tons of dry matter per hectare per year under optimal water and nitrogen conditions. This information emphasizes Arundo donax's potential as a useful biomass source under the right circumstances, providing a viable choice for sustaining energy production on less productive ground [22].

1.2 Arundo fibre extraction

Similar to the majority of natural fibres, extracting Arundo fibres, from reed stems and leaves, is possible by mechanical means, chemical means, or by combining the two. The physical structure of the fibres is mostly affected by mechanical processes like rolling and crushing[23]. On the other hand, chemical soaking modifies the fibres' chemical structure and composition[24]. The resulting fibre's chemical composition and mechanical qualities can be greatly impacted by the extraction technique used[25]. **Table 1.1** illustrates the composition of Arundo donax fibre samples extracted from different parts of the plant using various extraction methods. The samples were analyzed for cellulose, lignin, and hemicellulose content as well as fibre’s density.

Table 1.1 Composition of A. donax fibre samples (average values ± standard deviation) and shredded material (in percentage).

Fibre part	Methodes	Cellulose	Hemicellulose	Lignin	Ashes	Density (g/cm^3)	Ref
Shredded material	mechanical	38.0 ± 3.7	42.4 ± 1.3	32.4 ± 2.7	4.9 ± 1.1	1.1727	[24]
Fibres from stems	combining	67.5 ± 1.9	15.3 ± 4.6	25.7 ± 0.6	0.4 ± 0.2	1.5456	[24]
Fibres from leaves	combining	68.8 ± 4.3	20.0 ± 3.8	11.2 ± 2.2	1.8 ± 0.5	1.629	[24]
Fibres from stems	mechanical	43.2	20.5	17.2	1.9	1.168	[26]

1.3 Chemical Treatment of Arundo Donax L. Fibres

In order to increase Arundo donax's compatibility with polymers, chemical modification techniques are used.

1.3.1 Alkali treatment

Alkali treatment is one of the most common methods employed to modify natural fibres, including Arundo donax L. Alkalization is more than just a physical change because it also modifies the chemical composition of plant fibres during the treatment process. Similarly, it cannot be categorized as a purely chemical process because it does not entail the addition of extra coupling agents to the composite. This treatment improves the fibre's surface roughness and hydrophilicity by eliminating lignin and hemicellulose. As a result, the fibre's crystallinity and tensile strength both increases. Factors like temperature, treatment time, and alkali concentration affect how effective this procedure is [27], [28].

1.3.2 Mercerization

Mercerization involves treating Arundo donax L. fibres with concentrated alkali solutions, typically sodium hydroxide (NaOH), under tension. The fibres expand as a result of this process, increasing their surface area, tensile strength, and crystallinity. Additionally, mercerization gives the fibres better dye absorption capabilities and dimensional stability, which enhances their suitability for textile applications. However, excessive mercerization can cause fibre damage and loss of flexibility, highlighting the importance of optimizing the treatment conditions [24], [29].

1.3.3 Acetylation treatment

Acetylation is a chemical process that requires the use of an appropriate catalyst, most often acetic acid. This procedure attempts to extract hydrogen atoms from cellulose molecules' hydrophilic hydroxyl branches. It does this by grafting and placing acetyl groups at these originally hydrogenated locations on the cellulose molecule. This alteration improves certain cellulose characteristics, increasing its suitability for a range of industrial uses [30].

1.3.4 Acid treatment

Acid treatment can improve compatibility with specific polymers by removing impurities, roughening up the surface, and adding carboxylic acid groups to the fibre surface. The fibre is treated, using acids like hydrochloric acid (HCl) or sulfuric acid (H2SO4). The three-step process of alkaline pre-treatment, acid hydrolysis, and soxhlet-based extraction, as shown by Gaikwad et al.[28], significantly improved the qualitative and quantitative characteristics of the cellulose fibres that were isolated from Arundo donax.

1.3.5 Silane treatment

Arundo donax fibres can be treated with silane, a chemical surface modification method, to improve their adherence and compatibility with polymer matrices in composite materials. An organosilane chemical, such as γ-aminopropyltriethoxysilane (γ-APS), is dissolved in a suitable solvent, such as ethanol or water, to create a silane solution. After being cleaned, the fibres are submerged in the silane solution for a predetermined amount of time, usually between one and two hours, at either room temperature or a higher temperature, frequently about 60°C. The silane compounds undergo hydrolysis and condensation processes on the fibre surface during this treatment, resulting in the formation of a siloxane network that forms connections with the hydroxyl groups in cellulose. After treatment, the fibres are dried at high temperatures and rinsed with the solvent to get rid of any remaining, unreacted silane compounds[31], [32].

This silane treatment procedure can be applied alone or in combination with other chemical treatments, such as the alkali treatment (**Figure 1.3**), to improve the adherence and compatibility of the Arundo donax fibres with the polymer matrix. The main benefits of silane treatment for Arundo donax fibres are increased mechanical characteristics and better stress transmission due to improved fibre-matrix adhesion. Moreover, silane treatment improves

thermal stability, which allows processing at higher temperatures, and moisture resistance, which qualifies the composites for humid settings[33].

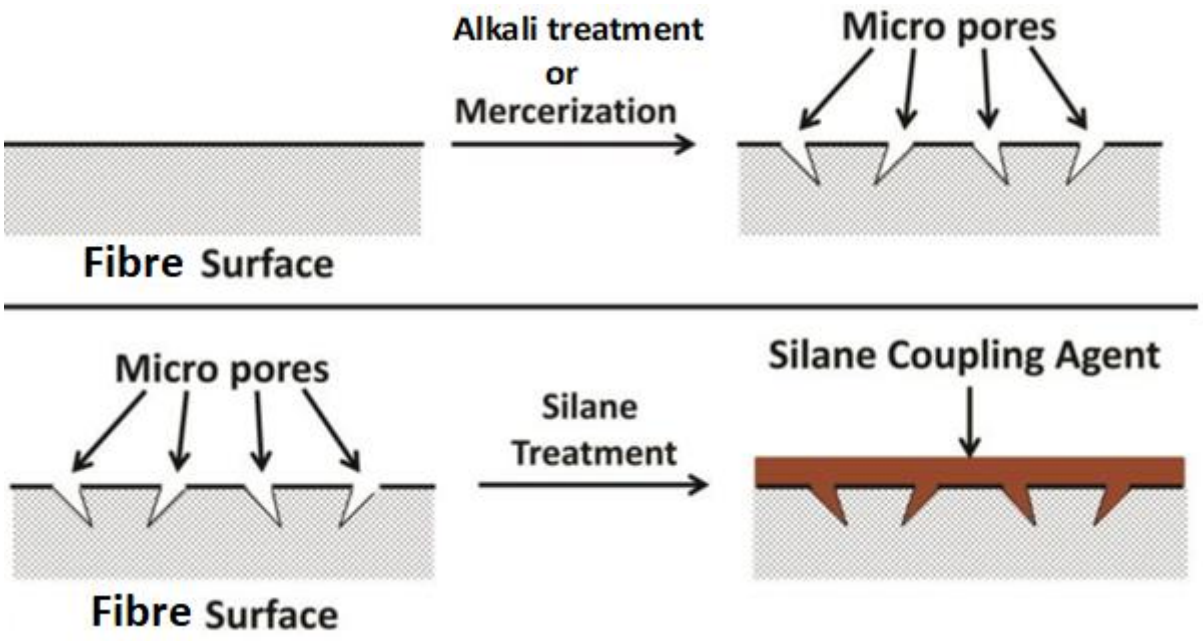


Fig. 1.3 Surface effects of chemical treatment and silane treatment process combined.

1.4 Arundo donax L. as a reinforcing agent

Arundo donax L. has been investigated for various applications such as bioethanol production[34], bioenergy generation[35], biomolecule extraction[36], paper and pulp manufacturing[37], biochar production[38], oil spill recovery[39], [40], traditional architectural restoration, and insulating material[41]. Additionally, its versatility extends to soil bioremediation, where it offers the added advantage of generating charcoal or methane[42], [43]. This section, however, will focus exclusively on Arundo's application as a reinforcing agent in thermoplastic matrices.

Arundo donax L. offers beneficial lignocellulosic fibres that are perfect for reinforcing composites. The potential of these fibres in polymer composites, which provide advantages in terms of strength and durability, has been investigated. Fiore et al.[44] utilized Arundo fibres extracted from the outer stem of the plant to fabricate a PLA-based composite, examining the impact of ADF content and size on morphology, as well as mechanical and thermal properties. A. donax fillers were segregated into two fractions based on size: 150 to 300 µm (A300) and 300 to 500 µm (A500). Composites, containing 10 and 20 wt% of ADF, were

manufactured using a modular co-rotating twin-screw extruder, and specimens for mechanical characterization were prepared via compression molding.

Table 1.2 Tensile properties of neat PLA and PLA–ADF composites[44].

Samples	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
PLA	3.22 ±0.17	48.9 ± 1.4	2.24 ± 0.26
C300-10	3.69 ±0.15	37.5 ± 1.8	1.35 ± 0.20
C500-20	3.85 ±0.09	37.3 ± 2.0	1.09 ± 0.10
C300-20	4.35 ±0.24	33.4 ± 4.5	0.86 ± 0.11
C500-20	4.47 ±0.16	31.5 ± 2.9	0.76 ± 0.07

When compared to pure PLA (**Table 1.2**), all composites showed greater tensile modulus, with filler content having a significant effect on modulus. In particular, the tensile modulus of C300-10 and C300-20 composites were found to be around 15% and 35% greater than those of PLA. All examined composites, however, showed tensile strengths that were lower than those of pure PLA; filler amount had a greater impact on these characteristics than size. In particular, C500-10 and C500-20 tensile strength that were roughly 13% and 26% lower than PLA.

Suarez et al. [45] explored the extraction of fibre bundles from the Arundo plant through a rolling mill. The fibre bundles were obtained by passing the wet strips through three pairs of rollers after being soaked in water for 1 to 2 days (**Figure 1.4**). Compression molding was used to create PE and PP-based composites with fibre contents up to 40%. Tensile, flexural, and impact loading tests were performed to evaluate the mechanical characteristics of the materials (**Table 1.3**). The impact characteristics were found to have drastically decreased by the authors, particularly for all PP composites and PE at loadings of 30 and 40%. As was noted in the earlier study, raising the filler ratio causes the elastic modulus to increase and the tensile strength to drop, but it has no noticeable effect on the flexural strength of PE.

(a) (b)

Fig 1.4 Fibre extraction: (a) Clum passing through the rolling mill; and (b) fibre bundles[45].

Table 1.3 Impact and Tensile properties of PP composites loading effect[45].

Composites	**Impact Strength (kJ/m2)**		**Ultimate Strength (MPa)**		**E (MPa)**		**Yield Strength (MPa)**	
C.PP.	32.5	±1.40	25.4	±0.15	857.2	±13.80	11.1	±0.41
C.PP.AD.10	6.9	±1.24	20.3	±0.37	955.4	±28.22	11.7	±0.66
C.PP.AD.20	5.4	±1.12	15.5	±1.34	1037.8	±29.77	10.4	±0.97
C.PP.AD.30	5.3	±0.49	13.7	±1.38	1142.0	±81.88	10.7	±1.08
C.PP.AD.40	4.6	±0.27	13.3	±0.94	1186.7	±29.89	10.4	±0.58

In this study, Suarez et al. [46] evaluated the characteristics of composite components made by rotational molding with Arundo donax fibres at 5 and 10 weight percent loading, utilizing two distinct matrices: PE and PLA. Composite materials' mechanical performance, morphology, and bio-disintegration have all been evaluated. **Figure 1.5** illustrates images of PLA composites featuring 10% untreated and treated fibres, while **Table 1.4** presents the average values along with standard deviations for mechanical characteristics of PLA/ADF composites.

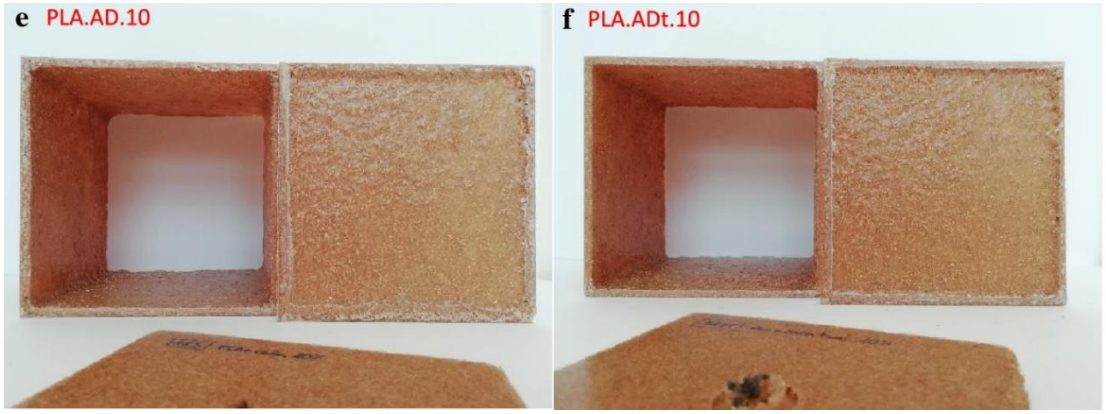


Fig. 1.5 Pictures of PLA composites with 10% treated PLA fibre (f)and 10% untreated PLA fibre(e)[46].

The addition of longer fibre lengths (3–4 mm) at loadings of 5 and 10% did not significantly change the rotomolded PE parts, except for impact strength. In contrast, the impact and flexural properties of PLA-based composites were found to be diminished, even after subjecting the fibres to NaOH solution. While the mechanical characteristics of the composites were maintained, the treatment produced fibres with increased thermal stability. Despite the substandard mechanical performance of PLA composites, adding Arundo fibres led to increased deterioration in a biodisintegration experiment, as shown by a decrease in melting and glass transition temperature after the experiment.

Table 1.4 The average values (± standard deviations) for PLA/ADF composite's mechanical.characteristics[46].

Material	Impact	Tensile properties		Flexural properties	
	Strength (kJ/m²)	Strength (MPa)	Modulus (MPa)	Strength (MPa)	Modulus (MPa)
PLA	21.1 ± 5.0	17.3 ± 5.6	865.4 ± 161.5	57.7 ± 4.5	3862.1 ± 412.1
PLA.AD 10	4.0 ± 1.4	20.1 ± 2.7	874.0 ± 179.0	33.7 ± 2.6	3148.3 ± 280.0
PLA.ADt 10	3.7 ± 0.7	18.5 ± 2.8	774.8 ± 108.4	33.4 ± 6.3	3007.3 ± 690.2

Ultimately, the utilization of Arundo donax L. as a reinforcing agent in thermoplastic matrices presents numerous advantages, fueling significant interest in its application. Arundo's lignocellulosic fibres have proven to be a very suitable material for reinforcing composites, hence augmenting their strength and durability. Researchers' investigations into the possibilities of Arundo fibres in polymer composites have produced encouraging findings. Still, there's a lot of room for more research in this area.

Future research endeavors could focus on examining diverse fibre treatment techniques and their impact on composite characteristics, as well as exploring different matrix materials. Furthermore, investigating composite production technologies, such 3D printing, may provide insightful information on cutting-edge uses and processing strategies. All things considered, further research into Arundo fibres as a reinforcing agent has great potential for the creation of high-performance, sustainable composite materials that may find use in a variety of sectors.

References

[1] Elfaleh I, Abbassi F, Habibi M, Ahmad F, Guedri M, Nasri M, Garnier C., "A comprehensive review of natural fibers and their composites: An eco-friendly alternative to conventional materials," *Results Eng.*, vol. 19, p. 101271, Sep. 2023, doi: 10.1016/j.rineng.2023.101271.

[2] R. Naghdi, "Advanced natural fibre-based fully biodegradable and renewable composites and nanocomposites: A comprehensive review," *Int. Wood Prod. J.*, vol. 12, no. 3, pp. 178–193, Aug. 2021, doi: 10.1080/20426445.2021.1945180.

[3] Aravindh, M., Sathish, S., Prabhu, L., Raj, R.R., Bharani, M., Patil, P.P., Karthick, A. and Luque, R., "Effect of Various Factors on Plant Fibre-Reinforced Composites with Nanofillers and Its Industrial Applications: A Critical Review," *J. Nanomater.*, vol. 2022, p. e4455106, Jul. 2022, doi: 10.1155/2022/4455106.

[4] G. Annapoorani," Sustainable textile fibers", Sustainable Innovations in textile fibres, p. 1-30, 2018.

[5] M. ADNAN ALI and M. IMRAN SARWAR, "Sustainable and Environmental freindly fibers in Textile Fashion (A Study of Organic Cotton and Bamboo Fibers)," Dissertation, University of Borås/Swedish School of Textiles, 2010.

[6] Li, M., Pu, Y., Thomas, V.M., Yoo, C.G., Ozcan, S., Deng, Y., Nelson, K. and Ragauskas, A.J., "Recent advancements of plant-based natural fiber–reinforced composites and their applications," *Compos. Part B Eng.*, vol. 200, p. 108254, Nov. 2020, doi: 10.1016/j.compositesb.2020.108254.

[7] S. Maiti, M. R. Islam, M. A. Uddin, S. Afroj, S. J. Eichhorn, and N. Karim, "Sustainable Fiber-Reinforced Composites: A Review," *Adv. Sustain. Syst.*, vol. 6, no. 11, p. 2200258, 2022, doi: 10.1002/adsu.202200258.

[8] T. Khan, M. T. B. Hameed Sultan, and A. H. Ariffin, "The challenges of natural fiber in manufacturing, material selection, and technology application: A review," *J. Reinf. Plast. Compos.*, vol. 37, no. 11, pp. 770–779, Jun. 2018, doi: 10.1177/0731684418756762.

[9] A. Lotfi, H. Li, D. V. Dao, and G. Prusty, "Natural fiber–reinforced composites: A review on material, manufacturing, and machinability," *J. Thermoplast. Compos. Mater.*, vol. 34, no. 2, pp. 238–284, Feb. 2021, doi: 10.1177/0892705719844546.

[10] L. Molari, F. S. Coppolino, and J. J. García, "*Arundo donax*: A widespread plant with great potential as sustainable structural material," *Constr. Build. Mater.*, vol. 268, p. 121143, Jan. 2021, doi: 10.1016/j.conbuildmat.2020.121143.

[11] M.-J. Le Guen, R. H. Newman, A. Fernyhough, S. J. Hill, and M. P. Staiger, "Correlations Between the Physiochemical Characteristics of Plant Fibres and Their Mechanical Properties," *Natural Fibres: Advances in Science and Technology Towards Industrial Applications*, pp. 35–47,2016, doi: 10.1007/978-94-017-7515-1_3.

[12] S. R. Djafari Petroudy, "3 - Physical and mechanical properties of natural fibers," Advanced *High Strength Natural Fibre Composites in Construction*, pp. 59–83,2017, doi: 10.1016/B978-0-08-100411-1.00003-0.

[13] Jakob, M., raj Mahendran, A., Gindl-Altmutter, W., Bliem, P., Konnerth, J., Müller, U., & Veigel, S. , "The strength and stiffness of oriented wood and cellulose-fibre materials: A review.",Progress in Materials Science,2021, doi:10.1016/j.pmatsci.2021.100916.

[14] Peças, P., Carvalho, H., Salman, H. and Leite, M., "| Free Full-Text | Natural Fibre Composites and Their Applications: A Review.", J. Compos. Sci., vol *2*, p.66,2018, https://doi.org/10.3390/jcs2040066.

[15] F. Ahmad, H. S. Choi, and M. K. Park, "A Review: Natural Fiber Composites Selection in View of Mechanical, Light Weight, and Economic Properties," *Macromol. Mater. Eng.*, vol. 300, no. 1, pp. 10–24, 2015, doi: 10.1002/mame.201400089.

[16] Ho, M.P., Wang, H., Lee, J.H., Ho, C.K., Lau, K.T., Leng, J. and Hui, D.,"Critical factors on manufacturing processes of natural fibre composites," *Compos. Part B Eng.*, vol. 43, no. 8, pp. 3549–3562, Dec. 2012, doi: 10.1016/j.compositesb.2011.10.001.

[17] Pulighe, Giuseppe, G. Bonati, S. Fabiani, T. Barsali, Flavio Lupia, S.Vanino, P. Nino, P. Arca, and P. P. Roggero, "Assessment of the Agronomic Feasibility of Bioenergy Crop Cultivation on Marginal and Polluted Land: A GIS-Based Suitability Study from the Sulcis Area, Italy," *Energies*, vol. 9, no. 11, Art. no. 11, Nov. 2016, doi: 10.3390/en9110895.

[18] M. Christou, E. Alexopoulou,S.L. Cosentino, V. Copani, S. Nogues, E. Sanchez,A. Monti, W. Zegada-Lizarazu, L. Pari, L. and A. Scarfone, "4 - Giant Reed: From Production to End Use," *Perennial Grasses for Bioenergy and Bioproducts*, pp. 107–151,2018, doi: 10.1016/B978-0-12-812900-5.00004-7.

[19] L. Suárez, Z. Ortega, M. Barczewski, and E. Cunningham, “Use of giant reed (Arundo donax L.) for polymer composites obtaining: a mapping review,” *Cellulose*, vol. 30, no. 8, pp. 4793–4812, May 2023, doi: 10.1007/s10570-023-05176-x.

[20] Shtein, I., Baruchim, P. and Lev-Yadun, S.,“Division of labour among culms in the clonal reed Arundo donax (Poaceae) is underlain by their pre-determined hydraulic structure ", *Botanical Journal of the Linnean Society*, vol.*195*,no. 3, pp.348-356,2021.

[21] J. Jiménez-Ruiz, L. Hardion, J. P. Del Monte, B. Vila, and M. I. Santín-Montanyá, “Monographs on invasive plants in Europe N° 4: Arundo donax L.,” *Bot. Lett.*, vol. 168, no. 1, pp. 131–151, Jan. 2021, doi: 10.1080/23818107.2020.1864470.

[22] M. Borin, A. C. Barbera, M. Milani, G. Molari, S. M. Zimbone, and A. Toscano, “Biomass production and N balance of giant reed (*Arundo donax* L.) under high water and N input in Mediterranean environments,” *Eur. J. Agron.*, vol. 51, pp. 117–119, Nov. 2013, doi: 10.1016/j.eja.2013.07.005.

[23] V. Sadrmanesh and Y. Chen, “Bast fibres: structure, processing, properties, and applications,” *Int. Mater. Rev.*, vol. 64, no. 7, pp. 381–406, Oct. 2019, doi: 10.1080/09506608.2018.1501171.

[24] L. Suárez, M. Barczewski, P. Kosmela, M. D. Marrero, and Z. Ortega, “Giant Reed (Arundo donax L.) Fiber Extraction and Characterization for Its Use in Polymer Composites,” *J. Nat. Fibers*, vol. 20, no. 1, p. 2131687, Apr. 2023, doi: 10.1080/15440478.2022.2131687.

[25] A. Gholampour and T. Ozbakkaloglu, “A review of natural fiber composites: properties, modification and processing techniques, characterization, applications,” *J. Mater. Sci.*, vol. 55, no. 3, pp. 829–892, Jan. 2020, doi: 10.1007/s10853-019-03990-y.

[26] V. Fiore, T. Scalici, and A. Valenza, “Characterization of a new natural fiber from Arundo donax L. as potential reinforcement of polymer composites,” *Carbohydr. Polym.*, vol. 106, pp. 77–83, Jun. 2014, doi: 10.1016/j.carbpol.2014.02.016.

[27] F. M. Alasti, N. Asefi, R. Maleki, and S. S. SeiiedlouHeris, “The influence of three different types and dosage of alkaline on the inherent properties in cocoa powder,” *J. Food Sci. Technol.*, vol. 57, no. 7, pp. 2561–2571, Jul. 2020, doi: 10.1007/s13197-020-04293-w.

[28] A. Gaikwad, K. Debnath, and M. K. Gupta, “Effects of alkaline-acid treatment on the physiochemical attributes of natural cellulosic fiber of Arundo donax L,” *J. Appl. Polym. Sci.*, vol. 140, no. 48, p. e54724, 2023, doi: 10.1002/app.54724.

[29] B. NagarajaGanesh and B. Rekha, “Effect of mercerization on the physico-chemical properties of matured and seasoned Cocos nucifera fibers for making sustainable composites,” *Mater. Res. Express*, vol. 6, no. 12, p. 125102, Nov. 2019, doi: 10.1088/2053-1591/ab5395.

[30] I. O. Oladele, O. S. Michael, A. A. Adediran, O. P. Balogun, and F. O. Ajagbe, “Acetylation Treatment for the Batch Processing of Natural Fibers: Effects on Constituents, Tensile Properties and Surface Morphology of Selected Plant Stem Fibers,” *Fibers*, vol. 8, no. 12, Art. no. 12, Dec. 2020, doi: 10.3390/fib8120073.

[31] H. Long *et al.*, “Mechanical and thermal properties of bamboo fiber reinforced polypropylene/polylactic acid composites for 3D printing,” *Polym. Eng. Sci.*, vol. 59, no. s2, pp. E247–E260, 2019, doi: 10.1002/pen.25043.

[32] Long, H., Wu, Z., Dong, Q., Shen, Y., Zhou, W., Luo, Y., Zhang, C. and Dong, X., “Characterization of raw and treated Arundo donax L. cellulosic fibers and their effect on the curing kinetics of bisphenol A-based benzoxazine,” *Int. J. Biol. Macromol.*, vol. 164, pp. 2931–2943, Dec. 2020, doi: 10.1016/j.ijbiomac.2020.08.179.

[33] P. F. Alao, L. Marrot, M. D. Burnard, G. Lavrič, M. Saarna, and J. Kers, “Impact of Alkali and Silane Treatment on Hemp/PLA Composites’ Performance: From Micro to Macro Scale,” *Polymers*, vol. 13, no. 6, Art. no. 6, Jan. 2021, doi: 10.3390/polym13060851.

[34] Corno, Luca, Roberto Pilu, and Fabrizio Adani, "Arundo donax L.: a non-food crop for bioenergy and bio-compound production." *Biotechnology advances* ,vol. 32, no. 8, pp. 1535-1549, 2014.

[35] Amaducci, Stefano, and Alessia Perego. "Field evaluation of Arundo donax clones for bioenergy production." *Industrial Crops and Products* ,vol.75,pp. 122-128, 2015.

[36] N. H. Shafik, A. M. Al-sayed, H. N. Michael, F. Abd-Elhai, A. A. Ali, and T. Ragab, “Phytochemical Investigations by LC– ESI–MS and Biological Activities of Arundo Donax Leaves Extract and Its Silver Nanoparticles,” *Egypt. J. Chem.*, vol. 67, no. 5, pp. 451–461, May 2024, doi: 10.21608/ejchem.2023.233124.8557.

[37] Shatalov, Anatoly A., and Helena Pereira. "Influence of stem morphology on pulp and paper properties of Arundo donax L. reed." *Industrial Crops and Products,vol.* 15, no. 1,pp.: 77-83,2002.

[38] Y. Zhao, L. Huang, and Y. Chen, “Biochars derived from giant reed (Arundo donax L.) with different treatment: characterization and ammonium adsorption potential,” *Environ. Sci. Pollut. Res.*, 2017, doi: 10.1007/s11356-017-0110-3.

[39] E. Piperopoulos, A. Khaskhoussi, V. Fiore, and L. Calabrese, “Surface Modified Arundo Donax Natural Fibers for Oil Spill Recovery,” *J. Nat. Fibers*, vol. 19, no. 14, pp. 8230–8245, Oct. 2022, doi: 10.1080/15440478.2021.1961343.

[40] Calabrese, Luigi, Elpida Piperopoulos, and Vincenzo Fiore. "Arundo donax fibers as green materials for oil spill recovery." *Biofibers and biopolymers for biocomposites: Synthesis, characterization and properties* ,pp: 259-283,2020.

[41] N. Amarone, G. Iovane, D. Marranzini, R. Sessa, M. C. Guedes, and B. Faggiano, “Arundo donax L. as sustainable building material,” *Sustain. Build.*, vol. 6, p. 2, 2023, doi: 10.1051/sbuild/2023005.

[42] Fernando, A. Luisa, B. Barbosa, L. A. Gomes, J. Costa, and E. G. Papazoglou. "Giant reed (Arundo donax L.)—A multi-purpose crop bridging phytoremediation with sustainable bioeconomy." In *Bioremediation and bioeconomy*, pp. 119-144. Elsevier, 2024.

[43] Zhang, Deng, Q. W. Jiang, D. Y. Liang, S. Huang, and J. Liao, "The potential application of giant reed (Arundo donax) in ecological remediation." ,*Frontiers in Environmental Science,vol.* 9,pp.: 652367,2021.

[44] Fiore, Vincenzo, L. Botta, R. Scaffaro, A. Valenza, and A. Pirrotta. "PLA based biocomposites reinforced with Arundo donax fillers.", *Composites Science and Technology,vol.* 105, pp: 110-117,2014.

[45] L. Suárez, J. Castellano, F. Romero, M. D. Marrero, A. N. Benítez, and Z. Ortega, “Environmental Hazards of Giant Reed (Arundo donax L.) in the Macaronesia Region and Its Characterisation as a Potential Source for the Production of Natural Fibre Composites,” *Polymers*, vol. 13, no. 13, Art. no. 13, Jan. 2021, doi: 10.3390/polym13132101.

[46] L. Suárez, Z. Ortega, F. Romero, R. Paz, and M. D. Marrero, “Influence of Giant Reed Fibers on Mechanical, Thermal, and Disintegration Behavior of Rotomolded PLA and PE Composites,” *J. Polym. Environ.*, vol. 30, no. 11, pp. 4848–4862, Nov. 2022, doi: 10.1007/s10924-022-02542-x.

CHAPTER 2: INVESTIGATING POLYPROPYLENE AND SUSTAINABLE BLENDS FOR FDM 3D PRINTING

2.1 Polypropylene

Polypropylene (PP) is a versatile thermoplastic polymer with a wide range of advantageous properties, making it a popular material in various industries[1]. Its notable characteristics include high chemical resistance, excellent fatigue resistance, and low density, which contributes to its lightweight nature[2], [3]. PP is known for its ability to withstand high temperatures, making it suitable for applications requiring heat resistance. Moreover, it exhibits good electrical insulation properties, making it valuable in the electrical and electronic industries[4]. PP is easily moldable, enabling cost-effective manufacturing through injection molding and extrusion[5]. Its affordability, coupled with its durability and recyclability, makes PP an environmentally friendly choice[6]. Common applications encompass packaging materials, automotive components, household goods, medical devices, and textiles, illustrating the extensive and diverse utilization of polypropylene in modern industrial and consumer contexts[7], [8].

2.1.1 Market and applications of polypropylene

The polypropylene market stands as a dynamic and influential sector within the realm of thermoplastic, characterized by its broad applications and consistently growing demand. As a versatile thermoplastic polymer, polypropylene has cemented its place across diverse industries due to its exceptional combination of properties. In packaging, polypropylene finds extensive use for its lightweight, durable, and moisture-resistant characteristics, making it a preferred choice for various packaging solutions. Polypropylene is used widely in the automobile sector to provide lightweight components that help achieve sustainability and fuel economy goals. Because of its strength and abrasion resistance, the textile sector also benefits from its usage in fibres and non-woven textiles. Polypropylene's flexibility is further demonstrated by its use in consumer items, medical equipment, building materials, and other industries.

A detailed breakdown of the anticipated uses for polypropylene (PP) by 2030 is shown in the pie chart (**figure 2.1**). Particularly, packaging stands out as the leading industry,

accounting for a significant 50% of the use of PP. Additionally, by 2030, it is projected that 18% of PP uses will come from the automotive industry, underscoring the importance of this polymer in the production and development of automotive components. These percentages are shown visually in the picture, which gives a succinct and understandable summary of how PP applications are anticipated to be distributed throughout various industries over the next ten years[9].

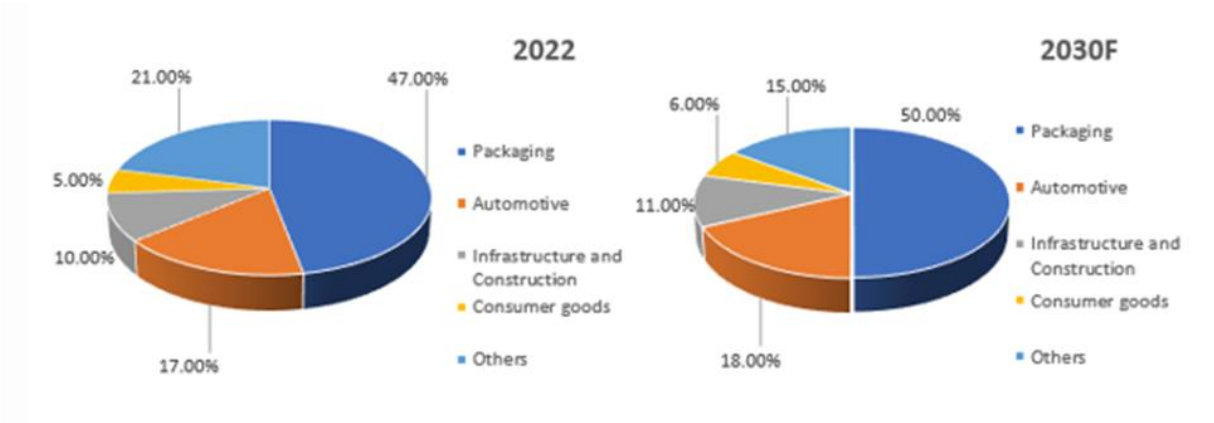


Fig. 2.1 polypropylene market share, by end-use volume, 2022 and 2030[9].

Given its affordability, recyclable nature, and capacity to adapt to new production techniques, the polypropylene industry is always changing and has a significant influence on how today's materials are used in a wide range of industries. By 2022, the global polypropylene (PP) market is expected to grow to 74 million tons. This suggests that until the end of the projected period in 2030, the industry is anticipated to expand at a decent compound annual growth rate (CAGR) of 5.54%[10]. **Figure 2.2** shows the market size of polypropylene from 2022 to 2032 in USD billions.

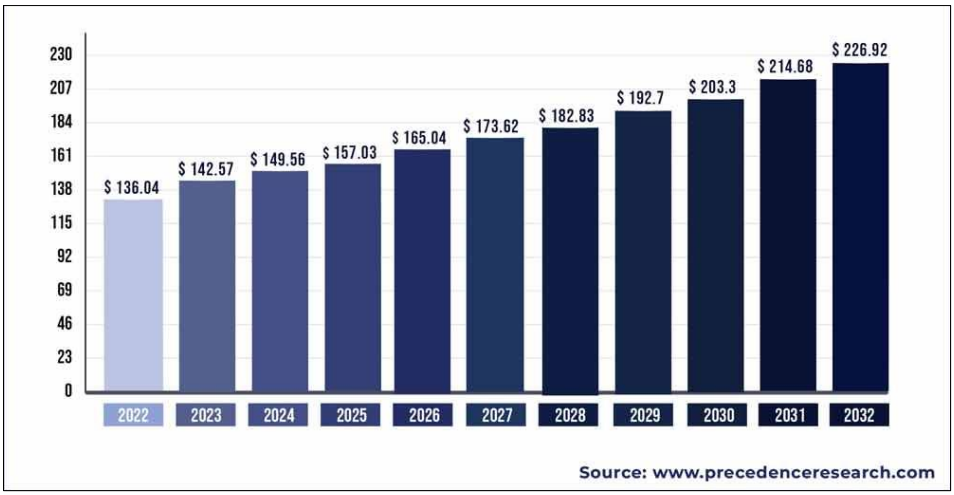


Fig. 2.2 Polypropylene market size, 2022 to 2032 (USD Billion)[10].

2.1.2 Challenges of plastic waste management

Plastic has become an integral part of our daily lives. However, the exponential growth in plastic production has led to a severe environmental challenge, plastic waste, The management of plastic waste poses significant challenges globally, affecting ecosystems, human health, and the overall well-being of the planet[11], [12].

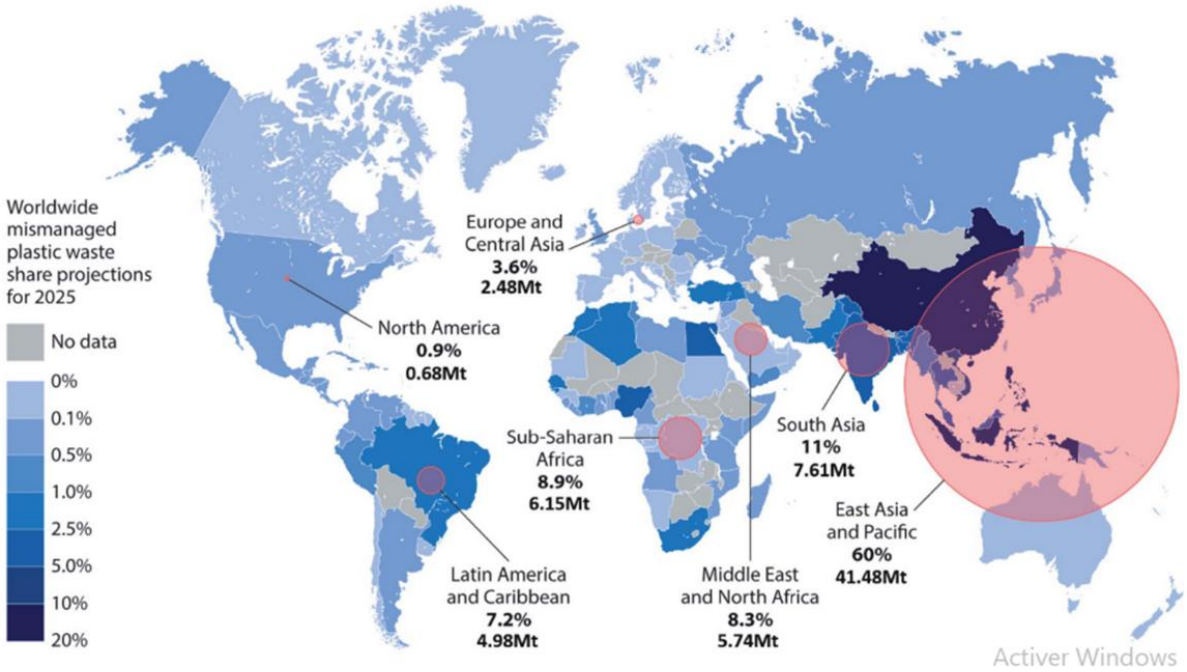


Fig.2.3 worldwide mismanaged plastic waste share projecting for 2025[13].

Based on an expected total volume of 69.14 million metric tons, **figure 2.3** shows the estimated global creation of mismanaged plastic garbage within a 50-kilometer radius of coasts by 2025, with each country's share contributions noted. Circles of representative sizes are used to visually and statistically partition the waste levels into areas. Algeria is expected to make a significant contribution of between 5% and 10%, which translates to 5.74 million metric tons of improperly handled plastic garbage in this coastal region. This highlights Algeria's significance in the larger picture of worldwide plastic waste management issues. Furthermore, estimates suggest that a considerable fraction of these poorly managed wastes, between 15% and 40%, may eventually become marine debris, underscoring the critical need for efficient waste management[13].

The management of plastic waste presents a variety of difficulties that seriously impede the sustainability of the environment. The global crisis of plastic pollution, the scarcity of single-use plastics, the issue of microplastics poisoning ecosystems, the lack of proper waste

collection and disposal methods, and the financial burden of managing plastic waste are some of the major problems. These challenges collectively contribute to the urgent need for comprehensive strategies to address the multifaceted nature of the plastic waste crisis[14], [15].

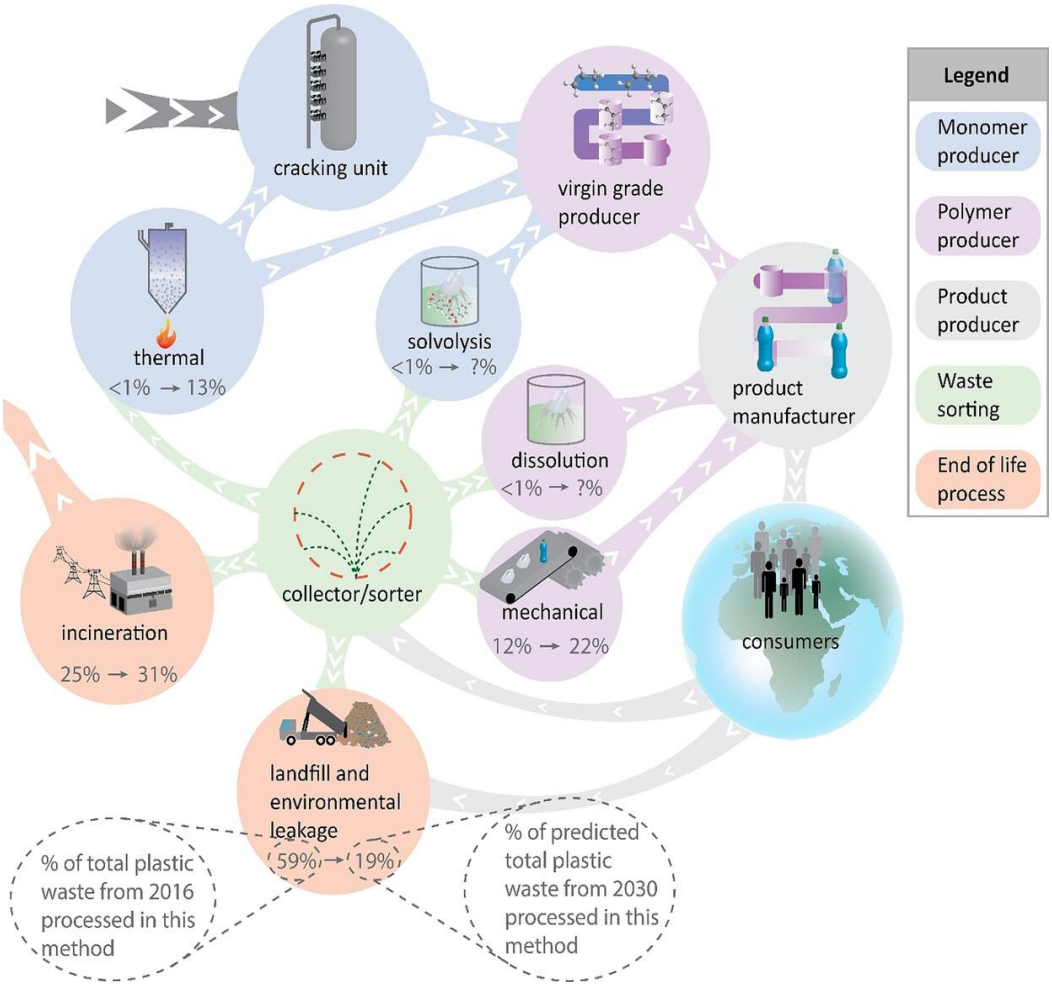


Fig. 2.4 An example of a potential plastics value chain that could simplify the circularity transition[16].

2.1.3 Recycling plastic waste

Over the years, significant strides have been made in the development of various methods for the disposal of plastics, **Figure 2.4** presents an outline of a plastics value-chain that has been envisioned and constructed to enable the transition towards circularity. Because of the difficulties in gathering and classifying plastic garbage, a large amount of it is being burned or ends up in landfills, creating highly polluted and mixed plastic waste streams[16]. Mechanical recycling is still important, especially for the cleanest streams of a single polymer;

its proportion increased from 12% in 2016 to a predicted 22% by 2030. These data, which are taken from the McKinsey study[17], show how waste processing techniques have strategically evolved, with an emphasis on improving mechanical recycling procedures.

Current methods of recycling plastic materials take a multifaceted approach to reduce the negative effects of plastic waste on the environment. The first step in the procedure is usually gathering plastic products from different places, such as residences and companies. Following collection, the plastics are sorted according to their resin codes, which divide the various types. One common recycling technique is mechanical recycling, which involves cleaning, shredding, and melting plastics to create recycled pellets that may be used to make new plastic items[18]. However, challenges such as contamination, limited recyclability of certain plastics, and the need for robust infrastructure have prompted a growing interest in innovative recycling technologies.

By physically reprocessing plastic waste to make new products, mechanical recycling helps to promote a more circular and sustainable usage of plastic. Furthermore, blending polymers has become a cutting-edge technique that combines many plastic varieties to improve their qualities and produce products with better properties. These strategies reflect a growing understanding within the scientific and industrial communities of the need for environmentally friendly ways to manage plastic trash, with the goal of promoting a more circular economy for these useful materials while reducing their negative effects on the environment[19].

2.1.4 Recycling Polypropylene for FDM

The potential benefits of using recycled polypropylene (PP) blends for 3D printing are multifaceted and include environmental, economic, and technical advantages. By utilizing recycled PP blends, several benefits can be realized:

Environmental Sustainability: The use of recycled PP blends reduces the amount of plastic waste that would otherwise end up in landfills or contribute to environmental pollution. This aligns with the principles of sustainable manufacturing and waste reduction.

Resource Conservation: Recycling PP reduces the demand for virgin plastic materials, thereby conserving natural resources and energy required for the production of new plastics.

Cost-Effectiveness: Recycling PP blends presents a cost-effective approach to obtaining feedstock for 3D printing, as it leverages existing waste materials, potentially reducing the need for new material procurement.

Designed Material Properties: Blending recycled PP with other polymers allows for the customization of material properties, such as mechanical strength, flexibility, and thermal characteristics, to meet specific application requirements in 3D printing.

Distributed Manufacturing: The use of recycled PP blends supports the concept of distributed manufacturing, where parts can be printed locally from readily available materials, reducing transportation costs and lead times.

Overall, the utilization of recycled PP blends for 3D printing aligns with the principles of circular economy and sustainable manufacturing, offering a promising avenue for environmentally conscious and cost-effective additive manufacturing processes.

2.2 **FDM technology and feedstock**

2.2.1 FDM technology

3D printing technique known as fused deposition modeling (FDM) has become a leading and exciting sustainable processing method. The use of a wide variety of feedstock, mostly thermoplastic polymers, which are deposited layer by layer to build three-dimensional objects, is essential to its efficacy. This versatile technology allows for the incorporation of recycled materials, including post-consumer plastic waste and specifically polypropylene, into the feedstock. The ability to use recycled materials not only addresses the growing concern of plastic pollution but also contributes to the reduction of virgin plastic consumption. FDM technology's advantage lies in its additive manufacturing process, minimizing material waste compared to traditional subtractive manufacturing methods. By enabling the transformation of recycled plastics into functional products, FDM technology plays a crucial role in advancing sustainable practices and fostering a circular economy. Its adaptability, coupled with its eco-friendly attributes, positions FDM technology as a key player in the pursuit of more environmentally conscious manufacturing processes[17], [19].

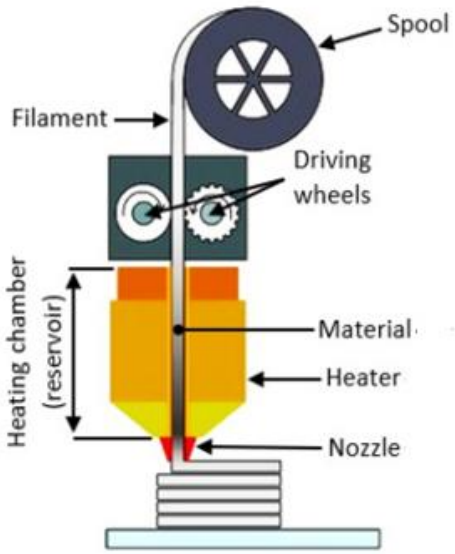


Fig. 2.5 Extrusion-based AM process (filament-based).

Two counter-rotating drive wheels draw a strong thermoplastic filament into a heated die as part of a cutting-edge ME-AM (Material Extrusion Additive Manufacturing) process, as shown in **Figure 1.5**[21]. These spooled filaments, which are normally created by extruding different thermoplastic polymers, are transferred onto a heated build platform using a mobile deposition device. This leads to the sequential building of a structural member using the layer contours provided by the CAD. The filament is heated in the liquefier and nozzle to a temperature that permits smooth flow and typically exceeds the melting point of semicrystalline thermoplastic filaments in order to assist extrusion through the nozzle. The material is deposited onto a build platform or an earlier layer in the horizontal plane after it is extruded from the nozzle[22], [23], [24].

2.2.2 feedstock

The filament material requirements for material extrusion-based additive manufacturing (ME-AM) can be summarized as follows:

- The filament needs to be a thermoplastic that can be extruded within a certain diameter and ovality tolerance for consistent 3D printing.
- It should be stiff yet flexible enough for spooling and despooling during printing.

- The filament should have a minimum strain at yield of approximately 5% to enable continuous spooling and despooling.
- For composites, strong filler-matrix adhesion is essential for high filament strength and stiffness.
- The viscosity of the filament material should be within a suitable range to allow controlled deposition without dripping, and high viscosities can be counteracted by increased nozzle temperatures or additional hardware. Highly viscous materials in composites tend to agglomerate, potentially leading to clogged printing nozzles[25].

These requirements are crucial for ensuring the successful and reliable 3D printing of polypropylene and other thermoplastic materials using material extrusion-based additive manufacturing[26], [27], [28].

Materials that are easily obtainable for FDM technology include ABS[29], PLA, polyethylene terephthalate glycol, polyamide or nylon, high-impact polystyrene, polycarbonate[30], polymethyl methacrylate, polycaprolactone (PCL), polyethylene, and polypropylene[31], [32]. The two most often utilized feedstocks are PLA and ABS, with PLA having clear processing and property benefits over ABS. A lower printing temperature, no smell emission, and a decreased chance of warping and breaking are some of these benefits. As a result, PLA is frequently used as the favored feedstock for FDM. The Nozzle temperature, characteristics, and uses of the most practical thermoplastic materials for FDM are shown in **Table 2.1**. The two most often utilized feedstocks are PLA and ABS, with PLA having clear processing and property benefits over ABS. A lower printing temperature, no smell emission, and a decreased chance of warping and breaking are some of these benefits. As a result, PLA is frequently used as the favored feedstock for FDM[33].

Table 2.1. Nozzle temperature, properties and applications of most useful thermoplastic materials in FDM[34].

Thermoplastic materials	ABS	PLA	PEEK	PEI	PETG
Nozzle temperature (°C)	220-250	190-220	350-400	355-390	220-265
properties	High flexibility and durability, good impact resistance, heat, chemical and abrasion resistance, good dimensional stability, tensile strength and high surface hardness	Good biodegradability, biocompatibility, resistance to temperature, high strength and better elasticity	Excellent mechanical strength, good toughness, high flexibility, chemical and heat resistance	Good mechanical properties such as tensile, flexural and compressive strengths, toughness and good electrical insulation chemical resistance	good impact resistance and chemical resistance
Applicaiopns	Automotive parts, Compressors, gardening tools, nebulizers	Medical implant, tissue engineering scaffolds, food packaging, drinking cup	Piston parts, pumps, medical implant	Medical implants, automotive components, chemical instruments	Fabricating bottles for liquid beverages, cooking oil containers, and food storage containers

2.3 Recycled polypropylene blends as novel 3D printing materials

Blending polypropylene (PP) with other polymers serves as a crucial strategy to improve its properties and overcome limitations when used as a material for 3D printing[35]. The main need and importance of blending PP with other polymers include:

1. Enhanced Mechanical Properties: Blending PP with other polymers can lead to improvements in mechanical properties such as tensile strength, elongation at break, and impact resistance. This enhancement is essential for ensuring the printed parts have the required strength and durability for various applications[36].

2. Improved Printability: Blending PP with other polymers can help optimize the printability of the filament, making it easier to extrude and ensuring better adhesion between layers during the printing process. This can result in higher-quality printed parts with improved dimensional accuracy[37].

3. Reduced War page and Shrinkage: Blending PP with other polymers can help mitigate issues related to war page and shrinkage, which are common challenges when 3D printing with pure PP due to its semicrystalline nature. By modifying the blend, the thermal properties can be adjusted to minimize these issues[38].

4. Customized Properties: PP can be combined with other polymers to create a filament whose characteristics are specifically suited for a given purpose. Because of its flexibility, the material may be tailored to have certain properties like flexibility, heat resistance, or chemical resistance.

5. Cost-Effectiveness: Blending PP with other polymers can offer a cost-effective solution to enhance the overall performance of the material. By utilizing a combination of polymers, it is possible to achieve a balance between performance and cost, making it a viable option for various 3D printing applications[39].

In summary, blending PP with other polymers in 3D printing is essential for improving its properties, enhancing printability, reducing war page, designing properties to specific needs, and achieving cost-effective solutions. This approach allows for the optimization of PP-based materials for a wide range of additive manufacturing applications[40].

2.4 Blending Polypropylene with Polylactic Acid (PLA)

2.4.1 Polylactic acid (PLA)

PLA is a thermoplastic polymer that is biobased and biodegradable. It is the most cost-effective biopolymer with the maximum manufacturing capacity. The ring-opening lactide polymerization or lactic acid's direct condensation polymerization are used to produce PLA. The fermentation of carbohydrates found in tapioca, sugarcane, or maize starch yields the raw

ingredient, lactic acid monomer. PLA has become more popular commercially as an alternative to polymers derived from petroleum[41], [42].

Its use in FDM is growing because of several reasons[40], including:

i) Good printability, which is demonstrated by less warping and cracking, no smell released during the FDM process, and a lower melting temperature than ABS.

ii) Environmental friendliness: Because PLA filament is renewable, biodegradable, and compostable, it may be used in FDM to solve waste issues and make 3D printing more accessible to a wider range of people.

iii) Superior mechanical qualities of 3D-printed components over conventional petrochemical polymers, such as increased elastic modulus and tensile strength.

While PLA offers various advantages, its adoption is not as extensive as conventional plastics due to higher costs and lower durability[43]. Efforts have been made to enhance PLA's mechanical properties and reduce expenses by exploring the incorporation of fibres, filler[44]s, and cellulose nanofibres[45] in the form of biocomposite blends[46].

2.4.2 PLA/PP blends for FDM application

The focus of the search for sustainable solutions has turned to creative applications of recycled materials. Of particular note is the possibility of using waste polypropylene to produce 3D printing-compatible filaments, which gives a viable solution to the problems associated with plastic waste and the need for environmentally friendly production methods Several thermoplastic blends have been investigated for enhancing functionality in 3D printing applications. However, there is limited prior research showcasing the 3D printing of filaments made from a blend of PP and PLA. Evaluations of 3D-printed blends' mechanical, chemical, thermal, and biodegradable qualities have been conducted regularly. The studies suggested that polymer blends displaying thermodynamic immiscibility could potentially serve as viable sources of filament for 3D printing, provided they exhibit acceptable printability. Additionally, the researchers proposed that the deficient printing performance of PP might be enhanced by blending it with a material characterized by high printability, such as PLA.

Choe et al. [47] evaluated the biodegradation behavior of 3D-printed prototypes, which were manufactured from various plastic blends. The materials included biodegradable polylactic acid (PLA), poly(3-hydroxybutyrate) (PHB), non-biodegradable high-density polyethylene (HDPE), and polypropylene (PP). The prototyping process involved creating letter-shaped specimens through fused deposition modeling (FDM) printing, utilizing various filaments such as PLA, PHB, HDPE, PP, PLA/HDPE, PLA/PP, PHB/HDPE, PHB/PP, and PLA/PHB. The study comprehensively assessed the printing performance and optimal printing conditions for these filaments. It is noteworthy that the FDM 3D printing of PP has traditionally presented challenges attributed to issues like poor adhesion, warping deformation, and crystallization-induced volume contraction. Nevertheless, the research demonstrated that PLA/PP blends exhibited improved printability under the given conditions.

The PLA and PP pellets were combined in weight ratios of 8:2, 5:5, and 2:8. The PLA/PP blends exhibited enhanced elongation at failure in comparison to neat PLA, with the most favorable outcomes observed for the 5:5 weight ratio blend. Specifically, the elongation at failure for PLA100 was 2.6%, whereas a significant improvement was observed for PLA50/PP50 (31.1%). However, there was a notable decrease in tensile strength from 53.2 to 15.2 and 16.2 MPa, respectively. The presence of ductile PP within the brittle PLA matrix acted as a site for stress concentration, allowing energy absorption through mechanical deformation and thereby increasing elongation. The reduction in tensile strength is attributed to a potential decline in interfacial bond strength. The thermal properties of the PLA/PP blends were also investigated, revealing a decrease in the glass transition temperature (Tg) of the blends with increasing PP content. The Tg for PLA100 was 60.5 °C, which decreased to 56.5 and 53.5 °C for PLA80/PP20 and PLA50/PP50, respectively. Overall, the study indicated that the mechanical and thermal characteristics of the PLA/PP blend, especially in the 5:5 weight ratio, were promising, implying that it may be a good option for several 3D printing applications.

In their study on bamboo fibre-reinforced polypropylene/polylactic acid composites, Long et al. [48]The findings revealed that the addition of polypropylene and bamboo fibre increased the elongation at break compared to pure PLA printed specimens, with silane treatment notably enhancing tensile strength. The study additionally highlights the commonly employed method in composite materials—the use of compatibilizers, such as maleated

polypropylene (MAPP), to improve compatibility between the fibre and polymer matrix. Furthermore, it was shown that surface alterations comprising silane and alkali treatments on bamboo fibres were efficient ways to enhance interfacial adhesion with the polymer matrix, leading to increased mechanical characteristics.

The study's conclusion states that when creating reinforced polymer composites for 3D printing applications, the concepts and methods shown here are transferable and adaptable to other natural fibres like jute, hemp, or flax. Researchers can improve the mechanical and thermal characteristics of a variety of natural fibre composites for use in additive manufacturing by optimizing surface treatments and adding appropriate compatibilizers.

2.5 Integrating natural fibre as reinforcement in 3D printing filament

In the domain of additive manufacturing, the use of natural fibres in Fused Deposition Modeling (FDM) has become a promising option[49]. The main construction material for FDM, a common 3D printing process, has historically been synthetic polymers. However, the addition of natural fibres to FDM methods brings about a paradigm change by providing a viable substitute that could even be good for the environment[50], [51]. This novel method not only solves material sustainability issues but also creates new opportunities to improve mechanical qualities and expand the range of applications for 3D-printed items. In this investigation, we examine the ramifications and developments related to the incorporation of natural fibres into FDM, examining the challenges prospects, and revolutionary influence on the field of additive manufacturing[52], [53], [54].

Table **2.2** presents a comprehensive overview of various studies investigating the impact of incorporating natural fibres into PLA or rPP matrices, outlining the research objectives, fibre types, ratios employed, and key findings.

Table 2.2: Overview of PLA and rPP biocomposites filled with different natural fibres for FDM application.

Matrix	Natural fibre	Filler content (wt.%)	Properties	Ref
PLA	Kenaf	3,5,7	The fatigue life increases as the amount of powder loading increases from 0 wt. % up to 7 wt	[55]
PLA	Hemp	10-40	Mechanical properties decreased	[56]
PLA	Kenaf	2.5	2.0% silane concentration exhibits lower strength compared to 1.0%	[57]
PLA	Rice Straw Powder	1	improve the overall performance of the composites, and combination pretreatment	[58]
PLA	Wood/Bamboo/Cork	30	effect of # infilling and # fibre have a similar effect on mechanical properties	[59]
rPP	Rice husk	5, 10	no significant change in the properties between 5% to 10%, except for water absorption	[60]
rPP	Wood Dust fibre	24	# chemical treatmenthas a significant impact on the yield of several mechanical, physical, Thermalproperties	[61]
rPP	waste paper/ cardboard/ wood flour	5,10,20	Dynamic mechanical Increased 20–30% in storage modulus.	[62]

Integrating fibres into 3D printing filament can offer several advantages, including:

- Enhanced Mechanical Properties: The stiffness, strength, and toughness of 3D printed components are all greatly increased with the inclusion of fibres. This reinforcement takes place when the polymer matrix is strengthened by the fibres, improving load distribution and breaking and deformation resistance.
- Personalized Properties: The characteristics of 3D printed items may be altered by changing the kind, amount, and orientation of fibres. The capacity to customize materials makes it possible to create distinctive materials with particular qualities that work well for a variety of applications[55].
- Cost Efficiency: By lowering the volume of polymer material needed to achieve specified mechanical qualities, fibre integration helps to save costs in 3D printing. Less polymer material is needed because of the reinforcing that fibres give.
- Sustainability: By using natural fibres instead of synthetic ones, 3D printing has a less negative effect on the environment. Compared to synthetic fibres, natural fibres have a reduced carbon impact, are renewable, and biodegradable.

All things considered, adding fibres turns out to be a viable tactic for improving the mechanical qualities of 3D-printed items, tailoring their features, cutting prices, and promoting sustainability.

2.6 limitations and challenges

Incorporating fibres into 3D printing materials presents various limitations and challenges that must be addressed for successful integration and to unlock the full potential of enhancing mechanical properties and broadening application possibilities. Firstly, the printability of the composite is a concern. The addition of fibres can lead to issues such as nozzle clogging, uneven extrusion, and poor layer adhesion, resulting in printing defects and a decline in part quality[63], [64]. Precise control over fibre orientation during the 3D printing process poses another challenge. Achieving optimal mechanical properties requires accurate alignment of fibres, especially in intricate geometries, which can be difficult to achieve[65], [66].

Ensuring the homogeneous distribution of fibres within the printing material is crucial for consistent mechanical properties. However, achieving uniform dispersion throughout the polymer matrix proves challenging, leading to variations in material properties[67], [68].

The selection of appropriate processing parameters, including printing temperature[69], speed[70], [71], and layer height[71], is critical for successfully 3D printing fibre-reinforced composites. Striking the right balance to accommodate fibres without compromising print quality is a complex task. Additionally, achieving strong interfacial bonding between fibres and the polymer matrix is essential for optimal mechanical performance. However, establishing good adhesion, particularly with natural fibres, can be challenging due to their inherent variability and surface characteristics[72], [73], [74].

Addressing these challenges is imperative to fully harness the benefits of fibre incorporation into 3D printing materials and to realize their potential in enhancing mechanical properties and expanding the scope of applications.

References

[1] H. A. Maddah, “Polypropylene as a Promising Plastic: A Review,” Am. J. Polym. Sci., vol. 6, no. 1, pp. 1–11, 2016.

[2] ADEDIRAN, A. Adeolu, AKINWANDE, A. Abayomi A, BALOGUN, A. Oluwatosin, et al., “Mechanical and optimization studies of polypropylene hybrid biocomposites,” Sci. Rep., vol. 12, no. 1, Art. no. 1, Feb. 2022, doi: 10.1038/s41598-022-06304-6.

[3] A. Alsabri, F. Tahir, and S. G. Al-Ghamdi, “Environmental impacts of polypropylene (PP) production and prospects of its recycling in the GCC region,” Mater. Today Proc., vol. 56, pp. 2245–2251, Jan. 2022, doi: 10.1016/j.matpr.2021.11.574.

[4] K. L. Pickering, M. G. A. Efendy, and T. M. Le, “A review of recent developments in natural fibre composites and their mechanical performance,” Compos. Part Appl. Sci. Manuf., vol. 83, pp. 98–112, Apr. 2016, doi: 10.1016/j.compositesa.2015.08.038.

[5] A. Abdennadher, “Injection Moulding of Natural Fibre Reinforced Polypropylene: Process, Microstructure and Properties,” phd thesis, Ecole Nationale Supérieure des Mines de Paris, 2015.

[6] SANCHEZ, Fabio A. Cruz, BOUDAOUD, Hakim, CAMARGO, Mauricio, "Plastic recycling in additive manufacturing: A systematic literature review and opportunities for the circular economy". Journal of Cleaner Production, vol. 264, p. 121602,2020.

[7] J. Karger-Kocsis and T. Bárány, Eds., "Polypropylene Handbook: Morphology, Blends and Composites.", Cham, 2019. doi: 10.1007/978-3-030-12903-3.

[8] A. Calhoun, “3 - Polypropylene,” Multilayer Flexible Packaging , pp. 35–45, 2016, doi: 10.1016/B978-0-323-37100-1.00003-X.

[9] “Polypropylene Market Size, Analysis | Global Report, 2030.” Accessed: Feb. 05, 2024. [Online]. Available: https://www.chemanalyst.com/industry-report/polypropylene-pp-market-640

[10] “Polypropylene market” Accessed: Feb. 01, 2024. [Online]. Available: https://www.precedenceresearch.com/polypropylenemarket#:~:text=The%20global%20polypropylene%20market%20size,5.3%25%20from%202023%20to%202032.

[11] AYELERU, O. Olaitan, DLOVA, Sisanda, AKINRIBIDE, O. Jeremiah., “Challenges of plastic waste generation and management in sub-Saharan Africa: A review,” Waste Manag., vol. 110, pp. 24–42, Jun. 2020, doi: 10.1016/j.wasman.2020.04.017.

[12] C. I. Idumah and I. C. Nwuzor, “Novel trends in plastic waste management,” SN Appl. Sci., vol. 1, no. 11, p. 1402, Oct. 2019, doi: 10.1007/s42452-019-1468-2.

[13] WATT, Ethan, PICARD, Maisyn, MALDONADO, Benjamin, “Ocean plastics: environmental implications and potential routes for mitigation – a perspective,” RSC Adv., vol. 11, pp. 21447–21462, Jun. 2021, doi: 10.1039/D1RA00353D.

[14] Z. S. Mazhandu and E. Muzenda, “Global Plastic Waste Pollution Challenges and Management,” in 2019 7th International Renewable and Sustainable Energy Conference (IRSEC), Nov. 2019, pp. 1–8. doi: 10.1109/IRSEC48032.2019.9078268.

[15] MAZHANDU, Zvanaka S., MUZENDA, Edison, MAMVURA, Tirivaviri A., et al. "Integrated and consolidated review of plastic waste management and bio-based biodegradable plastics: Challenges and opportunities". Sustainability, vol. 12, no 20, p. 8360, 2020.

[16] VOLLMER, Ina, JENKS, Michael JF, ROELANDS, Mark CP, et al. "Beyond mechanical recycling: Giving new life to plastic waste". Angewandte Chemie International Edition, vol. 59, no 36, p. 15402-15423, 2020.

[17] “Recycling and the future of the plastics industry | McKinsey.” Accessed: Feb. 03, 2024. [Online]. Available: https://www.mckinsey.com/industries/chemicals/our-insights/how-plastics-waste-recycling-could-transform-the-chemical-industry

[18] L. Shen and E. Worrell, “Chapter 31 - Plastic recycling,” in Handbook of Recycling (Second Edition), C. Meskers, E. Worrell, and M. A. Reuter, Eds., Elsevier, 2024, pp. 497–510. doi: 10.1016/B978-0-323-85514-3.00014-2.

[19] M. Z. Shiferaw and H. S. Gebremedhen, “Recycled Polymer for FDM 3D Printing Filament Material: Circular Economy for Sustainability of Additive Manufacturing,” Advances of Science and Technology, pp. 243–261,2022,doi: 10.1007/978-3-030-93712-6_17.

[20] BHAGIA, Samarthya, BORNANI, Kamlesh, AGRAWAL, Ruchi, “Critical review of FDM 3D printing of PLA biocomposites filled with biomass resources, characterization,

biodegradability, upcycling and opportunities for biorefineries," Appl. Mater. Today, vol. 24, p. 101078, Sep. 2021, doi: 10.1016/j.apmt.2021.101078.

[21] S. C. Altıparmak, V. A. Yardley, Z. Shi, and J. Lin, "Extrusion-based additive manufacturing technologies: State of the art and future perspectives," J. Manuf. Process., vol. 83, pp. 607–636, Nov. 2022, doi: 10.1016/j.jmapro.2022.09.032.

[22] EDGAR, Jonathan , TINT, Saxon, "Additive manufacturing technologies: 3D printing, rapid prototyping, and direct digital manufacturing", Johnson Matthey Technology Review, vol. 59, no 3, p. 193-198,2015.

[23] Hashmi, M. Saleem J. "Comprehensive materials processin", Newnes, 2014.

[24] B. Kianian, Wohlers Report 2017: 3D Printing and Additive Manufacturing State of the Industry, Annual Worldwide Progress Report: Chapters titles: The Middle East, and other countries. FORT COLLINS, COLORADO, USA: Wohlers Associates, Inc., 2017. Accessed: Feb. 03, 2024. [Online]. Available: https://wohlersassociates.com/2017report.htm

[25] GOLAB, Mark, MASSEY, Sam, and MOULTRIE, James," How generalisable are material extrusion additive manufacturing parameter optimisation studies? A systematic review", Heliyon, vol. 8, no 11, 2022.

[26] REITER, Martin, MIRON, Veronika M., LÄMMERMANN, Sebastian," Comparing the mechanical properties of additively manufactured post-consumer polypropylene to injection molded specimens," Materials Today: Proceedings, vol. 70, p. 55-60, 2022.

[27] W. M. H. Verbeeten, M. Lorenzo-Bañuelos, and P. J. Arribas-Subiñas, "Anisotropic rate-dependent mechanical behavior of Poly(Lactic Acid) processed by Material Extrusion Additive Manufacturing," Addit. Manuf., vol. 31, p. 100968, Jan. 2020, doi: 10.1016/j.addma.2019.100968.

[28] G. Papazetis, "Extrusion based Additive Manufacturing: Trajectory Design and Material Deposition Optimisation," Jul. 2020, doi: 10.26240/heal.ntua.18612.

[29] C. Abeykoon, P. Sri-Amphorn, and A. Fernando, "Optimization of fused deposition modeling parameters for improved PLA and ABS 3D printed structures," Int. J. Lightweight Mater. Manuf., vol. 3, no. 3, pp. 284–297, Sep. 2020, doi: 10.1016/j.ijlmm.2020.03.003.

[30] M. Kumar,R. Ramakrishnan, “Effect of Fused Filament Fabrication Parameters and Tetrabromobisphenol-A/Microcrystalline Cellulose Additives on the Dynamic Mechanical Behavior of Polycarbonate/Acrylonitrile–Butadiene–Styrene Blends for Precision Structures,” J. Mater. Eng. Perform., Jul. 2022, doi: 10.1007/s11665-022-07143-2.

[31] H. S. Ashrith, T. P. Jeevan, H. G. V. Divya, “3D Printing of Crystalline Polymers,” in Polymer Crystallization, John Wiley & Sons, Ltd, 2023, pp. 233–254. doi: 10.1002/9783527839247.ch9.

[32] S. Wickramasinghe, T. Do, and P. Tran, “FDM-Based 3D Printing of Polymer and Associated Composite: A Review on Mechanical Properties, Defects and Treatments,” Polymers, vol. 12, no. 7, Art. no. 7, Jul. 2020, doi: 10.3390/polym12071529.

[33] T. Swetham, K. M. M. Reddy, A. Huggi, and M. N. Kumar, “A Critical Review on of 3D Printing Materials and Details of Materials used in FDM,” Int. J. Sci. Res. Sci. Eng. Technol., vol. 3, no. 2, pp. 353–361, Mar. 2017, doi: 10.32628/IJSRSET173299.

[34] G. Nyiranzeyimana, J. m. Mutua, B. r. Mose,T. o. Mbuya, “Optimization of process parameters in fused deposition modelling of thermoplastics: A review,” Mater. Werkst., vol. 52, no. 6, pp. 682–694, 2021, doi: 10.1002/mawe.202000193.

[35] M. Spoerk, C. Holzer, J. Gonzalez-Gutierrez, “Material extrusion-based additive manufacturing of polypropylene: A review on how to improve dimensional inaccuracy and warpage,” J. Appl. Polym. Sci., vol. 137, no. 12, p. 48545, 2020, doi: 10.1002/app.48545.

[36] N. E. Zander, M. Gillan, Z. Burckhard, F. Gardea, “Recycled polypropylene blends as novel 3D printing materials,” Addit. Manuf., vol. 25, pp. 122–130, Jan. 2019, doi: 10.1016/j.addma.2018.11.009.

[37] M. Bertolino, D. Battegazzore, R. Arrigo, A. Frache, “Designing 3D printable polypropylene: Material and process optimisation through rheology,” Addit. Manuf., vol. 40, p. 101944, Apr. 2021, doi: 10.1016/j.addma.2021.101944.

[38] M. Jin, C. Neuber,H.-W. Schmidt, “Tailoring polypropylene for extrusion-based additive manufacturing,” Addit. Manuf., vol. 33, p. 101101, May 2020, doi: 10.1016/j.addma.2020.101101.

[39] IFTEKAR, Syed Fouzan, AABID, Abdul, AMIR, Adibah," Advancements and limitations in 3D printing materials and technologies: a critical review.", Polymers, vol. 15, no 11, p. 2519, 2023.

[40] T. M. Joseph , “3D printing of polylactic acid: recent advances and opportunities,” Int. J. Adv. Manuf. Technol., vol. 125, no. 3, pp. 1015–1035, Mar. 2023, doi: 10.1007/s00170-022-10795-y.

[41] Y. Wu, X. Gao, J. Wu, T. Zhou, T. T. Nguyen, and Y. Wang, “Biodegradable Polylactic Acid and Its Composites: Characteristics, Processing, and Sustainable Applications in Sports,” Polymers, vol. 15, no. 14, Art. no. 14, Jan. 2023, doi: 10.3390/polym15143096.

[42] J. Prendiz, J. Vega-Baudrit, and M. Mena, “Polylactic Acid (PLA) As A Bioplastic And Its Possible Applications In The Food Industry,” Food Sci. Nutr., vol. 5, Oct. 2019, doi: 10.24966/FSN-1076/100048.

[43] BIKIARIS, D. Nikolaos, KOUMENTAKOU, Ioanna, SAMIOTAKI, Christina," Recent advances in the investigation of poly (lactic acid)(PLA) nanocomposites: incorporation of various nanofillers and their properties and applications.", Polymers, vol. 15, no 5, p. 1196, 2023.

[44] M. R. Foruzanmehr, P. Vuillaume, S. Elkoun,M. Robert, “Physical and mechanical properties of PLA composites reinforced by TiO2 grafted flax fibres,” Mater. Des., vol. 106, May 2016, doi: 10.1016/j.matdes.2016.05.103.

[45] A. Frone, S. Berlioz, J. F. Chailan, D. Panaitescu, “Morphology and thermal properties of PLA-cellulose nanofibres composites,” Carbohydr. Polym., vol. 91, pp. 377–84, Jan. 2013, doi: 10.1016/j.carbpol.2012.08.054.

[46] A. Z. Naser, I. Deiab, F. Defersha, S. Yang, “Expanding Poly(lactic acid) (PLA) and Polyhydroxyalkanoates (PHAs) Applications: A Review on Modifications and Effects,” Polymers, vol. 13, no. 23, p. 4271, Dec. 2021, doi: 10.3390/polym13234271.

[47] CHOE, Shinhyeong, KIM, Yujin, PARK, Geunyong., “Biodegradation of 3D-Printed Biodegradable/Non-biodegradable Plastic Blends,” ACS Appl. Polym. Mater., vol. 4, no. 7, pp. 5077–5090, Jul. 2022, doi: 10.1021/acsapm.2c00600.

[48] H. LONG, Haibo, WU, Zhiqiang, DONG, Qianqian, “Mechanical and thermal properties of bamboo fibre reinforced polypropylene/polylactic acid composites for 3D printing,” Polym. Eng. Sci., vol. 59, no. s2, pp. E247–E260, 2019, doi: 10.1002/pen.25043.

[49] H. J. Aida, R. Nadlene, M. T. Mastura, L. Yusriah, D. Sivakumar, R. A. Ilyas, “Natural fibre filament for Fused Deposition Modelling (FDM): a review,” Int. J. Sustain. Eng., vol. 14, no. 6, pp. 1988–2008, Nov. 2021, doi: 10.1080/19397038.2021.1962426.

[50] MAZZANTI, Valentina, MALAGUTTI, Lorenzo, and MOLLICA, Francesco," FDM 3D printing of polymers containing natural fillers: A review of their mechanical properties.", Polymers, vol. 11, no 7, p. 1094, 2019.

[51] T. N. A. Tuan Rahim, A. Abdullah, H. Md Akil, “Recent Developments in Fused Deposition Modeling-Based 3D Printing of Polymers and Their Composites,” Polym. Rev., vol. 59, pp. 1–36, Apr. 2019, doi: 10.1080/15583724.2019.1597883.

[52] N. R. Rajendran Royan, J. S. Leong, W. N. Chan, J. R. Tan, Z. S. B. Shamsuddin, “Current State and Challenges of Natural Fibre-Reinforced Polymer Composites as Feeder in FDM-Based 3D Printing,” Polymers, vol. 13, no. 14, Art. no. 14, Jan. 2021, doi: 10.3390/polym13142289.

[53] C. H. Lee, F. N. B. M. Padzil, S. H. Lee, Z. M. A. Ainun, L. C. Abdullah, “Potential for Natural Fibre Reinforcement in PLA Polymer Filaments for Fused Deposition Modeling (FDM) Additive Manufacturing: A Review,” Polymers, vol. 13, no. 9, Art. no. 9, Jan. 2021, doi: 10.3390/polym13091407.

[54] S. C. Daminabo, S. Goel, S. A. Grammatikos, H. Y. Nezhad, V. K. Thakur, “Fused deposition modeling-based additive manufacturing (3D printing): techniques for polymer material systems,” Mater. Today Chem., vol. 16, p. 100248, Jun. 2020, doi: 10.1016/j.mtchem.2020.100248.

[55] SHAHAR, F. Syazwani, SULTAN, M. T. Hameed, SAFRI, S. N. Azrie," Fatigue and impact properties of 3D printed PLA reinforced with kenaf particles.", Journal of materials research and technology, vol. 16, p. 461-470, 2022.

[56] X. Xiao, V. S. Chevali, P. Song, D. He, H. Wang, “Polylactide/hemp hurd biocomposites as sustainable 3D printing feedstock,” Compos. Sci. Technol., vol. 184, p. 107887, Nov. 2019, doi: 10.1016/j.compscitech.2019.107887.

[57] A. H. Jamadi, N. Razali, M. Petrů, M. M. Taha, N. Muhammad, R. A. Ilyas, “Effect of Chemically Treated Kenaf Fibre on Mechanical and Thermal Properties of PLA Composites Prepared through Fused Deposition Modeling (FDM),” Polymers, vol. 13, no. 19, Art. no. 19, Jan. 2021, doi: 10.3390/polym13193299.

[58] YU, Wangwang, DONG, Lili, LEI, Wen," Effects of rice straw powder (RSP) size and pretreatment on properties of FDM 3D-printed RSP/poly (lactic acid) biocomposites.", Molecules, vol. 26, no 11, p. 3234, 2021.

[59] MAZUR, Karolina E., BORUCKA, Aleksandra, KACZOR, Paulina," Mechanical, thermal and microstructural characteristic of 3D printed polylactide composites with natural fibres: wood, bamboo and cork.", Journal of Polymers and the Environment, vol. 30, no 6, p. 2341-2354, 2022.

[60] M. A. Morales, C. L. Atencio Martinez, A. Maranon, C. Hernandez, V. Michaud, and A. Porras, “Development and Characterization of Rice Husk and Recycled Polypropylene Composite Filaments for 3D Printing,” Polymers, vol. 13, no. 7, Art. no. 7, Jan. 2021, doi: 10.3390/polym13071067.

[61] NAFIS, Z. A. S., NUZAIMAH, M., KUDUS, SI Abdul., “Effect of Wood Dust Fibre Treatments Reinforcement on the Properties of Recycled Polypropylene Composite (r-WoPPC) Filament for Fused Deposition Modelling (FDM),” Materials, vol. 16, no. 2, Art. no. 2, Jan. 2023, doi: 10.3390/ma16020479.

[62] N. E. Zander, J. H. Park, Z. R. Boelter, and M. A. Gillan, “Recycled Cellulose Polypropylene Composite Feedstocks for Material Extrusion Additive Manufacturing,” ACS Omega, vol. 4, no. 9, pp. 13879–13888, Aug. 2019, doi: 10.1021/acsomega.9b01564.

[63] N. V. Santos and D. C. T. Cardoso, “3D printing of vegetable yarn-reinforced polymer components,” J. Clean. Prod., vol. 415, p. 137870, Aug. 2023, doi: 10.1016/j.jclepro.2023.137870.

[64] A. Sola, “Materials Requirements in Fused Filament Fabrication: A Framework for the Design of Next-Generation 3D Printable Thermoplastics and Composites,” Macromol. Mater. Eng., vol. 307, no. 10, p. 2200197, 2022, doi: 10.1002/mame.202200197.

[65] C. Armstrong, N. Todd, A. Alsharhan, D. Bigio, and R. Sochol, “A 3D Printed Morphing Nozzle to Control Fibre Orientation during Composite Additive Manufacturing,” Adv. Mater. Technol., vol. 6, p. 2000829, Nov. 2020, doi: 10.1002/admt.202000829.

[66] D. Battini, L. Giorleo, and A. Avanzini, “Effects of fibre layout on strength and failure of 3D printed notched composites,” Compos. Struct., vol. 327, p. 117644, Jan. 2024, doi: 10.1016/j.compstruct.2023.117644.

[67] M. Robakowska, I. Gibson, R. Akkerman, F. R. Wurm,H. Gojzewski, “Towards more homogeneous character in 3D printed photopolymers by the addition of nanofillers,” Polym. Test., vol. 129, p. 108243, Dec. 2023, doi: 10.1016/j.polymertesting.2023.108243.

[68] WANG, Xin, JIANG, Man, ZHOU, Zuowan," 3D printing of polymer matrix composites: A review and prospective.", Composites Part B: Engineering, vol. 110, p. 442-458, 2017.

[69] DICKSON, N. Andrew, ABOURAYANA, M. Hisham, DOWLING, P. Denis," 3D printing of fibre-reinforced thermoplastic composites using fused filament fabrication—A review.", Polymers, vol. 12, no 10, p. 2188, 2020.

[70] PRABHAKAR, M. Manoj, SARAVANAN, A. K., LENIN, A. Haiter," A short review on 3D printing methods, process parameters and materials.", Materials Today: Proceedings, vol. 45, p. 6108-6114, 2021.

[71] S. Valvez, A. P. Silva, P. N. B. Reis, “Optimization of Printing Parameters to Maximize the Mechanical Properties of 3D-Printed PETG-Based Parts,” Polymers, vol. 14, no. 13, p. 2564, Jun. 2022, doi: 10.3390/polym14132564.

[72] Y. Zhou, M. Fan, L. Chen, “Interface and bonding mechanisms of plant fibre composites: An overview,” Compos. Part B Eng., vol. 101, pp. 31–45, Sep. 2016, doi: 10.1016/j.compositesb.2016.06.055.

[73] HUANG, Silu, FU, Qiuni, YAN, Libo," Characterization of interfacial properties between fibre and polymer matrix in composite materials–A critical review.", Journal of Materials Research and Technology, vol. 13, p. 1441-1484, 2021.

[74] MOHAMMED, Mohammed Muhanna, RASIDI, M., MOHAMMED, Aeshah M., “Interfacial Bonding Mechanisms of Natural Fibre-Matrix Composites: An Overview,” BioResources, vol. 17, Aug. 2022, doi: 10.15376/biores.17.4.Mohammed.

CHAPTER 3: METHODOLOGY

3.1 Research workflow

The research workflow for this study is outlined in **Figure 3.1**, providing a schematic overview of the background experimental methods employed to achieve the research objectives. The initial step involves chemical modification and preparing Arundo fibre, where FTIR, morphology, and thermal properties are examined to assess the impact of chemical modification.

The second step involves producing and characterizing PLA/PP/Arundo fibre biocomposite pellets to study the effect of fibre treatment on the properties of the biocomposites. The analysis includes evaluating melt flow and thermal properties.

Moving on to the third step, the biocomposite pellets are extruded into standard filament for quality assessment and FDM-printed as ASTM-standard specimens for further examination. This phase involves investigating the interface morphology, mechanical properties, and water absorption of the FDM-printed items.

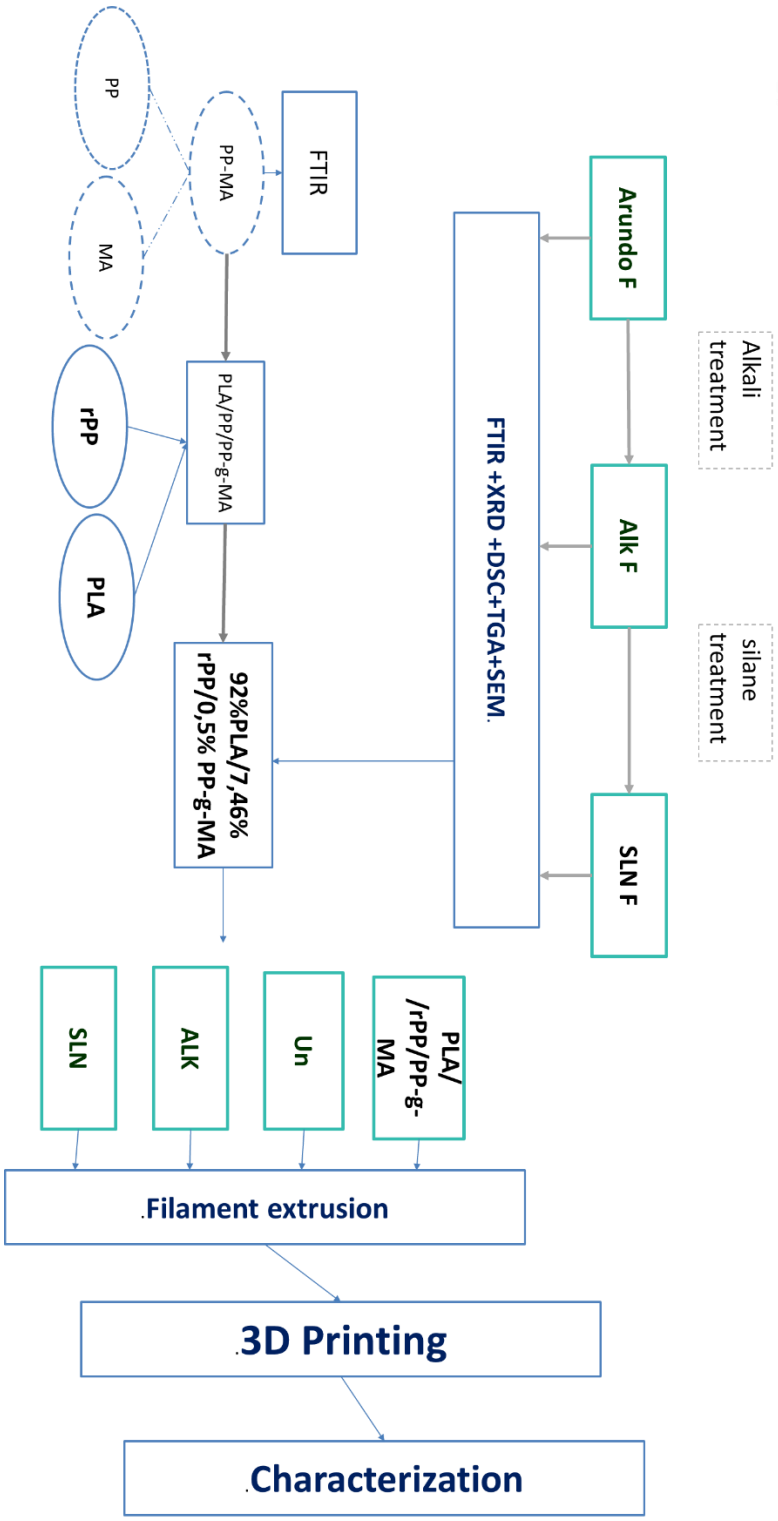


Fig. 3.1 Diagram of the experimental framework of this research work.

3.2 Materials

3.2.1 Arundo donax L.

Arundo donax L. is a large perennial grass that belongs to the Poaceae family and is commonly known as giant reed or Spanish cane. It has notoriously fast growth and can reach up to 10 meters in height with stems that are up to 5 centimeters wide. This plant is native to Mediterranean regions but has been introduced all over the world as an ornamental plant, for erosion control, biomass production, and even musical instruments such as pipes and harps have been made from its hollow stems. Its potential as a reinforcing agent is highlighted by recent research, making it an important resource for industrial and sustainable uses. The Arundo donax L. plant is displayed in **Figure 3.3 a**, and **Table 3.1** lists some of its compositions and characteristics.

Table 3.1 Arundo donax L. compositions and its properties [1].

Fibre	Tensile strength (MPa)	Young's modulus(GPa)	Elongation at break (%)	Density (g/cm³)	T_{onset} (°C)	Cellulose (wt.%)	Hemicellulose (wt.%)	Lignin (wt.%)	Ash (wt.%)
Arundo clum	248	9.4	3.24	1.168	275	43.2	20.5	17.2	1.9
Bamboo	140-230	11-17	-	0.60-1.10	214	26-43	30	21-31	-

3.2.2 polypropylene waste

Granules of recycled polypropylene (rPP) were employed as a sustainable substitute for virgin plastic products, effectively decreasing the volume of plastic waste entering landfills. Specifically, industrial waste of polypropylene sheet.

3.2.3 PolyLactic Acid (PLA)

The PLA used in this study is a NatureWorks LLC product, known under the trade name Ingeo 2003D, it is a resin made from annually renewable resources for use in food packaging. Transparent general-purpose extrusion grade Ingeo bio-polymer 2003D can be used on its own or in a blended product. This PLA has a high molecular weight and can be processed with ease using standard extrusion machinery, granule form, and its different characteristics are mentioned in **Table 3.2**.

Table 3.2 PLA physical and mechanical properties.

Physical Properties	**Ingeo 2003D**
Specific Gravity /D792	1.24
MFR, g/10 min (210°C, 2.16 Kg) /D1238	6
Mechanical Properties	
Tensile Strength break ,MPa /D882	53
Tensile Yield Strength ,MPa /D882	60
Tensile Modulus ,GPa /D882	3.5
Tensile Elongation ,% /D882	6
Notched Izod Impact , J/m /D256	16
Heat Distortion Temperature, °C/ E2092	55

3.2.4. Compatibilizers

3.2.4.1 polypropylene

The maleated polypropylene was created using an injection-grade copolymer polypropylene. With an MFR value of 20 g/10min (190°C, 2.16 kg), this Borouge product exhibits a superb balance between stiffness and impact strength.

3.2.4.2 Dicumyl peroxide

The peroxide used to functionalize PP is dicumyl peroxide (DCP) which is presenting in the form of a white crystalline solid.

3.2.4.3 Maleic anhydride (MA)

The maleic anhydride used in this study to prepare PP-g-AM by Panreac. with M.= 98.06, white to transparent crystals.

3.2.5 Sodium Hydroxide (NaOH):

Sodium hydroxide pellets were manufactured by Quality Reagent Chemicals (QReC) for experimental, research, and industrial purposes, exhibiting a specific gravity of 2.13 and a molecular weight of 40 g/mol; Grade: AR.

3.2.6 silane coupling agent (n-octyltriethoxy):

N-octyltriethoxysilane, IUPAC name triethoxy(octyl)silane, is a product of Thermo Scientific.It has a molecular weight of 276.49 g/mol and a purity level of 97%. Its chemical structure is shown in Figure **3.2** and its molecular formula is C14H32O3Si.

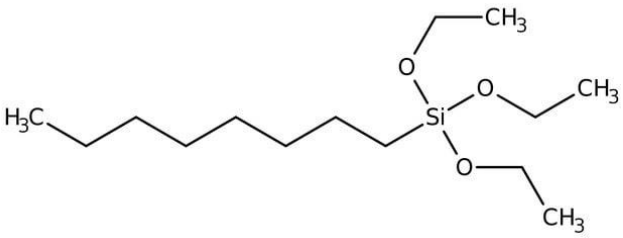


Fig.3.2 N-octyltriethoxysilane chemical structure.

3.3 Methodology

3.3.1 Fibre preparation

The stems were separated from the leaves and cleaned by tapping to remove any visible dirt. Next, the stems were chopped into small pieces using pruning shears to ensure they could fit through the lab crusher, where it was crushed and later sieved under 250 µm.

Fig.3.3 Fibre preparation: (a) Arundo donax L. plant, (b) Arundo steams, (c) Alkali-treated ArF, and (d) Silane-treated ArF.

3.3.2 Alkaline treatment

The sieved Arundo fibre was first treated with hot water at 100° C for 1h, then washed and dried overnight at 60°C. Second, the treated ArF was dipped in a 5 % NaOH solution for 3 hours at ambient temperatures with agitation. The mass ratio of ArF to NaOH was 1:15. Subsequently, the ArF solution was filtered, neutralized with distilled water, and dried overnight at 60°C.

3.3.3 Silane treatment

Initially, a 5% silane coupling agent and ethanol solution (9:1 ethanol/water mass ratio) were combined. The alkali-treated Around fibres (A-ArF) were added to the prepared solution. The silane coupling agent's dry mass ratio to the A-ArF was set at 1:50. At ambient temperature, the mixture was agitated for 3 hours[2]. The silane treated fibre was dried for 24 hours at 105°C. Finally, all fibres, both untreated and treated, were sealed in a plastic bag and stored in a dry location for future processing.

3.3.4 Maleated polypropylene (PPgMA) preparation:

In an internal mixer of the Brabender type with a 60 cm3 mixing chamber, the compatibilizing agent PP-g-AM was synthesized. Therefore, for sevn minutes, PP was combined with 7 and 1 phr maleic anhydride and DCP, respectively, at 180°C and 40 rpm of speed. The PP-g-AM was then pulverized in a mill of the Brabende type. An FTIR analysis validated the synthesis of maleated polypropylene (PPgMA).

3.3.5 Blending stage

A blend of 3 wt. % of fibre (Unmodified or modified ArF), 96.5 wt.% (92.5: 7.5) PLA: PP, and 0.5 wt. % PP-g-MA was achieved using a Brabender at 180 °C, V= 50rpm, for 8 min. The composites were then granulated through the smallest crusher sieve. This step significantly influences the filament's quality and diameter, with finer grains resulting in more uniform filament extrusion. Composites terminology and abbreviation are mentioned in **Table 3.3.**

Table 3.3 Nomenclature of composites based on weight % and treatment.

	PLA (wt.%)	PP (wt.%)	PP-g-MA (wt.%)	ArF (wt.%)
PLA/PP	92.0375	7.4625	0.5	0
Un	89.2625	7.2375	0.5	3 (untreated)
Alk	89.2625	7.2375	0.5	3 (Alkali treated)
SLN	89.2625	7.2375	0.5	3 (Alkali+ 5% silane)

3.3.6 Filament extrusion stage

The preceding stage's ArF/PLA/PP pellets were dried at 60°C for 1 hour before being fed into a mini filament extruder of a 1.75 mm nozzle head diameter (Well zoom C). For all materials, the two extrusion zone temperatures were kept at 170°C- 175°C.Whereas The speed was adjusted based on filament flow and diameter consistency. The ArF/PLA/PP filament was cooled in two steps, first with air, then with water. Thereafter, these filaments were employed to print the specimens used in the traction, impact, and water absorption tests.

3.4 The 3D printing of ArF/PLA/PP specimen

3.4.1 3D printing setting

A commercial 3D printer, the Flash Forge Creator Pro, was used to generate the specimen samples, and the produced filaments in Figure 2.3 were used as the primary printing substance. In our case, The 3D models of the tensile, Izod impact, and water absorption specimens were received as a .stl file.[3]. Before printing, many factors have to be considered, including nozzle temperature, bed temperature, and printing speed. As a result, all three specimens' .stl files (tensile, impact, and water absorption) were loaded into Flash Print software for additional slicing and printing settings.

The test specimens were printed flat on the printing bed with a 100% infill density, and the layer height was fixed at 0.18 mm; for printing and traveling, a regular print speed of 40 mm/s was used. The temperatures of the nozzle and bed were held at 210°C and 50°C

respectively. During this investigation, the specimens were printed along the horizontal axis and a +45/-45 raster angle /orientation was employed.

The configuration of the 3D Print in the FlashPrint program is displayed in Table **3.4** Once everything was configured, the file was saved as a.x3g file and inserted using a memory card into the 3D printer to begin creating 3D objects.

Table 3.4 Printer setup using Flashprint software

Nozzle Temperature (°C)	210
Bed Temperature (°C)	50
Filler Percentage (%)	100
Shape of Filler	line
Orientation (°)	+45/-45
Perimeter shells	2
Top/Bottom solid layers	3
Nozzle Diameter (mm)	0.5
Print Speed (mm/s)	40
Travel Speed (mm/s)	80
Layer Height	0.18 mm
First layer height	0.27 mm
Printing direction	Along the build plate horizontal axis

The specimens were printed out flat onto the build plate, and Figure **3.4** illustrates the location of the raster angle that was employed in this investigation.

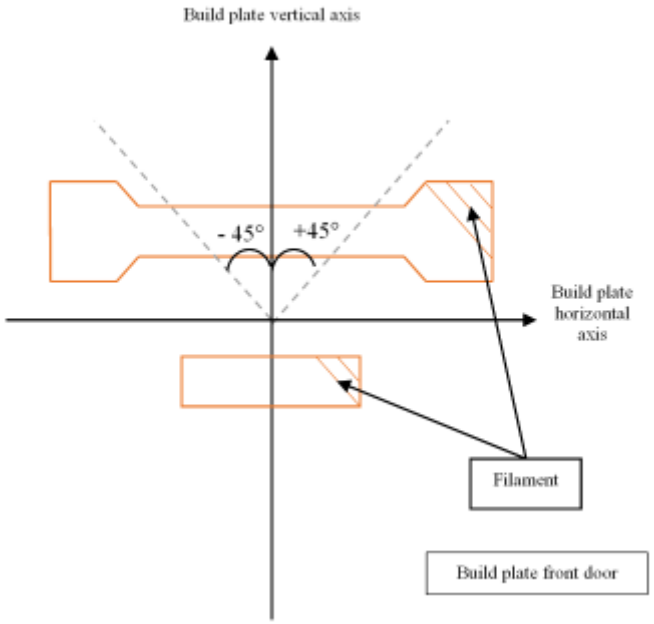


Fig. 3.4 Raster Angle used while printing specimens [4].

Figure **3.5** shows the various produced filaments, including PLA/PP filament, ArF reinforced filament, Un, Alk, and SLN.

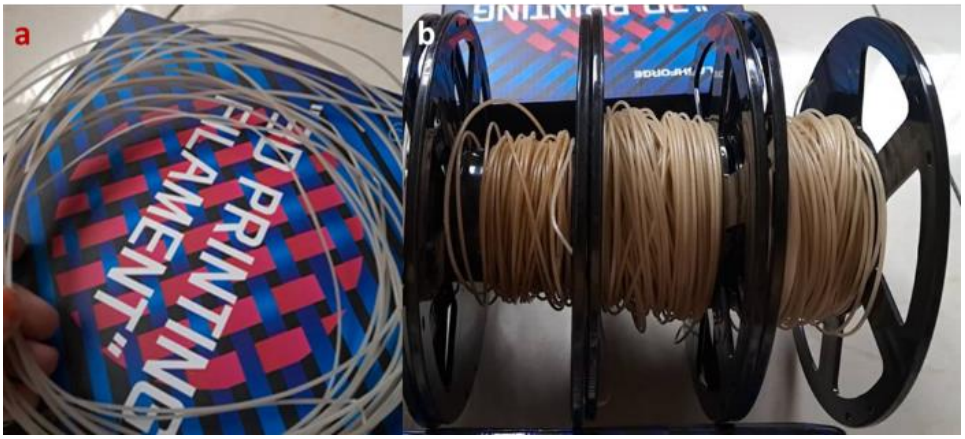


Fig. 3.5 The various composite filaments, (a) PLA/PP filament, (b) ArF reinforced filament, from left to right, Un, Alk, and SLN respectively.

3.4.2 Preparation of Tensile test specimen

The dog-bone-shaped 3D-printed tensile test specimen, shown in **Figure 3.6**, complies with the requirements given in ASTM D638 Type I [5], One hour and four minutes was the expected amount of time needed for the printing procedure.

Fig. 3.6 Tensile test specimens: from left to right, PLA/PP, Un, Alk, and SLN respectively.

3.4.3 Preparation of Impact test specimen

From each filament, five specimens were made. The specimens were made in accordance with ASTM D256 specifications for size and shape[6]. The rectangular Izod specimen had a notch in the centre, about 64 * 12.7 * 3.2 mm in dimension (length x breadth x height). **Figure 3.7** displays the 3D-printed specimen. The expected print time was 30 minutes.

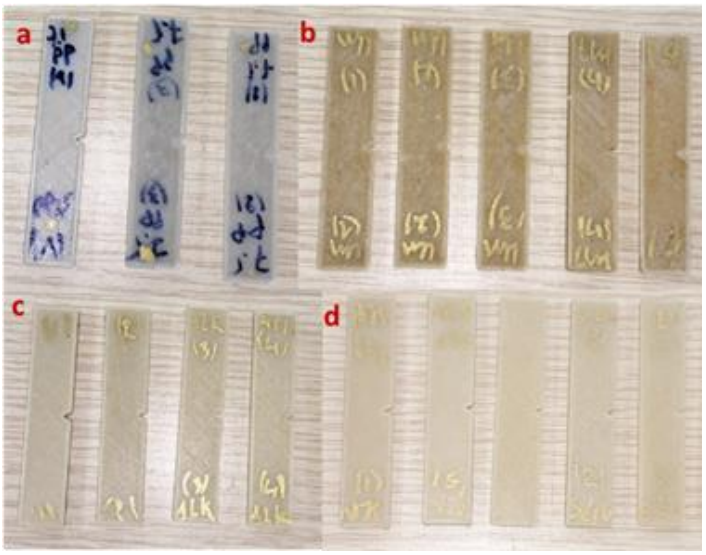


Fig. 3.7 Impact specimens, (a) PLA/PP, (b) Un, (c) Alk, and (d) SLN.

3.4.4 Water absorption and thickness swelling test specimen

Following the ASTM D570 standard [7], Figure **3.8** depicts a 3D model of each sample in a square, measuring 20 * 20 * 3.2 mm (height x breadth x thickness). These specimens were employed for dual purposes, serving as subjects for both water absorption testing and thickness swelling evaluation

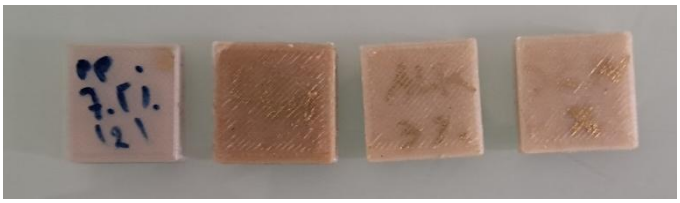


Fig. 3.8 Water absorption specimens.

3.5 Material Characterization

3.5.1 Fourier Transform Infrared Spectroscopy (FTIR)

Using a FTIR spectrometer (Perkin Elmer, PE 1600), reflection attenuated total Fourier transform infrared analysis is used to study the impact of chemical change on Arundo fibre structure over a range of 4000 to 400cm-1.

3.5.2 X-ray diffraction

Using a diffractometer (SIEMENS D 5000 X-ray and SHIMADZU XRD-6000, Kyoto, Japan) equipped with Cu Kα radiation, The crystallinity of the fibres (raw and treated Arundo fibre) was studied within the angular incidence range of 5° to 60° at 2θ angle. The crystallinity index (CrI) was determined using Equation (1)[8]:

$$\mathrm{Crl} = \left(\frac{(\mathrm{I200}-\mathrm{Iam})}{\mathrm{I200}}\right) * 100\% \quad (1)$$

where Iam is the minimum intensity point and I200 is the maximum intensity point.

3.5.3 Differential Scanning Calorimetry (DSC)

Using a TA Instrument Q200 V24-type calorimeter, the melting point, crystallization temperature, and enthalpy of the composites' were determined. 5 mg of each sample was heated to 200°C at a rate of 2°C per minute. The samples were then cooled to 50°C at a rate of 10°C per minute before being heated to 100°C and 150°C at the same cooling rate[9].The samples percentage crystallinity (Xc) was calculated using the following equation (2):

$$\mathrm{Xc} = \left(\frac{\Delta \mathrm{Hcc}}{\Delta \mathrm{H}*}\right) * 100\% \qquad (2)$$

ΔHcc is the cold crystallization enthalpy of the composites, while ΔH* is the melting enthalpy of 100% crystalline PLA (equal to 93.7 J/g).

3.5.4 Thermogravimetric Analysis (TGA)

The TGA technique was performed to study the thermal stability of the composites using a TA-SDT Q500 thermogravimetric analyzer. The weight variations of the samples were measured over a temperature range from 50 to 600°C, with a regulated rate of 10°C per minute. The TGA and DTG curves provided crucial information on the thermal properties and breakdown behaviour of the materials.

3.5.5 Melt Flow Index (MFI)

The MFI of the thermoplastic composite was determined in accordance with ASTM D 1238 [10]. The MFI is defined by measuring the amount of material that passes through a die in grams per 10 minutes. The MELT-INDEXER model 5 type was used to carry out the measurements under a weight of 2.16 kg and a predetermined temperature of 190°C. The numbers are provided as an average of many measurements, with the standard deviation included.

3.5.6 Tensile testing

The tensile strength and modulus of biocomposites were determined according to the ASTM D638 type 1 [5]. The measurements were taken at room temperature, with sample conditioning at 21.5°C, 50%RH and room conditioning at 24°C, 47%RH, using a Zwick/Z010 testing machine. The traverse speed was 5 mm/min, with a gauge length (GL) of 50 mm. Five samples of each biocomposites composition were evaluated to assess the tensile properties.

3.5.7 The Izod Impact test

The Izod impact test was conducted in accordance with ASTM D256, Test C, using a Ceast brand device. For each composite, five notched specimens were tested. Prior testing, the samples were subjected to a 48-hour conditioning period at 23 °C. The experiment was performed at laboratory temperature. The average value of the five repeats was then computed.

3.5.8 Scanning Electron Microscopy (SEM)

A scanning electron microscope was utilized to examine the fracture surface of the composites. The InTouch Scope SEM microscope offered an optical magnification range of 20-135, an electron magnification range of 80-1.3 105, a maximum digital zoom of 12, and operated with acceleration voltages set at 10 kV.

3.5.9 Water absorption and Thickness Swelling

The water absorption test was conducted according to ASTM D570 standars [7]. Eight specimens were made, two for each composite. The specimens were immediately weighed, following a 24-hour drying period at 60°C. Then, the samples were weighed again after 24 hours of soaking in distilled water, and so on every 24 hours until the samples' weight was

saturated (the weight increase remains 1% after three weeks). The water absorption percentage Wa and thickness swelling TS was calculated using the following formula (3,4):

$$Wa\ (\%) = \left(\frac{(\mathrm{mt} - \mathrm{mi})}{\mathrm{mi}}\right) * 100\% \quad (3)$$

Here; mt represents the $mass\ after$ the $nth\ time$, while mi is the initial $mass$.

$$TS\ (\%) = \left(\frac{(\mathrm{TSt} - \mathrm{TSi})}{\mathrm{TSi}}\right) * 100\% \quad (4)$$

Here; TSt represents the thickness $after$ the $nth\ time$, while TSi is the initial thickness.

References

[1] V. Fiore, T. Scalici and A. Valenza, *Characterization of a new natural fibre from Arundo donax L. as potential reinforcement of polymer composites,* Carbohydr. Polym, vol. 106, pp. 77–83, Jun 2014, doi: 10.1016/j.carbpol.2014.02.016.

[2] W. Bessa, D. Trache, M. Derradji," *Effect of different chemical treatments and loadings of Arundo donax L. fibres on the dynamic mechanical, thermal, and morphological properties of bisphenol A aniline based polybenzoxazine composites,"* Polymer Composites, doi:10.1002/pc.26215.

[3] F. S.Shahar, M. T. H. Sultan, S. N. A.Safri," *Fatigue and impact properties of 3D printed PLA reinforced with kenaf particles", Journal of materials research and technology, vol. 16, p. 461-470,2022,*doi:10.1016/j.jmrt.2021.12.023.

[4] F. S.Shahar, "*Development Of Kenaf/Pla Filament For Ankle-Foot Orthosis Using Fused Deposition Modelling (Fdm) 3d Printer",* the Degree of Doctor of Philosophy, Universiti Putra Malaysia, Malaysia, 2015.

[5] E. Cuit, *Standard Test Method for Tensile Properties of Plastics*, https://www.academia.edu/35737193/Standard_Test_Method_for_Tensile_Properties_of_Plastics.

[6] *D256 Standard Test Methods for Determining the Izod Pendulum Impact Resistance of Plastics,* https://www.astm.org/standards/d256.

[7] *D570 Standard Test Method for Water Absorption of Plastics,* https://www.astm.org/standards/d570.

[8] R. L. Segal, J. J. Creely, A. E. Martin and C. M. Conrad, *An Empirical Method for Estimating the Degree of Crystallinity of Native Cellulose Using the X-Ray Diffractometer, Text. Res. J*, Oct 1959, doi: 10.1177/004051755902901003.

[9] H. Long, Z.Wu, Q.Dong ," *Mechanical and thermal properties of bamboo fibre reinforced polypropylene/polylactic acid composites for 3D printing,* Polym", Eng. Sci, vol. 59, no. s2, pp. E247–E260, 2019, doi: 10.1002/pen.25043.

[10] *D1238 Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer,* https://www.astm.org/d1238-10.html.

CHAPTER 4: RESULTS AND DISCUSSIONS- part 1

4.1 EFFECT OF CHEMICAL TREATMENTS ON ARUNDO DONAX L. FIBRE

4.1.1 FTIR Spectroscopy

Figure 4.1 represents the infrared analysis of Arundo Donax L. fibres (untreated, treated with alkali (Alk), and fibres treated with alkali followed by silane treatment (Alk+SLN). The purpose of the study was to verify the chemical alteration made to the fibre. The absorbance bands observed in the range of 3300 cm^{-1} to 3500 cm^{-1} are attributed to the presence of hydroxyl groups (OH) in all samples, Subsequently, peaks are observed in the range of 2990 cm^{-1} to 2911 cm^{-1}, indicating the stretching and vibration of C-H and CH_2 groups, which are characteristic of cellulose, hemicellulose, and other organic components. Another prominent peak is observed at 1720 cm^{-1}, attributed to the stretching of C=O groups, indicative of aldehyde functionalities. The last spectrum peaks are noted in the range of 1052 cm^{-1} to 900 cm^{-1}, which corresponds to the vibrational stretch of C-O bonds, specifically associated with acetyl groups in lignin. This result aligns with previous studies [1-5].

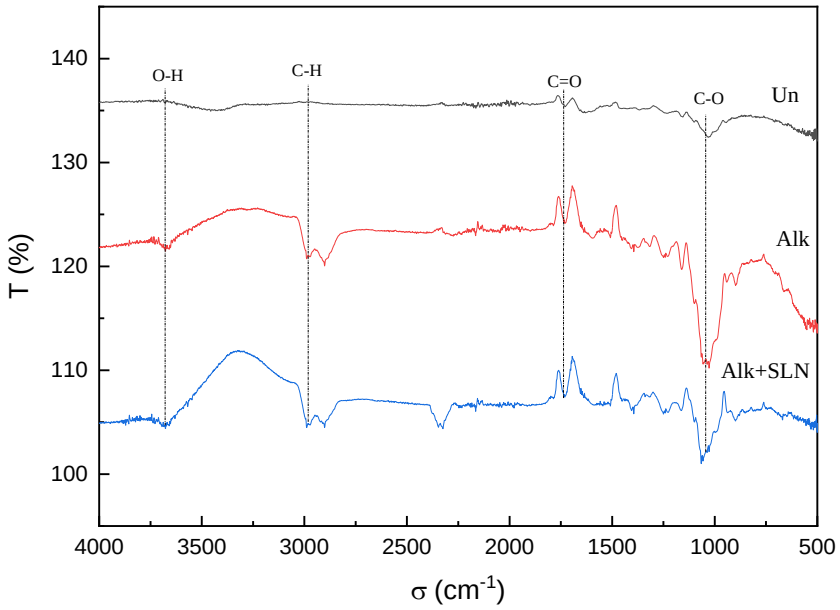


Fig. 4.1 FTIR spectra of Un, Alk, and Alk+SLN.

4.1.2 X-Ray Diffraction (XRD)

XRD analysis was conducted on the Un, Alk, and Alk+SLN samples to evaluate their crystallinity properties, as illustrated in **Figure 4.2** and the results are summarized in **Table 4.1**. In all spectra of the samples, two prominent peaks emerged at 2θ = 16.25° and 2θ = 22.4°, indicating the presence of crystalline regions within the Arundo fibres component. Additional peaks were observed, indicating that all fibres possessed a native cellulose Iβ type structure [1]. However, after treatments, the crystallinity index was increased from 30.40% to 35% for Un and Alk-SLN samples. The high crystallinity of Alk-SLN fibres implied high rigidity, making them suitable for utilization as a biofilter in composite materials to enhance their mechanical properties[6].

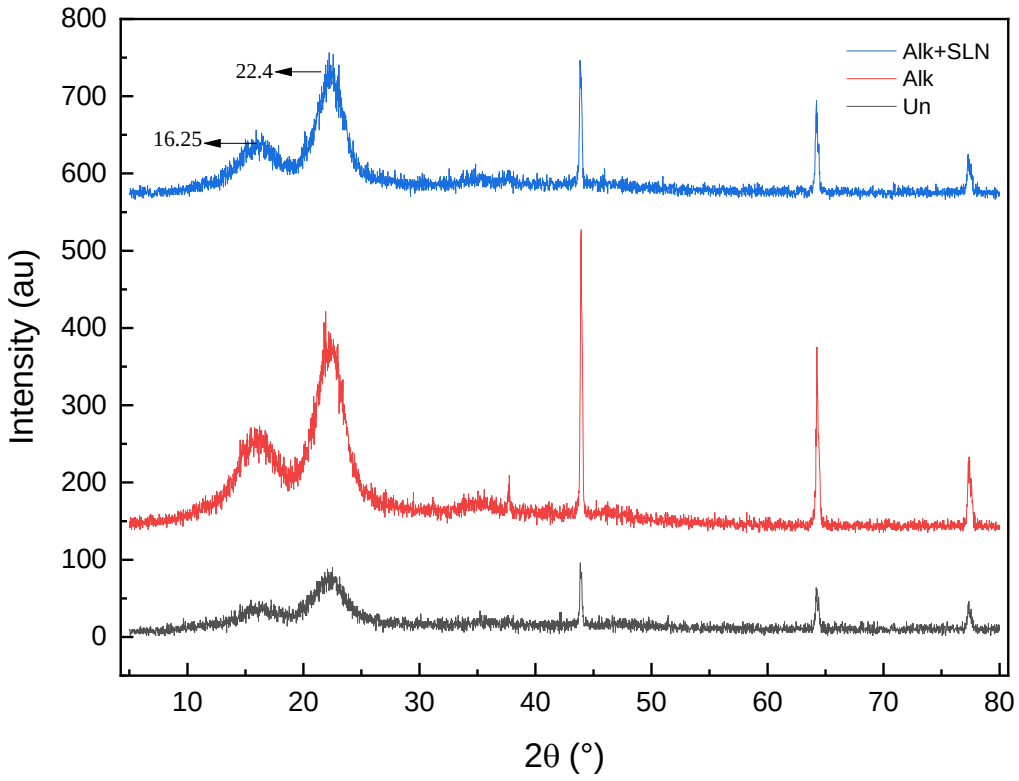


Fig. 4.2 XRD of Un, Alk, and Alk+SLN.

Table 4.1 The crystallinity index of Un, Alk, and Alk+SLN Arundo fibres.

Samples	**CrI (%)**
Un	30.40
Alk	34.69
Alk+SLN	35

4.1.3 Thermal Properties

Figure 4.3 (a and b) represents the TGA and DTG curves respectively, for Un, Alk, and Alk+SLN fibres. The thermal degradation of all samples exhibits a two-stage process. The initial stage, occurring between 30 to 180 °C, signifies the weight loss for all fibres due to the evaporation of water and volatile compounds from their surfaces. In the second stage, beyond 200 °C, the Un sample initiates thermal decomposition at 245.65 °C, indicating relatively lower thermal stability compared to the Alk of 311.86 °C and Alk-SLN of 319.73 °C. Additionally, it was also seen that the degradation peak was reduced and degradation temperature increased for the silane-treated Arundo fibres leading to the sustainment of the thermal stability [4], [6].

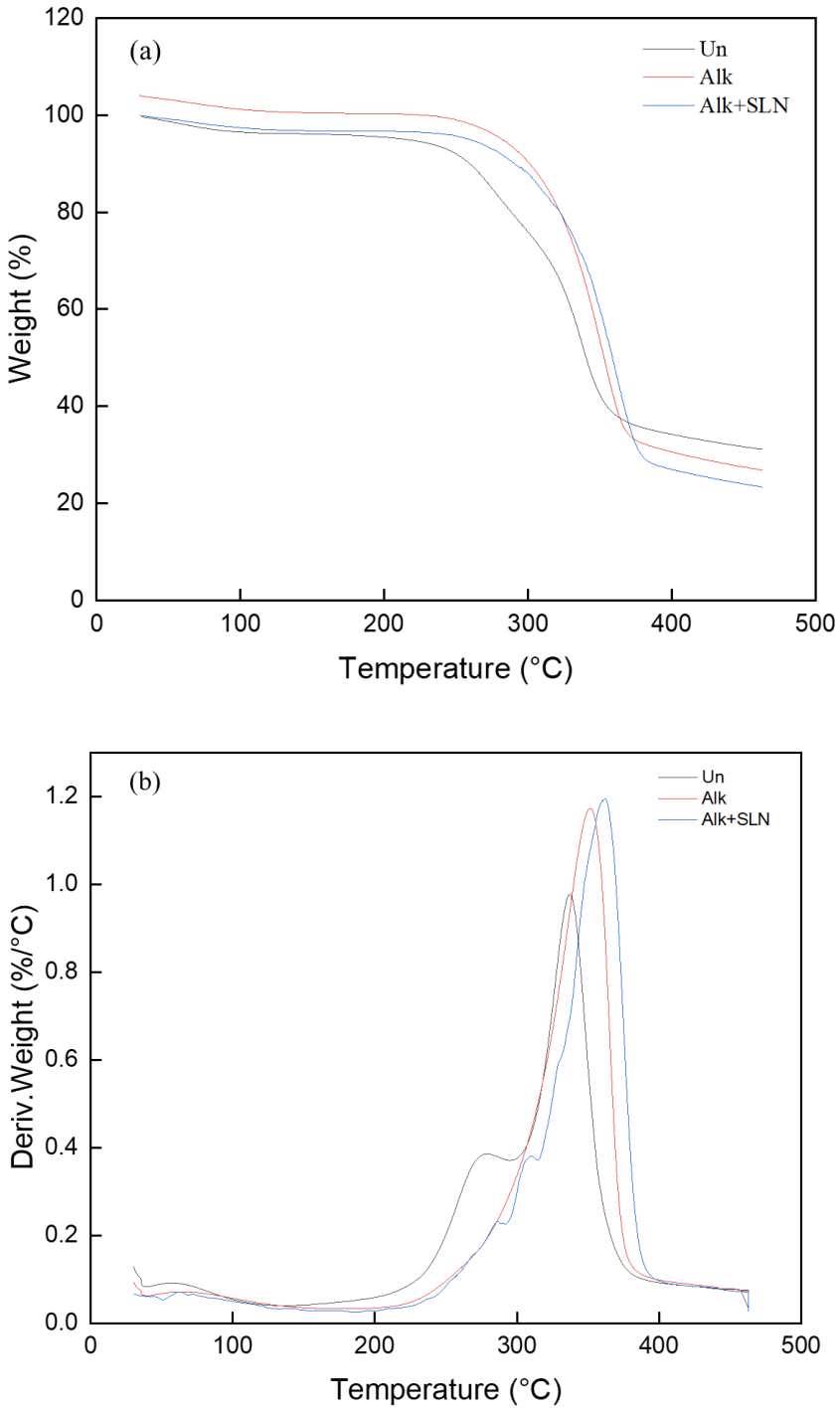


Fig 4.3 TGA (a) and DTG (b) of Un, Alk, and Alk+SLN Arundo fibres.

4.1.4 Scanning electron microscopy (SEM)

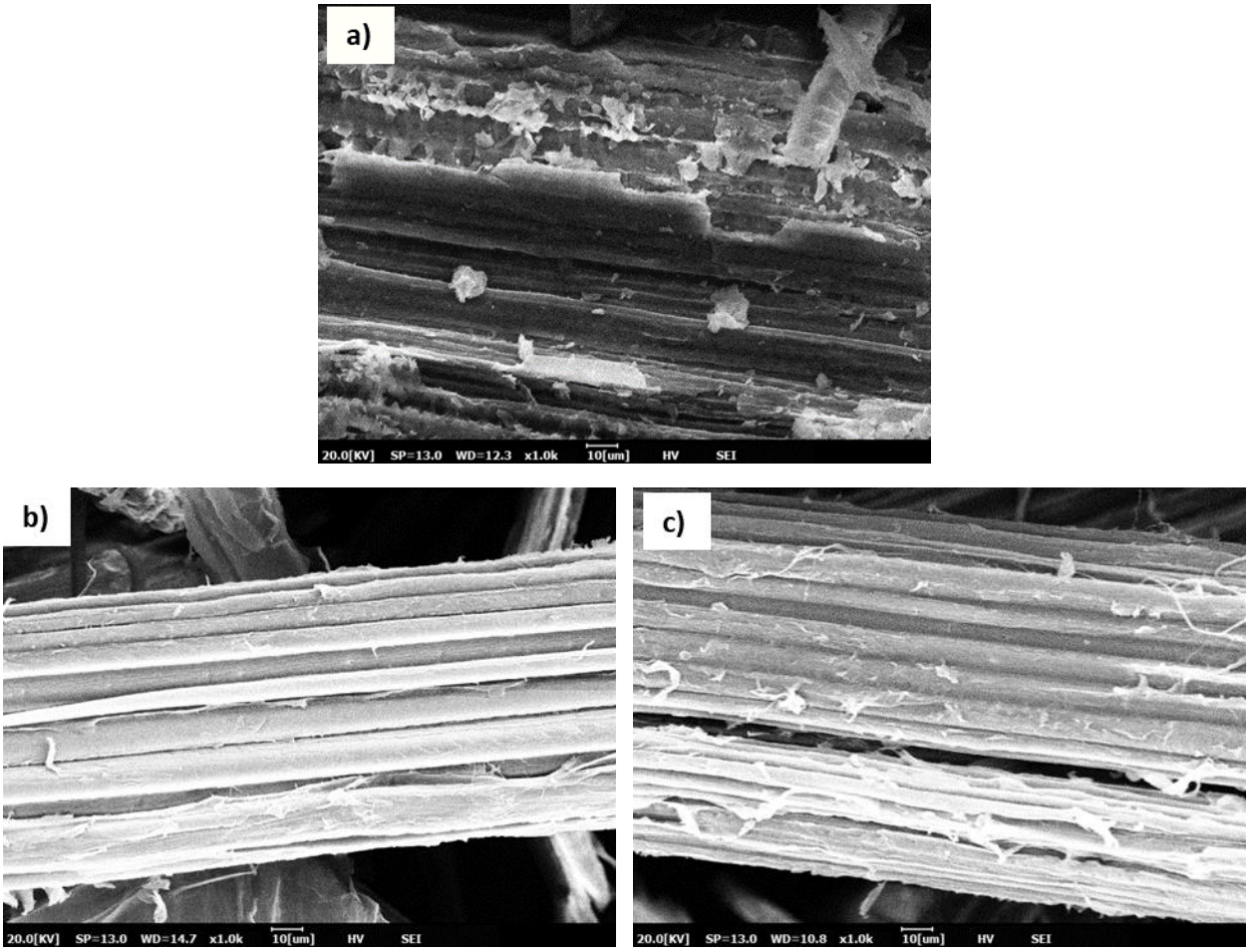


Fig 4.4 SEM images of a) raw ArF , b) ALK-ArF and c) SLN-ArF .

The surface morphology of Arundo fibre treated with silane, alkali, and raw was found to have significantly changed. The SEM micrographs of these samples are shown in **Figure 4.4** a to c**. Figure 4.4 a** illustrates the surface structure of untreated Arundo fibre (ArF). Like other natural fibres, the surface appearance of Arundo fibres consists of numerous basic fibres, also known as fibrils or fibre cells, which are connected lengthwise by non-cellulosic substances such as pectin. As is typical of raw natural fibres, certain contaminants are also visible on the fibre's surface[7], [8], [9]. Natural fibres are frequently chemically treated to remove these contaminants and improve interfacial adhesion with polymer matrices[10], [11].

Typically, the application of chemical treatment results in the lumens becoming apparent, as illustrated in Figures **4.4 b and c.** Moreover, the treated fibres appear «cleaner» along their entire length compared to the untreated ones [12]. The fibre treated with 5% alkali has also a slightly rougher surface and fibrils are visible on the surface of the fibre (**Fig**. **4.4 b**). This helps to improve the interlocking of the fibre and matrix, which makes it easier for tangential stresses to interchange. The improvement is ascribed to the alkali treatment process's elimination of wax, oils, and contaminants from the untreated ArF fibre's main wall [13]. Furthermore, the hydroxyl groups of cellulose, hemicellulose, and lignin form intra- or intermolecular hydrogen bonds that are separated by the alkali solution [14].

Comparing the surfaces of silane-treated and alkali-treated fibres (**Fig. 4.4** c and b) does not reveal whether silane is present on Arundo fibre surfaces, even though the silane treatment alters the surface's aspect. This could be result from creating a smooth silane coating on the fibre surface upon reaching the adsorption equilibrium and the silane coupling agents covering the whole fibre surface [15]. Moreover, the silane served as a bridge, highlighting the bond between the ArF and composite matrix through chemical connections, thereby enhancing the interfacial interaction [16].

Finally. Arundo fibres could benefit from surface treatments and chemical alterations, that strengthen the link between the fibres and the composite matrix. Alkali treatment enhances mechanical characteristics and fosters improved bonding with the matrix by dissolving fibre bundles and raising the fibre aspect ratio. Conversely, silane treatment strengthens the fibre-matrix contact and improves compatibility with polymeric matrices by adding more chemical groups to the fibre surface. The mechanical and thermal qualities of natural fibres can be improved by a combination of various treatments, increasing their usefulness for a range of composite applications [17].

4.2 Filament Production and Printing Processes Analysis

This section explores the effects of varying PLA: PP ratios and the addition of Ar fibre on the extruded filament's physical structure and behavior throughout the extrusion and printing process. Achieving a homogenous filament with a smooth surface, and ideal diameter is contingent upon the ratio of PLA to PP, all of which directly affect the quality of printed specimens. In addition, determining the fibre loading threshold that ensures the appropriate mechanical qualities of the finished products is also crucial in order to consistently get high-quality filament and prints.

4.2.1 The filament extrusion

An extensive study into improving the mechanical qualities of printed items by adding waste polypropylene served as the basis for choosing the blending PLA:PP ratio. A thorough examination of academic literature showed that the incorporation of PP had a substantial effect on the material's ultimate mechanical and rheological properties. The choice was then taken to mix PP and PLA in an effort to maximize the advantages noted in earlier research. The ideal ratio of PLA:PP and PP GMA was established following a thorough review of the literature and a number of lab tests. This study's conclusion, which includes the results of unsuccessful tests, is condensed into a **table 4.2** that offers a clear explanation of the reasoning for the blend ratio selection.

Table 4.2 PLA: PP ratio's effects on the printing and extrusion of filaments.

PLA:PP	Extrusion flow	Filament condition	Printing process
0:1	Filament flow freely	Good	tends to shrink and does not stick to the 3D printer bed.
9:1	Filament flow easily	Smooth surface and a constant diameter	went well and mostly steady.

A study with the Wellzoom C Mini Desktop Filament Extruder was conducted to determine the best formula for the extrusion procedure and subsequent printing. Variations in the PLA: PP ratio did not affect filament synthesis during the extrusion stage. However, when PP dominated the ratio, it was necessary to cool the filament with air at first since water made it cool too quickly and become ductile, preventing it from rewinding.

The extrusion of the 3 weight percent ArF/PLA/PP filament went easily and consistently between 170 and 175 degrees Celsius at a rotating speed (v) of 50 rpm, which is suitable. This performance was in line with the neat filament's, suggesting that the processing conditions were adequate. The filament spooling process also went smoothly.

Granule diameter was shown to be the most influencing element during the extrusion stage in all samples, as the fibre content was just 3%. The main reason for uneven filament diameter was found to be variations in granule diameter. In our case, this problem was resolved by reducing the particle size choice on the crusher sieve. However, achieving a uniform granule particle size through enhancement of the granulation process would represent the optimal solution to this problem. It was also observed that it was essential to pre-dry the granules at 60 °C for at least 30 minutes before extrusion. If this wasn't done, water would have evaporated during extrusion, damaging the filament and lowering its quality.

4.2.2 The impact of the quality of the extruded filament on the printed composite specimen

One of the most important variables affecting the success of 3D printing is filament quality. Low-quality filaments can lead to issues like clogging or inadequate filament grip by extruder gears, causing failed prints[18]. Performance, consistency, and overall quality of 3D printing are all directly impacted by the quality of the filaments. Several important factors come into play, including the shelf life, packaging, composition, and tolerance of the filament, as consistent diameter along the entire spool length allows the extruder to deliver filament to the hot tip at the correct, consistent rate[19], [20].

The temperature, speed, and bed temperature during printing also have a significant impact on the print quality. A temperature that is too high for printing may cause filament leakage, while a temperature that is too low may cause filament clogging inside the extruder.

Furthermore, the printing process is greatly impacted by the printing speed; therefore, obtaining a well-balanced value is essential to producing quick and seamless printing results, maintaining an appropriate bed temperature was also important to prevent part shrinking due to the presence of PP. Towards the end of the project, I encountered significant difficulties printing the last formula (SLN), requiring me to raise the temperature about 5°C. This adjustment became necessary due to poor storage conditions, which led to the filament absorbing humidity.

Lastly, when PP dominated the formula, the printed component shrank uncontrollably. This stopped the printed part from sticking to the print bed and from staying in place even when the bed temperature was raised and an adequate adhesive (PP magigoo).

References

[1] A. Hachaichi, B. Kouini, L. K. Kian, M. Asim, M. Jawaid, "Extraction and Characterization of Microcrystalline Cellulose from Date Palm Fibers using Successive Chemical Treatments," *J. Polym. Environ.*, vol. 29, no. 6, pp. 1990–1999, Jun. 2021, doi: 10.1007/s10924-020-02012-2.

[2] N. R. J. Hyness, N. J. Vignesh, P. Senthamaraikannan, S. S. Saravanakumar, M. R. Sanjay, "Characterization of New Natural Cellulosic Fiber from Heteropogon Contortus Plant," *J. Nat. Fibers*, vol. 15, no. 1, pp. 146–153, Jan. 2018, doi: 10.1080/15440478.2017.1321516.

[3] P. Manimaran, M. R. Sanjay, P. Senthamaraikannan, M. Jawaid, S. S. Saravanakumar, and R. George, "Synthesis and characterization of cellulosic fiber from red banana peduncle as reinforcement for potential applications," *J. Nat. Fibers*, vol. 16, no. 5, pp. 768–780, Jul. 2019, doi: 10.1080/15440478.2018.1434851.

[4] R Vijay, A Vinod, R Kathiravan, S Siengchin, D Lenin Singaravelu, "Evaluation of Azadirachta indica seed/spent Camellia sinensis bio-filler based jute fabrics–epoxy composites: Experimental and numerical studies," journal of industrial textiles, vol. 49, no. 9, p.,2020, doi:10.1177/1528083718811086.

[5] A. Vinod, R. Vijay, D. L. Singaravelu, M. R. Sanjay, S. Siengchin, M. M. Moure, "Characterization of untreated and alkali treated natural fibers extracted from the stem of Catharanthus roseus," *Mater. Res. Express*, vol. 6, no. 8, p. 085406, May 2019, doi: 10.1088/2053-1591/ab22d9.

[6] R. Vijay, S. Manoharan, S. Arjun, A. Vinod, D. L. Singaravelu, "Characterization of Silane-Treated and Untreated Natural Fibers from Stem of Leucas Aspera," *J. Nat. Fibers*, vol. 18, no. 12, pp. 1957–1973, Dec. 2021, doi: 10.1080/15440478.2019.1710651.

[7] V. Fiore, A. Valenza, G. Di Bella, "Artichoke (*Cynara cardunculus* L.) fibres as potential reinforcement of composite structures," *Compos. Sci. Technol.*, vol. 71, no. 8, pp. 1138–1144, May 2011, doi: 10.1016/j.compscitech.2011.04.003.

[8] I. M. De Rosa, J. M. Kenny, D. Puglia, C. Santulli, F. Sarasini, "Morphological, thermal and mechanical characterization of okra (*Abelmoschus esculentus*) fibres as potential reinforcement

in polymer composites," *Compos. Sci. Technol.*, vol. 70, no. 1, pp. 116–122, Jan. 2010, doi: 10.1016/j.compscitech.2009.09.013.

[9] V. Fiore, T. Scalici, A. Valenza," Characterization of a new natural fiber from Arundo donax L. as potential reinforcement of polymer composites," *Carbohydrate polymers*, vol. 106, p. 77-83,2014, doi: 10.1016/j.carbpol.2014.02.016.

[10] D. P. Ferreira, J. Cruz,R. Fangueiro, "Chapter 1 - Surface modification of natural fibers in polymer composites," *Green Composites for Automotive Applications*, pp. 3–41,2019, doi: 10.1016/B978-0-08-102177-4.00001-X.

[11] B. Nunez, H.-FRANCO, P. J. FÉLIX," Surface modification and performance of jute fibers as reinforcement on polymer matrix: an overview", *Journal of Natural Fibers*, Vol 16, No 7, 2019, doi: 10.1080/15440478.2018.1441093.

[12] I. M. De Rosa , "Effect of chemical treatments on the mechanical and thermal behaviour of okra (*Abelmoschus esculentus*) fibres," *Compos. Sci. Technol.*, vol. 71, no. 2, pp. 246–254, Jan. 2011, doi: 10.1016/j.compscitech.2010.11.023.

[13] LIU, Yucheng, MA, Yunhai, YU, Jiangtao, "Development and characterization of alkali treated abaca fiber reinforced friction composites," *Composite Interfaces*, vol. 26, no 1, p. 67-82, 2019, doi: 10.1080/09276440.2018.1472456.

[14] K. O. Reddy, C. U. Maheswari, D. J. P. Reddy, A. V. Rajulu, "Thermal properties of Napier grass fibers," *Mater. Lett.*, vol. 63, no. 27, pp. 2390–2392, Nov. 2009, doi: 10.1016/j.matlet.2009.08.035.

[15] F. Zhou, G. Cheng,B. Jiang, "Effect of silane treatment on microstructure of sisal fibers," *Appl. Surf. Sci.*, vol. 292, pp. 806–812, Feb. 2014, doi: 10.1016/j.apsusc.2013.12.054.

[16] Y. Liu, "Characterization of silane treated and untreated natural cellulosic fibre from corn stalk waste as potential reinforcement in polymer composites," *Carbohydr. Polym.*, vol. 218, pp. 179–187, Aug. 2019, doi: 10.1016/j.carbpol.2019.04.088.

[17] A. Gholampour, T. Ozbakkaloglu, “A review of natural fiber composites: properties, modification and processing techniques, characterization, applications,” *J. Mater. Sci.*, vol. 55, no. 3, pp. 829–892, Jan. 2020, doi: 10.1007/s10853-019-03990-y.

[18] S. Farah Syazwani Binti, “Development of kenaf/pla filament for ankle-foot orthosis using fused deposition modelling (fdm) 3d printer,” the Degree of Doctor of Philosophy, Universiti Putra Malaysia, Malaysia, 2015.

[19] L. Santana, C. H. Ahrens, A. da Costa Sabino Netto, C. Bonin, “Evaluating the deposition quality of parts produced by an open-source 3D printer,” *Rapid Prototyp. J.*, vol. 23, no. 4, pp. 796–803, Jan. 2017, doi: 10.1108/RPJ-05-2016-0078.

[20] V. M. Bruère, A. Lion, J. Holtmannspötter, M. Johlitz, “Under-extrusion challenges for elastic filaments: the influence of moisture on additive manufacturing,” *Prog. Addit. Manuf.*, vol. 7, no. 3, pp. 445–452, Jun. 2022, doi: 10.1007/s40964-022-00300-y.

CHAPTER 5: EFFECT OF CHEMICAL TREATMENTS OF ARUNDO DONAX L. FIBRE ON MECHANICAL AND THERMAL PROPERTIES OF THE PLA/PP BLEND COMPOSITE FILAMENT FOR FDM 3D PRINTING

5.1 Thermal properties

5.1.1 Differential Scanning Calorimetry (DSC)

Figure 5.1 and **Table 5.1** illustrate the results of the DSC analysis, which was conducted to evaluate the melting and crystallization characteristics of PLA/PP/Arundo donax L. fibre biocomposites. Based on the DSC plots, three clear transitions occurred during the first heating process of the samples. The temperature ranges in which the transitions occurred were as follows: the glass transition (T_g) happened between 57 and 59°C, cold crystallization (T_{CC}) took place between 100 and 110°C, and melting (T_m) occurred between 149 and 164°C.

The findings are consistent with earlier studies on PLA reinforced with natural [1]since only 7.5 wt.% of rPP was added[2]. In comparison to the neat PLA/PP matrix, the Tg values of PLA/PP-ArF biocomposites have increased somewhat with the inclusion of untreated and treated Arundo fibres.

Table 5.1 The DSC testing outcomes of PLA/PP blend and its ArF biocomposites.

	T_g (°C)	T_{cc} (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔH_{cc} (J/g)	ΔH_m (J/g)	χ (%)
First heating							
PLA/PP	57,16	-	153,58	163,43	-	35,91	-
Un	59,68	-	154,75	-	-	58,37	-
Alk	58,58	102,11	149	155,75	16,16	40,93	17,25
SLN	58,48	-	154,08	159	-	32,55	-
Second heating							
PLA/PP	60,91	108,12	-	-	20,02	-	21,37
Un	61,26	110,06	-	-	18.43	-	19,67
Alk	61,16	110,93	-	-	18,31	-	19,54
SLN	61,18	109,42	-	-	18.64	-	19.89

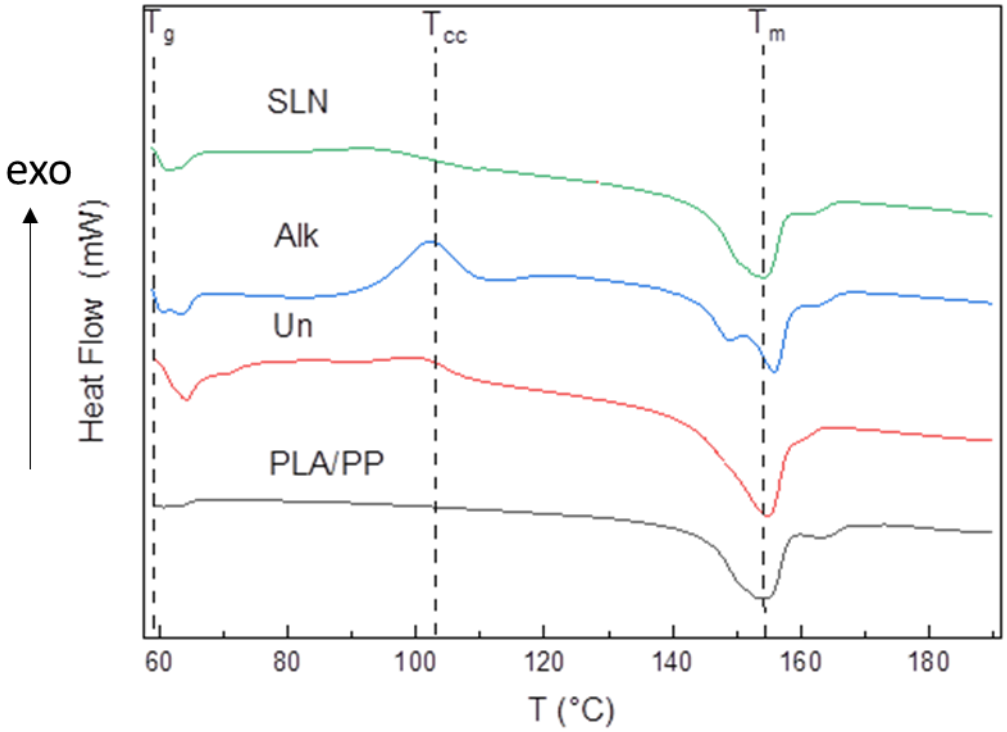


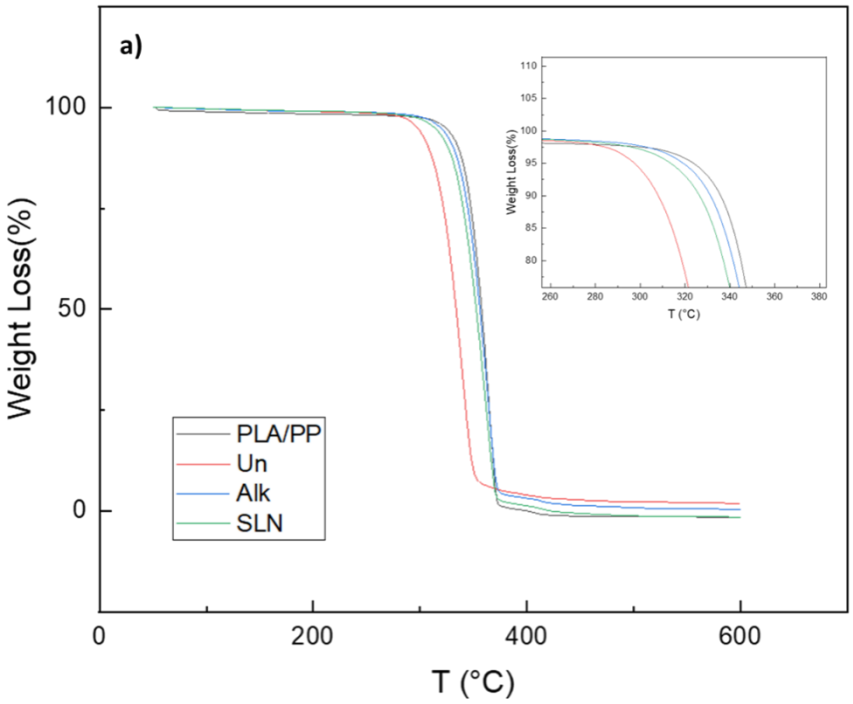
Fig.5.1 The first heating DSC thermograms of PLA/PP/ArF biocomposites.

The first heating plots **(Figure 5.1**) reveal that with a heating rate of 2°C/min, the PLA/PP blend could not crystallize. The addition of 3 wt.% alkali-treated Arundo fibre to the PLA/PP mix, on the other hand, resulted in the formation of a cold crystallization peak at Tcc = 102.11°C. PLA crystallization usually takes a long time, but when natural fibres are added they can either restrict polymer chain mobility or act as nucleation sites for the polymer crystallization [3], [4]. Nucleation events were most likely prominent when alkali-treated fibre was introduced. Additionally, the emergence of two distinct melting peaks suggests the formation of metastable and perfected crystals[5]. Nevertheless, after the Arundo fibre was treated with silane, the exothermic peak of crystallization nearly faded. This significant reduction represents the decrease in the activation energy required to rearrange PLA molecule chains and their incorporation into the lattice structure, as indicated by Yang et al.[6].This study suggests that the modified ArF fibres play a role in improving the cooling crystallization of PLA, hence increasing its overall crystallinity.

5.1.2 Thermogravimetric Analysis (TGA)

The thermal stability of both treated and untreated fibre composites was investigated using TGA analysis. **Figure 5.2** and **Table 5.2** demonstrate the thermo-analysis plots (TGA and DTG) and TGA outcomes of the PLA/PP mix and its ArF-reinforced biocomposites. In the case of PLA/PP blend, a single-step deterioration was observed. The initial degradation temperature (ID) was recorded at 332,89°C, and the maximum degradation temperature (MD) was at 366,54°C.

The addition of ArF significantly impacted the thermal degradation process of PLA/PP. The degradation temperature of all composites was lower than that of PLA/PP. The ID and MD values for the untreated ArF composite (Un) were 305,67°C and 339,69 °C, respectively, which are about 8% lower than PLA/PP. Previous research found that natural lignocellulosic fibres, possibly when mixed with the matrix, the compatibility and interfacial bonding diminish[7], which at high temperatures, enhances the deformation of the crystalline structure of PLA [8].DSC analysis has confirmed the presence of equivalent variables, revealing a decrease in crystallinity percentage upon including ArF.



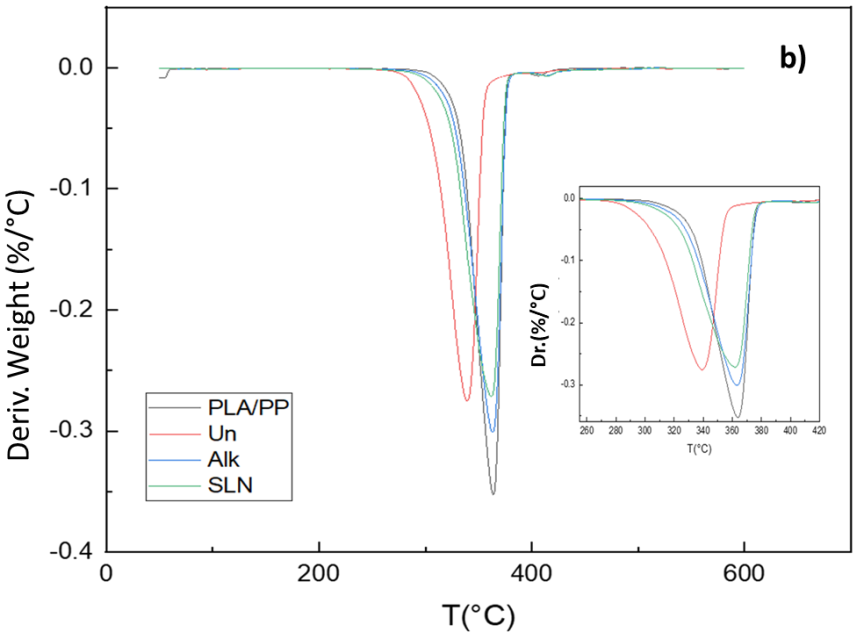


Fig.5.2 a) TGA thermograms of composites. **b)** DTG curves of composites.

Table 5.2 The results of TGA analysis of PLA/PP mix and its biocomposites.

Samples	**I_D T (°C)**	**M_D T (°C)**
PLA/PP	332,89	366,54
Un	305,67	339,69
Alk	327,76	363,62
SLN	321,73	362,42

However, for the treated Arundo fibre composites, the Thermal stability increased. When compared to Un, both Alk and SLN showed a slight increase in ID, with Alk increasing by 7% and SLN increasing by 5%. In terms of MD, Alk increased by 7% while SLN increased by 6.69%. The removal of organic impurities from the surface of the Arundo fibre, such as pectin and wax, contributes to the improvement in the thermal stability of the composites.

In the case of NaOH treatment, the thermal stability was higher because the treatment removed most of the impurities, exposing more cellulose molecules. The silane treatment, on the other hand, resulted in a coating on the surface. This phenomenon led to a lower thermal

stability than NaOH, but still higher than the untreated fibres[9]. A more extensive comparison of the alkali and silane treatments may be found elsewhere [10], [11]. The outcome validates that the treated fibres have greater thermal stability than the untreated ones in the following order: NaOH treated > silane treated > untreated. PLA/PP and biocomposites both degraded completely, with almost little residue remaining at the end of the testing cycle.

5.2 Melt flow index

The MFI value exhibits an inverse relationship to the dynamic viscosity, reflecting the rate at which a polymer material flows in its molten state. The MFI has a direct influence on polymer flowability during processing and also affects the bonding between printed layers. As a result, investigating this critical manufacturing feature is essential for both the printing process and the final quality of the product.

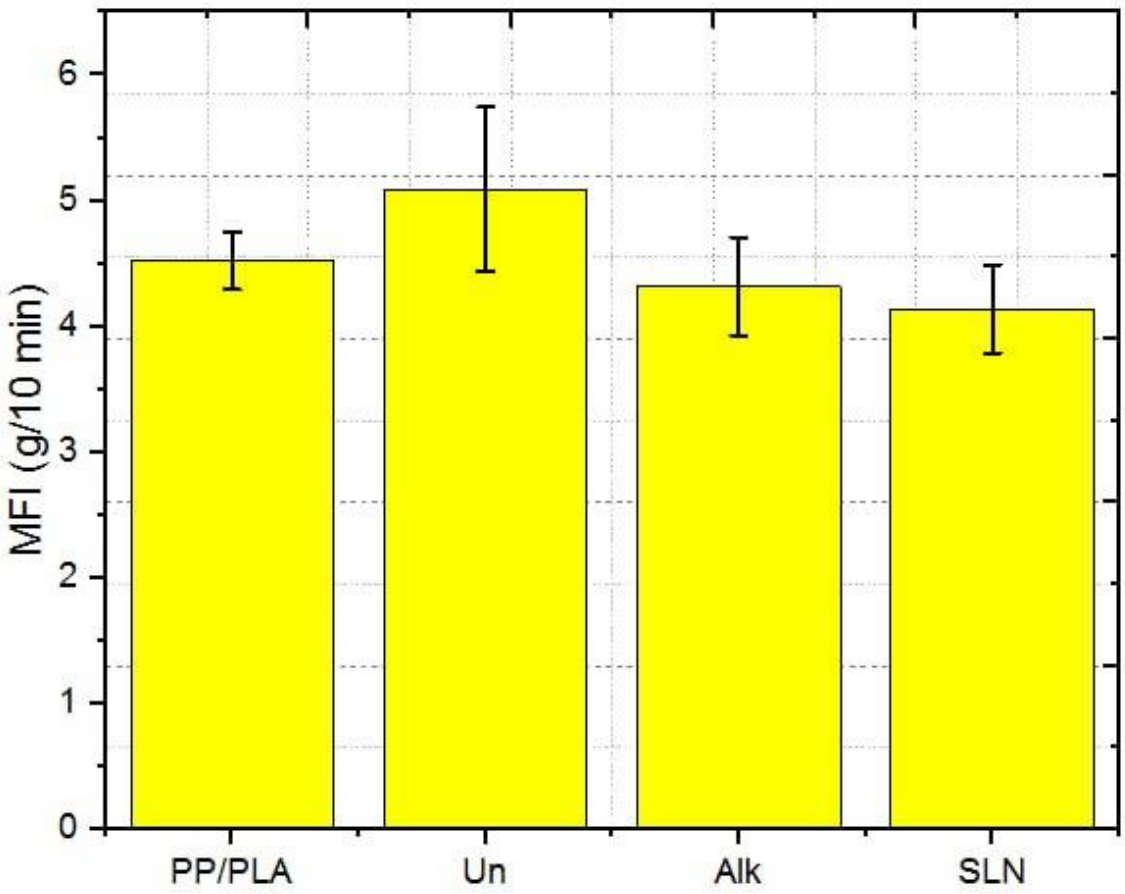


Fig. 5.3 The biocomposites' melt flow index.

Figure 5.3 depicts the MFI findings for the PLA/PP blend and its various Arundo fibre-reinforced biocomposites. The PLA/PP/PP-g-MA (92.0375/7.4625/0.5) MFI blend was 4.52 g/10min. This value implies that this system is suitable for FDM 3D printing. The result aligns with the literature, which demonstrates that PLA sets for FDM-based 3D printing applications should have MFI values less than 10 g/10 min (with a load of 2.16 kg and at 190°C)[12]. The MFI of ArF-reinforced composites also exhibited values between 4 and 5 g/10 min. Therefore, all composites are suitable for the FDM process.

The highest MFI value was of the untreated ArF composite (Un), probably due to the lack of fibre-matrix bonding. In this case, the untreated ArF acted more as an aggravating agent to the already immiscible PLA/PP blend, resulting in a higher MFI value. In contract, the treated fibre, the Alkali and silane treated fibre played as a reinforced agent to the mix, and the interface between the fibre-matrix was stronger. Therefore, the Alk and SLN composites functioned as one united system, leading to lower MFI values. These findings were further confirmed in the mechanical properties and morphological analysis discussion sections.

5.3 Mechanical properties

5.3.1 Tensile properties

The prepared specimens tested under static tensile conditions were grouped into four series, each containing five specimens. A total of 20 samples were used in this study: one series of PLA/PP neat blend specimens, one series of treated Arundo with NaOH solution composite (Alk), alkali and Silane-treated fibres composite (SLN), and untreated fibres composite (Un). All tensile outcome values are summarized in **Table 5.3. Figure 5.4** depicts a comparison of four curves of stress-strain derived from testing on all the biocomposites. Notably, the curves of untreated composite fibres and fibres treated with NaOH, which yielded the best results.

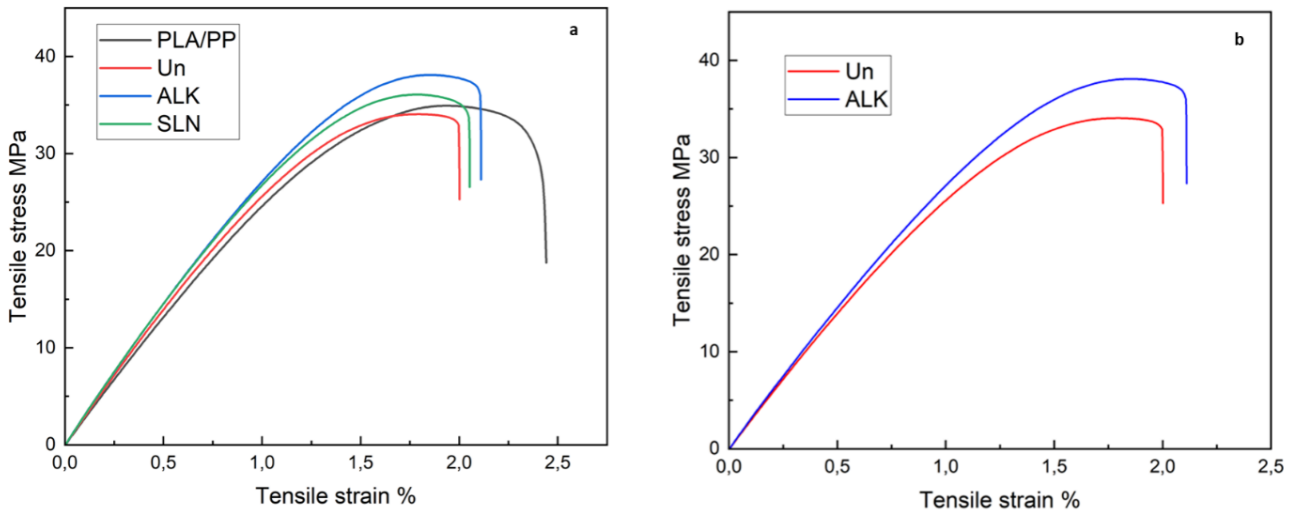


Fig. 5.4 The comparison of stress-strain curves generated from testing on :(a) all biocomposite ; (b) untreated, and alkali-treated fibre composites.

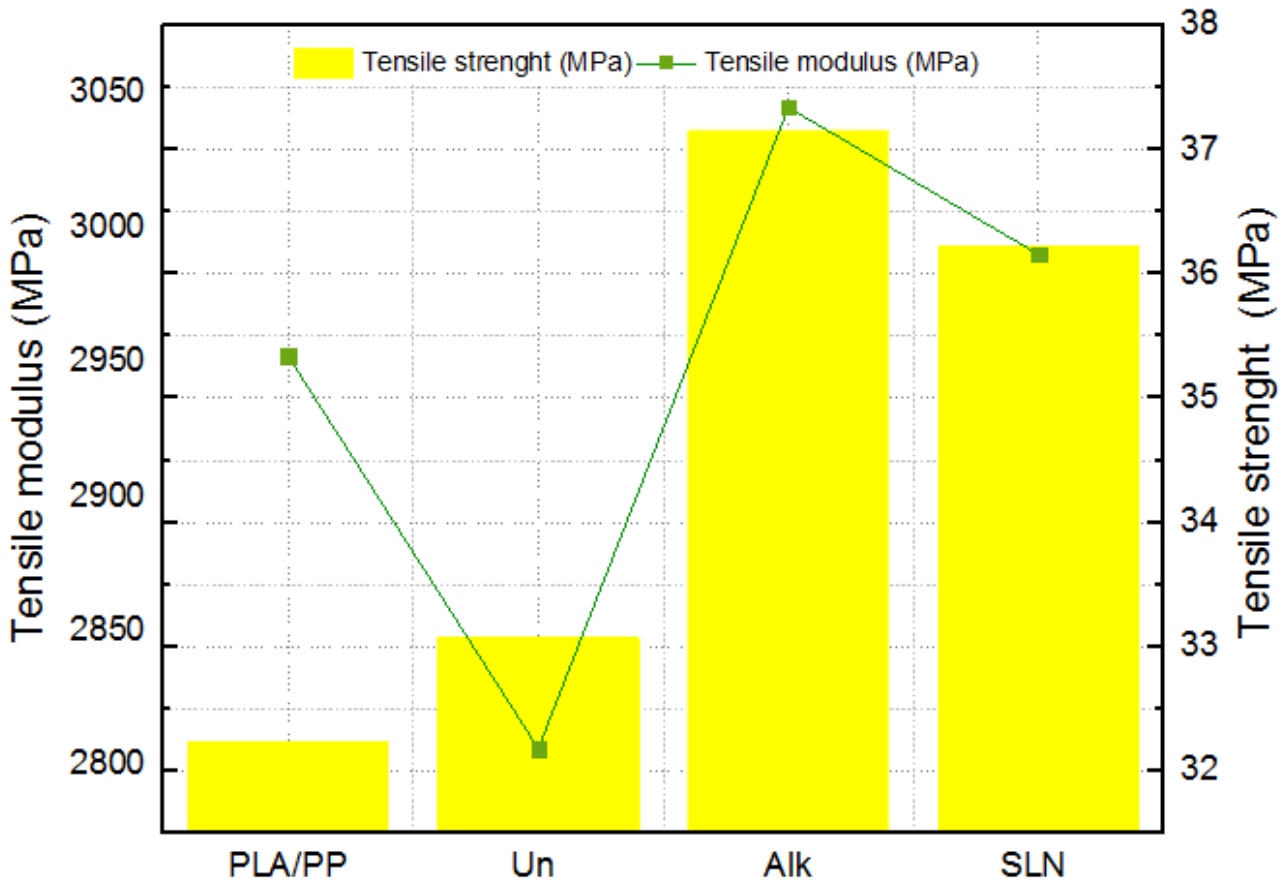


Fig. 5.5 The tensile strength and tensile modulus of all printed samples.

The tensile strength and modulus of neat polymer (PLA) reinforced with 7.5% waste PP (PLA/PP), untreated Arundo fibre (Un), and treated Arundo fibre are presented in **Figure 5.5.** Arundo fibre treatment involved immersion in alkali (Alk) and in both alkali and 5% silane (SLN), with the fibre ratio remaining constant at 3%. According to the findings, the tensile characteristics of the Arundo fibre composites (ArFC) altered drastically after chemical treatments of the fibres. Based on the results, the neat PLA/PP tensile strength was 35.34 MPa and the tensile modulus was 2808.5 MPa. However, the inclusion of untreated ArFs in the matrix reduced the tensile modulus. The lack of interaction between the fibres and the matrix might explain the poor transmission of stress from the matrix to the fibre[10], [13].

A marginal increase in strength and modulus of +16,05% and + 6,62 % respectively, was obtained for the Alk composite in comparison to the untreated composite (Un). The enhancement in interfacial bonding after the alkaline treatment of ArFs was presumably caused by the creation of more sites for mechanical interlocking. The strength of the composite was increased as a result of enhanced fibre interactions at the interface [8].

Yet, in the case of the SLN composite (ArF was treated with n-octyltriethoxysilane), a 12.37% increase in tensile strength and a 5.10% increase in tensile modulus were observed. Jamadi et al [13]suggested that By enduring higher concentrations of silane treatment, the elimination of lignin and hemicellulose showed promising results in achieving solid bonding between the fibre surface and the matrix, but a higher concentration might also have an adverse effect on the surface of the fibre and reduce its distinctive features. To summarize, higher concentrations of silane can be employed to eliminate impurities more efficiently, nonetheless, this may impair tensile strength due to surface fibre cracking and degradation of the chemical composition of the fibre. Regardless, a comparable study by Liu et al.[14]revealed that a 5 wt% concentration(considered high) increased both tensile strength and modulus.

Table 5.3 Tensile properties of 3D Printed Samples

Fibres	Type	GL [mm]	σ [MPa]	Ɛ [%]	E [MPa]	Ref
-	PLA/PP	50	35.34±2.76	0.018±0.008	2808,5±138	presentwork
ArF	Alkali	50	37.34±1.61	0.017±0.008	3036.0±47	
ArF	Silane	50	36.15±2.31	0.017±0.008	2992.8±133	
ArF	Un	50	32.17±3.33	0.016±0.008	2847.5±183	
BALF	Un	50	1572±2.33	1.45±0.03	67000± 1.2	[8]
BALF	Silane	50	2125±3.33	2.89±0.06	76000±1.9	[8]
RSF	Silane	50	10.3±1.33	-	671.42±0.8	[6]

Table 5.3 summarizes the different experimental results obtained for the tested specimens' stress, strain at rupture, and Young's modulus. Analysis of this table clearly demonstrates significant values and mechanical property values obtained.

5.3.2 Impact

To gain a comprehensive understanding of the material's toughness, the Izod impact test was conducted on various composites. Impact testing equipment was used to analyse the impact strength parameters of each composite.

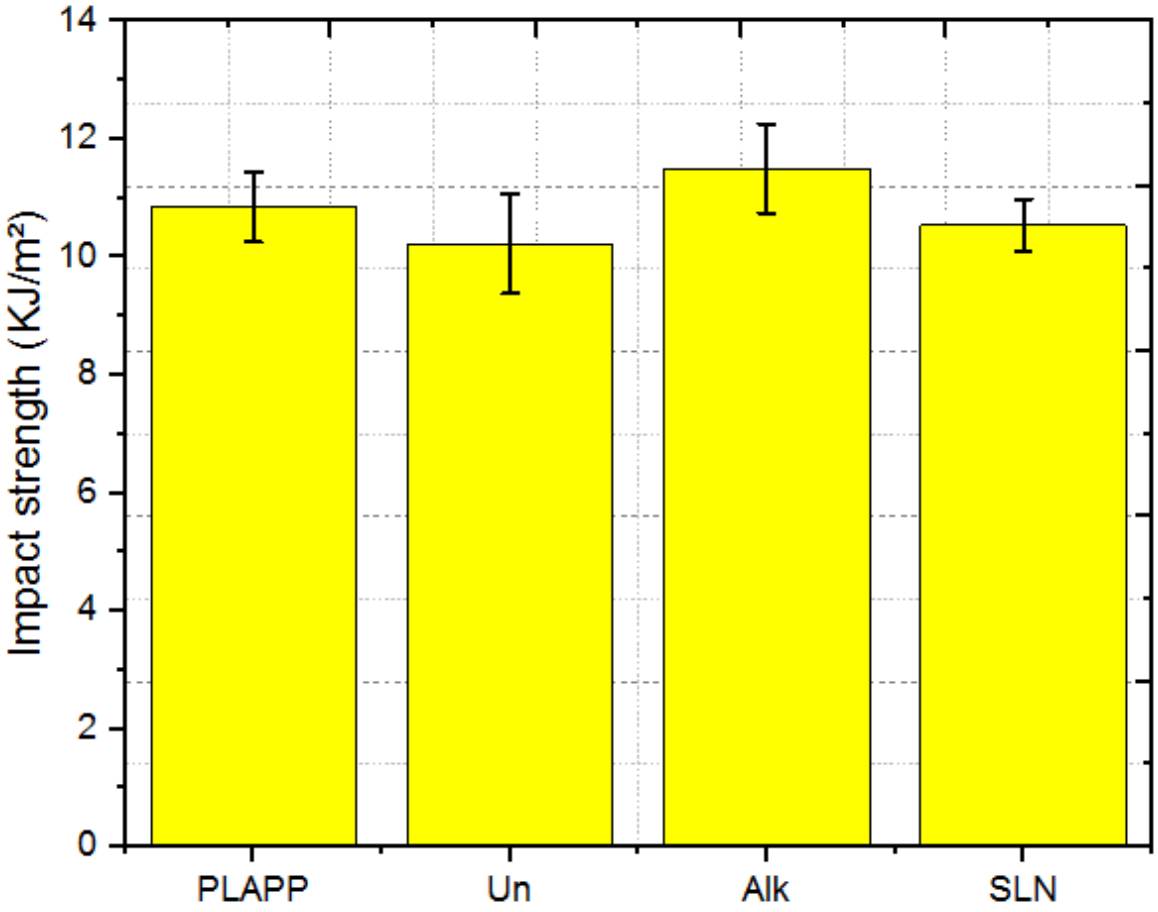


Fig.5.6 Impact strength of composites.

Figure 5.6 depicts the impact strength data acquired to evaluate the impact strength of PLA/PP, Un, ALK, and SLN reinforced polymer composites.It has been demonstrated that surface modifications increased the impact properties of the reinforced biocomposites. Despite the addition of 3% only alkali-treated Arundo fibre as reinforcement for the PLA/PP, impact strength improved by roughly 12% when compared to the Un. Also, compared to UN, the silane-treated composites exhibited a 3,01% increase in impact strength. This might be because the filler and matrix have a higher interfacial connection[8]. However, compared to Alk composite, silanization of the fibre leads to a small loss in impact strength. Ultimately, out of all the biocomposites, the Alk biocomposite exhibits the highest impact strength measuring 11.50 KJ/m^2.

5.4 Morphological Analysis

A typical specimen from each tensile specimen set that has been evaluated is shown in **Figure 5.7.** Fractures occurred in the gauge parts for all the samples tested. **Figure 5.8** displays

a series of scanning electron microscopy (SEM) images of the breaking surface. These images will give essential information about each material's microstructural characteristics and fracture behaviour.

Fig. 5.7 Broken specimens after tensile test from left to right, PLA/PP, Un, Alk, and SLN respectively.

It can be noted in **Figures 5.8.** a1-3 that the fracture surface of the PLA/PP specimen was rougher and more irregular. Physical separation of the PLA phase and the PP phase was seen in the multilayer system, which is characteristic of immiscible polymer blends[2]. Upon examining the pictures in **Figure 5.8** (b), (c), and (d), It can be observed that, in general, the filler dispersion is good, since no agglomeration was observed, and the fibre ratio in all composites was just 3wt.%.

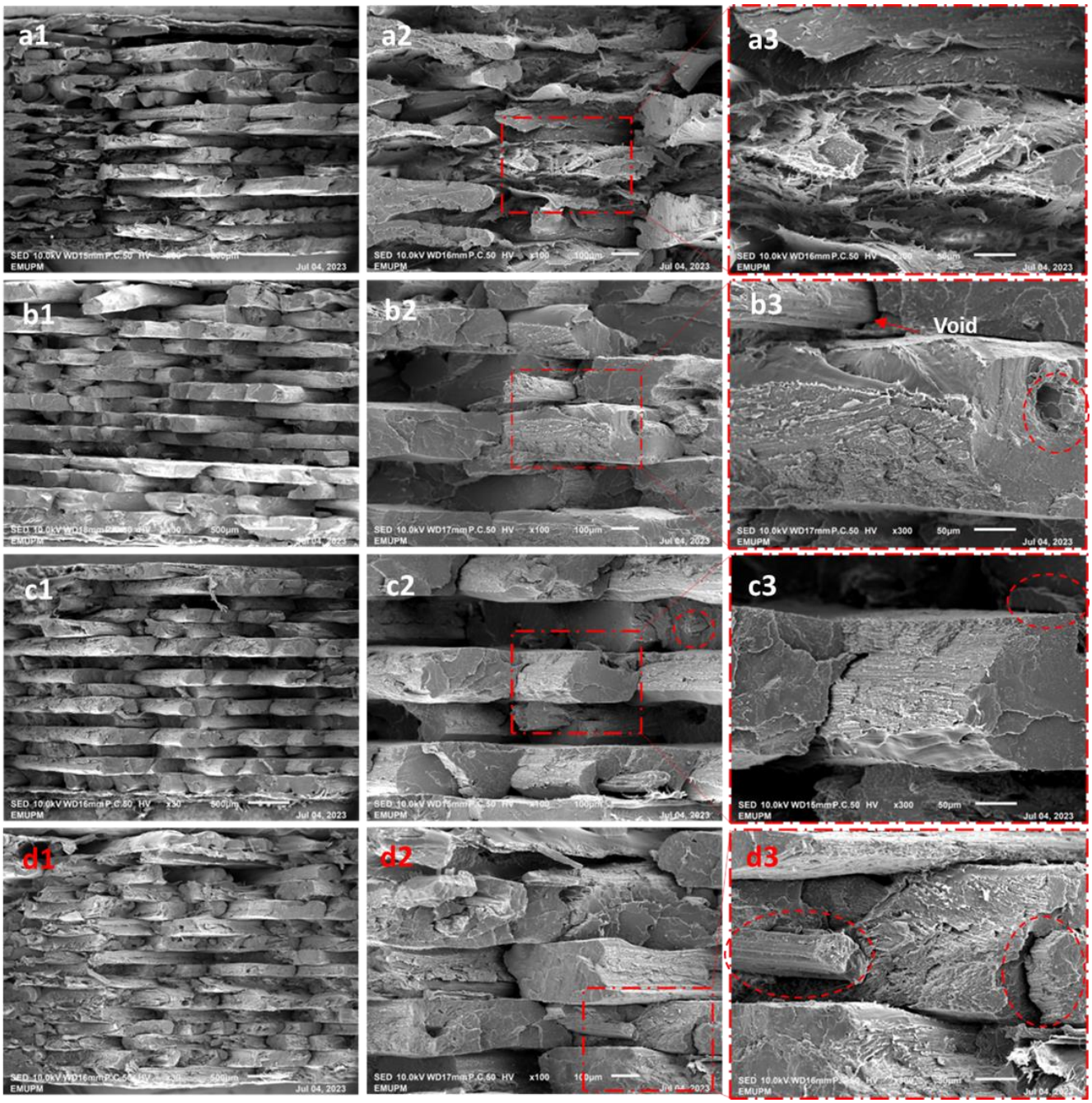


Fig. 5.8 SEM image shows a cross-section of a 3D-printed tensile specimen fracture of (a1-a3) neatPLA/PP, (b1-b3) Un, (c1-c3) Alk, and (d1-d3) SLN.

For the Un composites specimen in **Figure 5.8** b, void around the fibre- PLA/PP interface can be observed, along with the presence of gaps and fibre pullouts, which is expected given that no surface treatment was performed on the fibre. Whereas for both Alkali and later silane-treated fibre, the bonding strength between the Alkali-ArF surface and the matrix was evident.

Similar tendencies were observed in the results of studies by Yu et al. and Yang et al. [6],[15]. It can be shown that by treating the fibre, the elasticity and tensile strength improves, but the ability to deform decreases. To outline, this work also demonstrates that the chemical

treatment of the fibre optimizes tensile characteristics, as evidenced by data acquired on similar systems in the literature [16].

5.5 The Water Absorption

Figure 5.9 depicts all reinforced Arundo fibre composites' water absorption: Un, Alk, and SLN, immersed in water for several days.

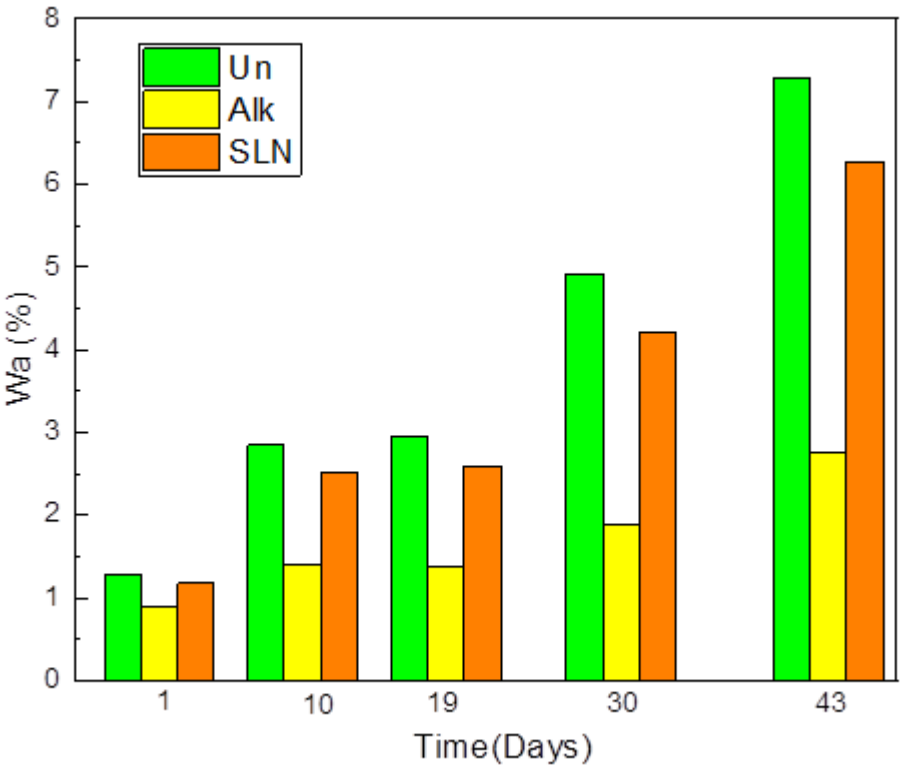


Fig. 5.9 Water absorption (WA) for PLA/PP and untreated and treated ArFocomposites immersed in water.

On the first day, Un samples absorbed water by around 1,30%, while Alk and SLN absorbed 0,9% and 1,17% respectively. Due to its hydrophilicity, the water absorption of Un composite continued increasing with time, reaching 7,30% on day 43. However, over the same time, water absorption was reduced by about 64% and 13.33% for Alk and SLN, respectively, compared to the Un specimens. These reductions were mostly because of enhanced matrix-ArF interfacial adhesion [17], as validated by SEM graphics. Lastly, the finding confirms that fibre treatment affects water absorption characteristics significantly.

5.6 Thickness swelling of the printed specimen

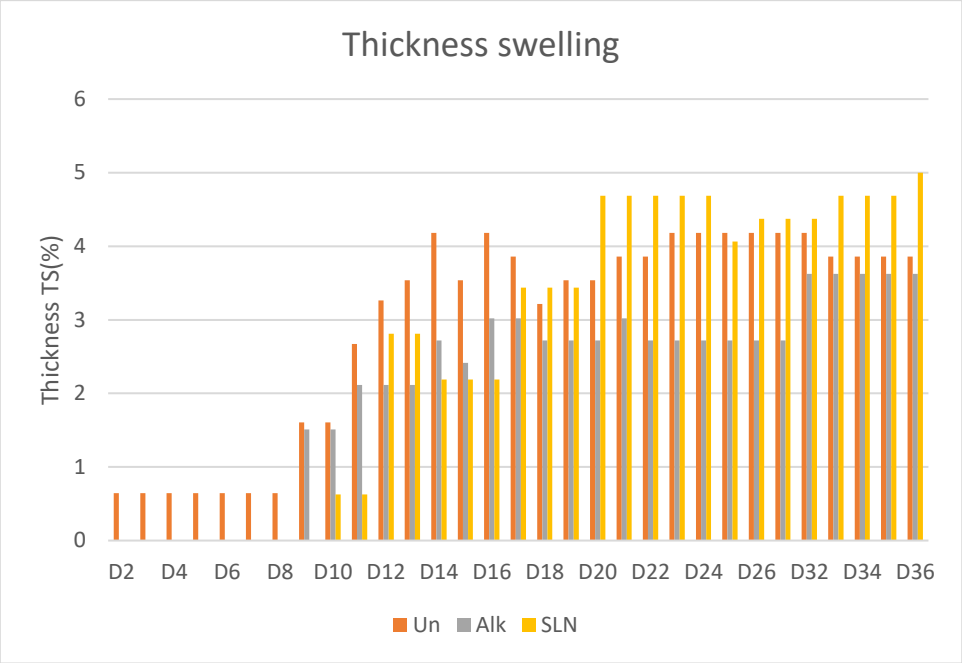


Fig. 5.10 Impact of chemical treatment on the specimen's thickness swelling.

The best method for examining dimensional stability is to use thickness swelling (TS) measurements to analyze the moisture resistance of composite materials. This study evaluated the stability of printed composites when exposed to prolonged water immersion. **Figure 5.10** demonstrates the impact of fibre treatment on the thickness swelling of the printed composite specimens. In general, the majority of natural fibres exhibit capillary action when immersed in water, facilitating water absorption in the sample, and consequently causing fibre swelling and an overall increase in the sample's dimensions[18].

The illustration reveals a consistent rise in thickness swelling for the untreated specimen during the initial 8 days, contrasting with the absence of swelling in the alkali and silane-treated composites. The principal cause of thickness swelling (TS) in untreated composite materials is a high porosity and void content. In addition, the thickness of lignocellulosic-based composites is affected by the amount of water in the lumen as well as the expansion—both irreversible and reversible—caused by the composites' swelling[19].However, After the eighth day, the thickness swelling rate begins to increase for

both the alkali and silane-treated composites. Out of all the tested samples, the composite treated with alkali exhibited the most substantial long-term dimensional stability (DS).It can be inferred that composites treated with alkali had fewer pores exposed to water and reduced void content. The surface treatment removed the –OH groups from the fibre surface, leading to enhanced interfacial bonds[20].Nevertheless, the variations in thickness swelling values among all composites were not statistically significant (3.85–4.68%, p = 0.83%). This suggests that the impact of fibre treatment on water swelling was minimal.

References

[1] F. Vincenzo, B. Luigi, S. Roberto,"PLA based biocomposites reinforced with Arundo donax fillers, " Composites Science and Technology, vol. 105, p. 110-117,2014, doi: 10.1016/j.compscitech.2014.10.005.

[2] N. Ploypetchara, P. Suppakul, D. Atong, C. Pechyen, “Blend of Polypropylene/Poly (lactic acid) for Medical Packaging Application: Physicochemical, Thermal, Mechanical, and Barrier Properties,” *Energy Procedia*, vol. 56, pp. 201–210, Jan. 2014, doi: 10.1016/j.egypro.2014.07.150.

[3] G. Moradkhani, J. Profili, M. Robert, G. Laroche, S. Elkoun, “Effects of Wet and Dry Treatments on Surface Functional Groups and Mechanical Properties of Flax Fibre Composites,” *Coatings*, vol. 13, no. 6, Art. no. 6, Jun. 2023, doi: 10.3390/coatings13061036.

[4] V. Mazzanti, R. Pariante, A. Bonanno, O. Ruiz de Ballesteros, F. Mollica, G. Filippone, “Reinforcing mechanisms of natural fibres in green composites: Role of fibres morphology in a PLA/hemp model system,” *Compos. Sci. Technol.*, vol. 180, pp. 51–59, Aug. 2019, doi: 10.1016/j.compscitech.2019.05.015.

[5] J. P. Mofokeng, A. S. Luyt, T. Tábi,J. Kovács, “Comparison of injection moulded, natural fibre-reinforced composites with PP and PLA as matrices,” *J. Thermoplast. Compos. Mater.*, vol. 25, no. 8, pp. 927–948, Dec. 2012, doi: 10.1177/0892705711423291.

[6] Q. Yang , “Effect of Chemical Treatment on Rice Straw Fibre Surface and Properties of Straw/Polylactic Acid Composites,” *J. Nat. Fibres*, vol. 20, no. 2, p. 2228486, Aug. 2023, doi: 10.1080/15440478.2023.2228486.

[7] M. S. Huda, L. T. Drzal, M. Misra, A. K. Mohanty, “Wood-fibre-reinforced poly(lactic acid) composites: Evaluation of the physicomechanical and morphological properties,” *J. Appl. Polym. Sci.*, vol. 102, no. 5, pp. 4856–4869, Dec. 2006, doi: 10.1002/app.24829.

[8] P. j. Jandas, S. Mohanty, S. k. Nayak, H. Srivastava, “Effect of surface treatments of banana fibre on mechanical, thermal, and biodegradability properties of PLA/banana fibre biocomposites,” *Polym. Compos.*, vol. 32, no. 11, pp. 1689–1700, 2011, doi: 10.1002/pc.21165.

[9] S. Oza, H. Ning, I. Ferguson, N. Lu, “Effect of surface treatment on thermal stability of the hemp-PLA composites: Correlation of activation energy with thermal degradation,” *Compos. Part B Eng.*, vol. 67, pp. 227–232, Dec. 2014, doi: 10.1016/j.compositesb.2014.06.033.

[10] T. Lu, M. Jiang, Z. Jiang, D. Hui, Z. Wang,Z. Zhou, “Effect of surface modification of bamboo cellulose fibres on mechanical properties of cellulose/epoxy composites,” *Compos. Part B Eng.*, vol. 51, pp. 28–34, Aug. 2013, doi: 10.1016/j.compositesb.2013.02.031.

[11] N. Lu and S. Oza, “Thermal stability and thermo-mechanical properties of hemp-high density polyethylene composites: Effect of two different chemical modifications,” *Compos. Part B Eng.*, vol. 44, no. 1, pp. 484–490, Jan. 2013, doi: 10.1016/j.compositesb.2012.03.024.

[12] S. Wang, L. Capoen, D. D’hooge, L. Cardon, “Can the melt flow index be used to predict the success of fused deposition modelling of commercial poly(lactic acid) filaments into 3D printed materials?,” *Plast. Rubber Compos.*, vol. 47, pp. 1–8, Nov. 2017, doi: 10.1080/14658011.2017.1397308.

[13] A. H. Jamadi, N. Razali, M. Petrů, M. M. Taha, N. Muhammad,R. A. Ilyas, “Effect of Chemically Treated Kenaf Fibre on Mechanical and Thermal Properties of PLA Composites Prepared through Fused Deposition Modeling (FDM),” *Polymers*, vol. 13, no. 19, Art. no. 19, Jan. 2021, doi: 10.3390/polym13193299.

[14] Y. Liu , “Characterization of silane treated and untreated natural cellulosic fibre from corn stalk waste as potential reinforcement in polymer composites,” *Carbohydr. Polym.*, vol. 218, pp. 179–187, Aug. 2019, doi: 10.1016/j.carbpol.2019.04.088.

[15] Y. Wangwang, D. Lili, L. Wen, «Effects of rice straw powder (RSP) size and pretreatment on properties of FDM 3D-printed RSP/poly (lactic acid) biocomposites". *Molecules*, vol. 26, no 11, p. 3234,2021.

[16] R. Scaffaro, M. C. Citarrella, M. Morreale, “Green Composites Based on Mater-Bi® and Solanum lycopersicum Plant Waste for 3D Printing Applications,” *Polymers*, vol. 15, no. 2, Art. no. 2, Jan. 2023, doi: 10.3390/polym15020325.

[17] Srinakharinwirot, “3D Printing Filaments Prepared from Modified Poly(Lactic Acid)/Teak Wood Flour Composites: An Investigation on the Particle Size Effects and Silane Coupling

Agent Compatibilisation," *J. Phys. Sci.*, vol. 30, no. 2, pp. 169–188, Sep. 2019, doi: 10.21315/jps2019.30.2.10.

[18] M. Jawaid, H. P. S. Abdul Khalil, "Cellulosic/synthetic fibre reinforced polymer hybrid composites: A review," *Carbohydr. Polym.*, vol. 86, no. 1, pp. 1–18, Aug. 2011, doi: 10.1016/j.carbpol.2011.04.043.

[19] H. P. S. Abdul Khalil, A. M. Issam, M. T. Ahmad Shakri, R. Suriani, A. Y. Awang, "Conventional agro-composites from chemically modified fibres," *Ind. Crops Prod.*, vol. 26, no. 3, pp. 315–323, Oct. 2007, doi: 10.1016/j.indcrop.2007.03.010.

[20] R. Siakeng, "Alkali treated coir/pineapple leaf fibres reinforced PLA hybrid composites: Evaluation of mechanical, morphological, thermal and physical properties," *Express Polym. Lett.*, vol. 14, pp. 717–730, Aug. 2020, doi: 10.3144/expresspolymlett.2020.59.

GENERAL CONCLUSION

With the main goal of creating an advanced reinforced composite made from plastic waste, a study on the PLA/PP Arundo donax L. fibre composite was conducted. Notably, previous research efforts have rarely addressed the chemical modifications of natural fibre in connection to 3D-printed specimens' properties. Thus, this present study delves into an examination of the effects of alkali and silane treatment on the Arundo fibre structure, along with the consequential impact on the thermal and rheological properties of the Arundo donax L. fibre/PLA/rPP composite. Furthermore, the study encompasses a thorough analysis of the mechanical properties exhibited by the 3D-printed specimens.

In comparison to the neat PLA/PP mix, DSC tests revealed that Tg increased with the inclusion of both untreated and treated Arundo fibre. Moreover, an observed cold crystallization peak during the first heating cycle in the case of alkali-treated fibre (Alk-ArF) indicated that Alk-ArF acted as a nucleation agent, accelerating the crystallinity of the PLA matrix. The TGA findings indicated that chemically treating Arundo fibre enhances its thermal stability. When compared to Un, both Alk and SLN showed a modest increase in onset temperature, with Alk increasing by 7% and SLN increasing by 5%. Despite adding only 3% fibre by weight. When compared to the Un composite, the maximum degradation of the ALK composite was increased by 7% and that of the SLN composite by 6.69%. The composites' MFI values ranged from 4 to 5 g/10 min (at 190 °C with a load of 2.16 kg), enabling the 3D printing of the material.

The tensile strength of the neat PLA/PP is 35.34 MPa, and the tensile modulus is 2808.5 MPa. In contrast, the addition of untreated ArFs to the matrix resulted in a decrease in tensile modulus. This might be attributed to a lack of adhesion between the fibres and the matrix. When compared to the untreated composite (Un), the Alk composite demonstrated an improvement in strength and modulus of +16,05 % and +6,62 % respectively. This improvement is attributed to the creation of additional mechanical interlocking sites, enhancing interfacial bonding after the alkaline treatment of ArFs. Similarly, the SLN composite showed gains in tensile strength and modulus of 12,37% and 5,10%, respectively. Furthermore, both chemical modifications improved the stability of impact strength.

The SEM image of the 3D-printed tensile specimen fracture cross-section confirmed that the chemical treatment of ArF had a significant impact on the bonding strength between the fibre interface and the matrix surface. Un composites specimen figures showed a void surrounding the fibre-PLA/PP mix interface, as well as the emergence of gaps and fibre pullouts. In contrast, a strong bonding strength at the interface was observed for Alkali and later silane-treated fibre.

A major reduction in material water absorptionand thickness swelling are key benefits of the treated composites. Water absorption drops dramatically with the addition of the treated fibre, from 7.30% for Un composite to 2.6% for the material having Alkali-treated fibre (ALK). Throughout the 43-day testing period, the water absorption of samples with silane-treated fibre (SLN) also remained lower than that of Un samples. In conclusion, ALK composites in our work provided the greatest performance demonstrating that chemical modification is a potential technique to improve the properties of 3D-printed NFRC.

RECOMMENDATIONS FOR FUTURE RESEARCH

Based on the findings of this study, several recommendations are proposed for further exploration to enhance the quality of composite filament for 3D printing:

- Conduct experiments with various concentrations of the silane coupling agent to optimize the interfacial bonding between fillers and the matrix. This can be achieved by modifying the surface of the fillers to potentially improve composite filament quality.
- Investigate the impact of altering the PLA:PP ratio on mechanical properties. Exploring different ratios may provide insights into achieving an optimal blend that enhances overall performance in 3D printing applications.
- Examine the effects of varying Arundo donax weight ratios on the final properties of the composite filament. This analysis could contribute to understanding the influence of different filler percentages on the overall characteristics of the 3D-printed material.
- Encourage the Algerian industry to focus on the development of Arundo donax L. fibres and composites based on different plastic waste. This can lead to the creation of locally sourced and produced materials with potential applications in 3D printing and other industries.

ABSTRACT:

The use of plastic waste and biomass fillers is increasing, as they constitute easily accessible and sustainable resources. This thesis significantly advances the use of plastic waste and a local natural fiber in 3D printing to create biosourced, sustainable and renewable raw materials.

Arundo donax L. is examined in this study as a suitable reinforcing agent for PLA/waste PP-based 3D printing filament. To improve the compatibility between fiber and polymer, Arundo fiber has been chemically modified by alkaline and silane treatment. The effect of chemical treatment on the thermal, mechanical and morphological properties of the composites was studied. The 3D printed specimens were also tested for tensile strength, Izod impact and water absorption. Composites treated with alkali (ALK) and combination of alkali and silane treatment (SLN) showed good results. The tensile strength and elastic modulus of the materials increased, as well as their stability maintained during the Izod impact test, demonstrating that the incorporation of Arundo fiber did not result in a loss of performance. Scanning electron microscopy (SEM) examination corroborated these findings by confirming the creation of beneficial interfacial contacts between the matrix and fiber components.

Keywords: polypropylene; 3D printed biocomposites; Arundo donax. Thermal properties; Morphological properties; Mechanical properties.

RÉSUMÉ

Les déchets plastiques sont largement utilisés dans la fabrication de produits abordables et respectueux de l'environnement, car ils constituent des ressources facilement accessibles et durables. Cette thèse fait progresser significativement l'utilisation de déchets plastiques et d'une fibre naturelle locale dans l'impression 3D pour créer des matières premières biosourcées, durables et renouvelables.

L'Arundo donax L. est examiné dans cette étude en tant qu'agent de renforcement approprié pour le filament d'impression 3D à base de PLA/déchets de PP. Afin d'améliorer la compatibilité entre la fibre et le polymère, la fibre Arundo a été modifiée chimiquement par traitement alcalin et au silane. L'effet du traitement chimique sur les propriétés thermiques, mécaniques et morphologiques des composites a été étudié. Les spécimens imprimés en 3D ont également été soumis à des tests de résistance à la traction, d'impact Izod et d'absorption d'eau. L'Arundo donax L. est examiné dans cette étude en tant qu'agent de renforcement approprié pour le filament d'impression 3D à base de PLA/déchets de PP. Afin d'améliorer la compatibilité entre la fibre et le polymère, la fibre Arundo a été modifiée chimiquement par traitement alcalin et au silane. Les composites traités aux alcalis (ALK) et à la combinaison de traitements aux alcalis et au silane (SLN) ont affiché de bons résultats. La résistance à la traction et le module d'élasticité des matériaux ont augmenté, ainsi que leur stabilité maintenue lors de l'essai de choc Izod, démontrant que l'incorporation de la fibre d'Arundo n'a pas entraîné de perte de performance. . L'examen au microscope électronique à balayage (MEB) a corroboré ces conclusions en confirmant la création de contacts interfaciaux bénéfiques entre la matrice et les composants de fibres.

Mots-clés : polypropylène; biocomposites imprimés en 3D; Arundo donax. Propriétés thermiques; Propriétés morphologiques; Propriétés mécaniques.

ملخص:

إن استخدام النفايات البلاستيكية والالياف النباتية كمعزز في ازدياد، نظرًا لتوفرها بسهولة وكونها مصادر مستدامة. هذه الرسالة العلمية تسهم بشكل كبير في استخدام نفايات البلاستيك وألياف نباتية طبيعية محلية في الطباعة ثلاثية الأبعاد لإنشاء مواد خام متجددة, مستدامة، ومأخوذة من مصادر حيوية.

تمت دراسة ألياف الأرندو دوناكس (Arundo donx L.) كعامل تعزيز مناسب للخيط المطبوع ثلاثي الأبعاد المكون منPLA / PP معاد تدويره .ومن أجل تحسين التوافق بين الألياف والبوليمر، تم تعديل ألياف أرندو كيميائيًا باستخدام المعالجة القلوية والسيلانية. تمت دراسة تأثير المعالجة الكيميائية على الخصائص الحرارية والميكانيكية والمورفولوجية للمركبات. كما تم اختبار الشدة وقوة الصدم وامتصاص الماء للعينات المطبوعة ثلاثية الأبعاد أيضًا. أظهرت المركبات التي تم معالجتها بالقلويات (ALK) ومزيج المعالجة القلوية والسيلانية (SLN) نتائج جيدة. زادت قوة الشد والمعامل للمواد ، وكذلك استقرارها في اختبار الصدمة بأداة إيزود، مما يظهر أن إدماج ألياف الأرندو لم يؤدي إلى ضعف في الأداء. دعم الفحص بالمجهر الإلكتروني هذه النتائج عن طريق تأكيد إنشاء اتصالات تفاعلية مفيدة بين مكونات المصفوفة والألياف.

الكلمات المفتاحية: مادة البولي بروبيلين؛ المركبات الحيوية المطبوعة ثلاثية الأبعاد؛ أرندو دوناكس. الخصائص الحرارية؛ الخصائص المورفولوجية. الخصائص الميكانيكية.