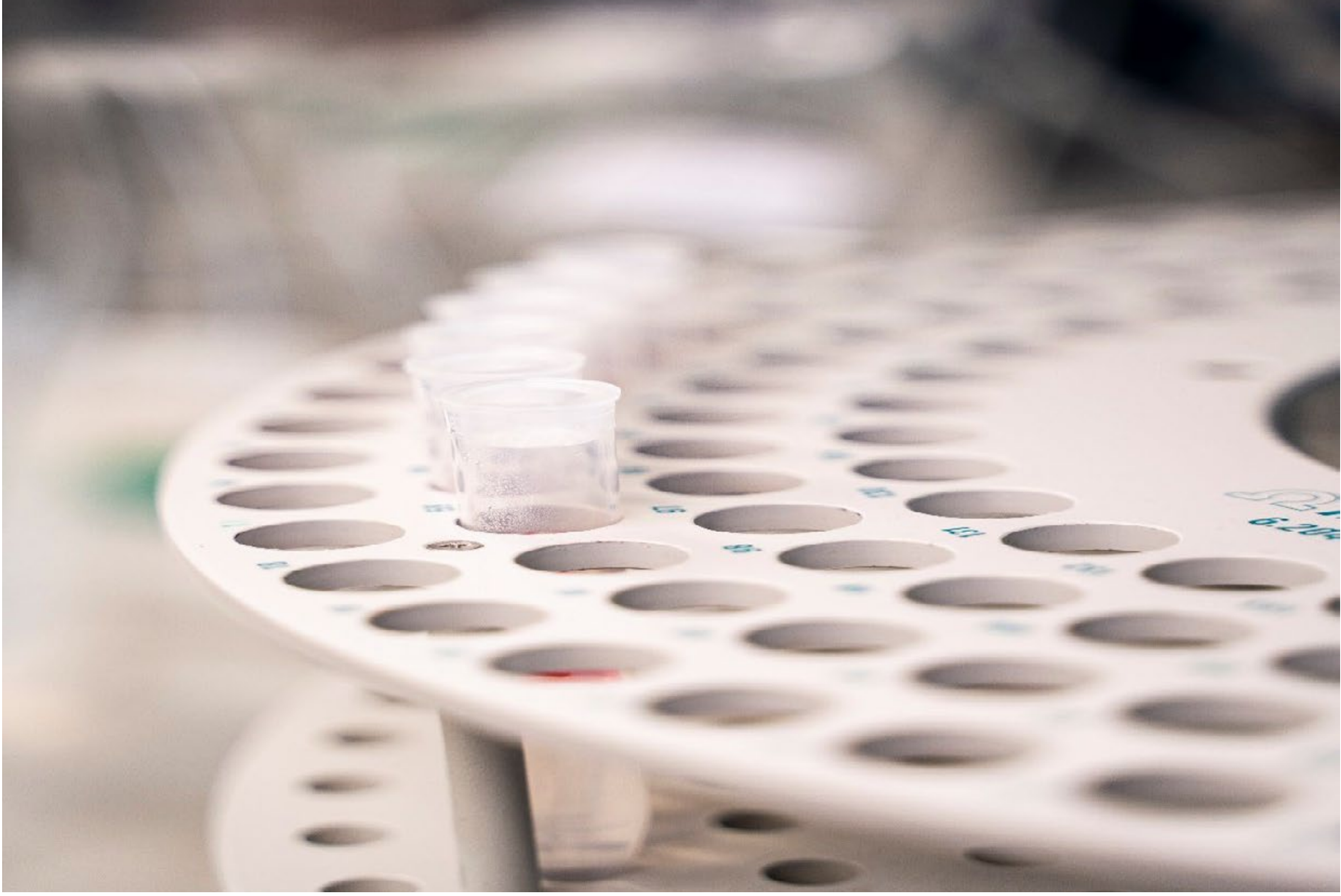

Rathish Rajan, Simo Huhtanen, Egidija Rainosalo

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CENTRIA UNIVERSITY OF APPLIED SCIENCES, 2023

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CONTENTS

1 INTRODUCTION

Fused granular fabrication (FGF) is a material extrusion type of 3D-printing method, which uses filled or unfilled thermoplastic granules (pellets) as printing material. Compared to fused filament fabrication (FFF), the FGF method can print large components for various end-use applications.

Among the thermoplastic materials used for FGF 3D-printing, wood plastic composites (WPC) carry the advantage of being made from wholly or partly bio-based materials. Moreover, it reduces the product's carbon footprint compared to synthetic fiber-reinforced composite material. Despite many benefits of this material, the main limitation is that WPC is restricted only to specific thermoplastic polymers because wood flour tends to degrade thermally when processed above 200°C (Poletto, Zattera, Forte & Santana 2012). Therefore, the thermoplastic polymers used to produce WPC are mainly polypropylene (PP), polyethylene (PE), and polyvinylchloride (PVC) (Khan, Srivastava & Gupta 2020).

Figure 1. Schematic representation of 3D-printed mold life cycle

Recently, Centria University of Applied Sciences (Centria) in Finland developed a method to produce WPC-based tooling for the composite industry by robot-assisted FGF method (Interreg Baltic Sea Region n.d.). The conventional method to produce composite tooling is a multistage, labor-intensive process involving multiple materials, making dismantling and recycling difficult. Molds are manufactured in two-stage process, which consists of making a plug in the first stage. Milling of the plug from the block generates a considerable amount of waste, depending on size and shape of the final part. The particles removed in milling process are very light and small, creating an undesirable working condition affecting the quality of lamination and the workers' health. By adopting the robot-assisted FGF method and using partly bio-based wood plastic composite as printing material, Centria demonstrated the possibility of producing composite tooling that can be recycled at its end-of-lifetime, as seen in Figure 1.

The above-discussed method can be used for direct 3D-printing of components for various industries. For example, the boat building industry widely uses glass and carbon fibre reinforced thermoset composites to build multiple components for boats. Due to strong chemical crosslinked structures, this material is very durable, making it impossible to recycle at the end of service life. Replacing the thermoset with thermoplastic raw material that can be processed by FGF method will provide the boat-building industry with sustainable materials that can be recycled and reused. However, some challenges must be addressed in the direct 3D-printing of boat components. For instance, direct 3D-printed components should have satisfactory mechanical, thermal, weathering resistance and other relevant properties compared to the conventional materials.

This report discusses the selection of thermoplastic composite materials potentially suitable for manufacturing boat components and composite tooling by 3D printing (FGF) based on different testing methods. Thermal expansion/

shrinkage of thermoplastic materials in 3D printing large-size products cause shape distortion. It is known fact, that thermoplastic materials require fibers or fillers to reduce material shrinkage from hot melt to room temperature. Therefore, wood-filled thermoplastic composites and glass fiber reinforced thermoplastic composites are selected for testing for various properties relevant to the service life of the printed products, boat components and moulds. The following sections of the report describe the chosen materials, testing methods and results in detail.

2 MATERIALS, METHODS AND CHARACTERIZATION

The main factors considered when selecting the materials are cost, commercial availability, printability, bio-based content, and long-term performance in outdoor conditions. Centria, in previous projects, had tested the chemical resistance of various thermoplastic polymers and concluded that polypropylene (PP) is best in terms of cost and performance. Therefore, commercially available wood-plastic composite and glass fiber-reinforced polymer composites based on polypropylene were selected for testing. Also, three bio-based polymers were used to produce wood-plastic composites to test as fully bio-based alternatives.

2.1 MATERIALS

Polypropylene-based wood plastic composite which is commercially available was chosen as a bio-based material for 3D printing. Three bio-based polyesters (bio-PES) named K35B, C73, and D55 were kindly provided by Brightplus Oy, Finland. According to the information from the supplier, all three polymers are UV-stabilized. The UV-stabilizers Chimassorb 2020 and Uvinal 4050 (HALS) and UV absorber Tinuvin 329 were kindly supplied by BASF Europe.

Table 1: Details on composites considered for 3D-printing

Composite name	Manufacturer	Fiber content (wt %)	Polymer	Density (g/cm3) **	MFI (g/10 min) **
Dura 50%	Storaenso	50	PP	1.11	1.0 (190oC/2.16 kg)
K35B+W20*	Brightplus Oy	20	Bio-PES	1.28	1.2 (190oC/2.16 kg)
C73+W20*	Brightplus Oy	20	Bio-PES	1.27	3.6 (190oC/2.16 kg)
D55+W20*	Brightplus Oy	20	Bio-PES	1.28	3.3 (190oC/2.16 kg)
D55+W30*	Brightplus Oy	30	Bio-PES	1.29	0.9 (190oC/2.16 kg)
ASA 20% GF	Polymaker	20	ASA	1.20	13.7 (230oC/2.16 kg)
PP 30% GF	CEAD	30	PP	1.09	4.9 (230oC/10.0 kg)

*Compounding done at Centria; **tested at Centria

The Durasense 50 3D was purchased from Storaenso. Considering that the ASA shows inherent UV-resistance properties, ASA filled with 20% GF (Polycore 3012) meant for 3D printing was purchased from Polymaker. As an alternative to PP-based wood plastic composites, polypropylene reinforced with 30% glass fiber purchased from CEAD was also considered a raw material for testing. Details about the selected composite materials are listed in Table 1.

2.2 METHODS

This report section discusses sample preparation by compounding, compression moulding and 3D-printing. The test plates made by the latter two methods were CNC machined to test specimens suitable for different testing described in Chapter 2.3.

2.2.1 COMPOUNDING

Bio-polyesters (Bio-PES) were compounded with wood flour in a twin-screw extruder Coperion ZSK18 MEGAlab (Figure 2). The wood flour obtained from the plywood industry was compounded with bio-PES polymers at the recommended processing temperature of each polymer.

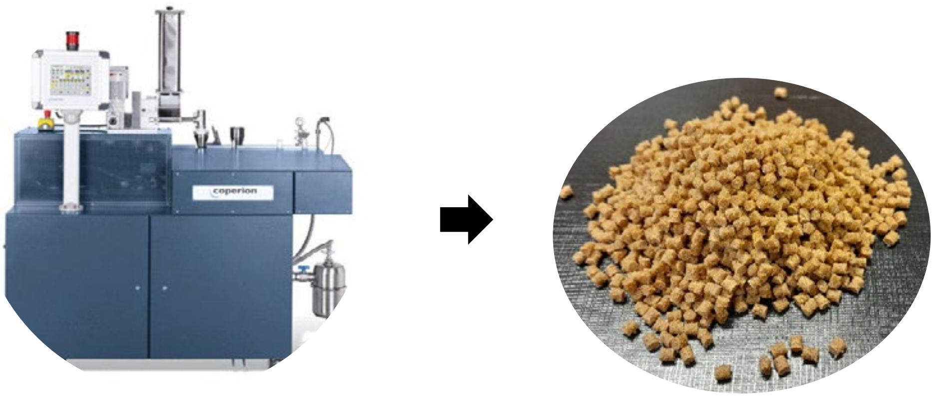


Figure 2. Continuous co-rotating twin-screw extruder used for compounding (left) and representation of compounded granules

The extruded strands were cooled and shredded to obtain granules. The fiber content of each composite can be seen in Table 1. Similarly, the UV-test samples were produced from composite granules made by compounding Durasense 50 3D with UV additives. Dura 30% was prepared by compounding Durasense 50 3D with PP and UV additives to obtain wood flour content of 30 wt.%. The two UV stabilizers and one UV absorber were used in 0.1% and 0.2% by weight of the compound.

2.2.2 COMPRESSION MOULDING

Test samples were prepared by compression molding of composite granules into plates. Mold consists of two steel plates, steel frame, and two polytetrafluoroethylenes (PTFE) sheets that prevent the sample from sticking to the mould. Mould was heated to desired temperature ranging from 190-220°C depending on the processing temperature of each composite material considered in the study. Before applying the load, the mold with the sample was kept at processing temperature without load for 15 minutes to let the remaining moisture in the pellets vaporize. Then load of 14 tons was applied for 3 minutes. Mold was cooled to room temperature and the plates were released. The Dura 50%, ASA 20% GF and PP 30% GF test plates were produced from the granules without further processing. A representation of the sample preparation process is seen in Figure 3.

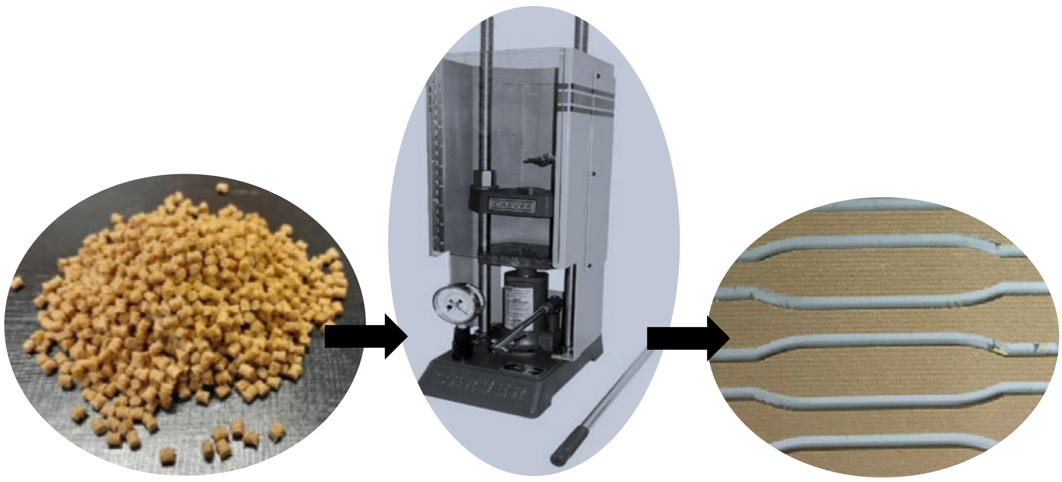


Figure 3. Representation of processing the test specimens by compression molding

2.2.3 3D-PRINTING OF TEST SAMPLES

3D-printed samples were printed using CEAD E25-printing head attached to ABB IBR 6700 robot. All samples, except ASA 20% GF, were printed on sanded polypropylene plate. ASA 20% GF was printed on an ABS-plate. All samples were cooled using airflow with constant speed. A representation of the test specimen preparation process is shown in Figure 4.

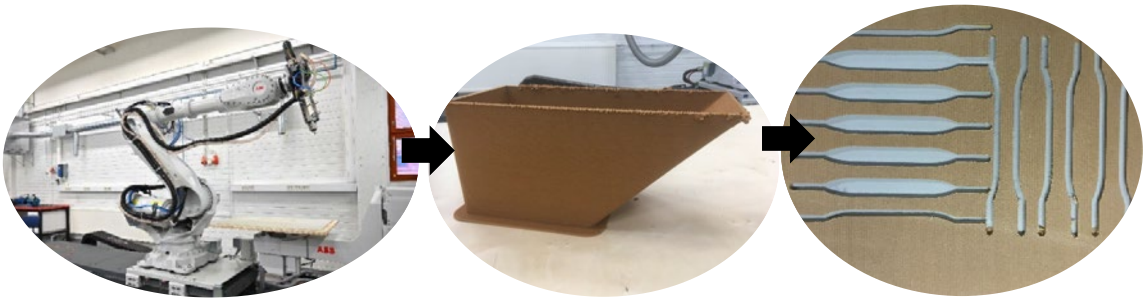


Figure 4. 3D-printing extruder attached to robot (left), the model printed to prepare test specimens (middle) and CNC machined test specimens (right)

Durasense samples were printed by varying one parameter (layer height, nozzle size, or printing speed) at a time. Samples were printed in temperatures according to technical datasheets. Note that ASA 20%GF and PP 30%GF had to be printed at slower speed due to the tendency to sag. The printing parameters used for producing the test samples are listed in Table 2.

Table 2: Parameters for preparing 3D-printed test samples

Sample name	Heating zone temperatures				Layer height (mm)	Nozzle Size (mm)	Speed (mm/s)
	Hz1	Hz2	Hz3	Hz4			
Dura 50%	170	180	190	200	1,5	4	30
Dura 50%	170	180	190	200	2	4	30
Dura 50%	170	180	190	200	2,5	4	30
Dura 50%	170	180	190	200	2	4	50
Dura 50%	170	180	190	200	3	6	30
K35B+W20	170	180	190	185	2	4	30
ASA 20%GF	210	240	240	230	2	4	10
PP 30%GF	170	180	195	190	2	4	10

2.3 CHARACTERIZATION

Various properties of the selected composite materials were tested to find the suitability of those in 3D-printing the boat components and composite tooling. Different aspects ranging from mechanical, physical, thermal and weathering were studied and is discussed in this sub-chapter.

2.3.1 MELT FLOW INDEX MEASUREMENT

A melt flow rate test was conducted for the composite materials considered in the study. Before the test, all samples were dried at 60°C for one day. The load is kept constant at 2.16 kg, and MFR was calculated from the average of 10 measurements for each material, whereas temperature and time interval were set according to how the material behaves.

2.3.2 TENSILE TESTING

Tensile properties of compression moulded samples were measured to compare the results with the 3D-printed samples. Tensile test for composites made by 3D printing and compression moulding method was done according to ISO 527-2. The test speed was 5 mm/minute.

2.3.3 STORAGE MODULUS BY DMA

Dynamic mechanical properties of the composites were analyzed using Netzsch DMA 242 analyzer. The measurement was conducted under tensile mode at a frequency of 1 Hz. The sample dimension was 30 mm x 3.7 mm (length x width). The free length of the sample was 10 mm, and the thickness was 2.2 mm – 2.4 mm. The testing temperature ranged from 25°C – 125°C at a heating rate of 2°C/minute.

2.3.4 COEFFICIENT OF THERMAL EXPANSION (CTE)

The coefficient of thermal expansion was measured for the compression molded and 3D printed samples using the same test parameters. Thermal expansion measurements were conducted on a dynamic mechanical analyzer (Netzsch DMA 242) using the tensile fixture. The sample dimension was 30 mm x 5.6 mm (length x width). The free length of the sample was 10 mm, and thickness was 2 mm. The sample was heated from 25°C to 150°C at a heating rate of 2°C/ minute. Displacement vs. temperature was plotted and the CTE values were calculated.

2.3.5 CYCLIC WEATHERING TESTS

During the cyclic weathering test, the samples were exposed to temperatures as high as 65°C and as low as -10°C. The samples were evaluated in terms of moisture gain during the selected interval of time until saturation. The detailed test conditions can be seen in Figure 5. The samples after the testing were dried, and the storage modulus was measured using a dynamic mechanical analyzer. The test was done in tension mode in a temperature range of 25°C – 125°C.

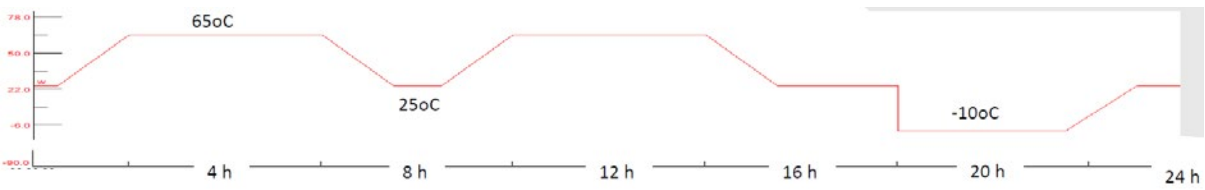


Figure 5. The test condition for the cyclic weathering test

2.3.6 UV-WEATHERING TEST

The accelerated UV exposure test is based on standard SFS-EN 927-6 (Paints and varnishes). Coating materials and coating systems for exterior wood. Part 6: Exposure of wood coatings to artificial weathering using fluorescent UV lamps and water). The test has used the equipment specified in the test, and the test has been carried out on the test sample with SFS-EN ISO 4628-4 (Paints and varnishes). Assessment of deterioration of coatings. Indication of the intensity, volume and size of the common type of error. Part 4: Assessment of the degree of fissure). The weathering conditions can be seen in Table 3. The weathering test equipment used was QUV 75-spray and the lamp type UVA 340. UVA-340 allows to imitate sunlight under different conditions:

Table 3: The table below shows a test cycle of 168 hours according to EN927-6

Program	Action	Radiation (W/m^2)	Temperature (C°)	Time (h:min)
1	Condensation		45	24:00
2	Sub-program; repeats programs 3-4 48 times			
3	Ultraviolet radiation	0,89	60	2:30
4	Spraying			0:30
5	Last period: goes to program 1			

- Maximum radiation (comparable to the midday sun) practical for quick results without sacrificing a correlation relationship
- Average Optimum (comparable to March/September sunlight in Finland)

3 RESULTS AND DISCUSSION

The results from testing the composites considered in the study are presented in this chapter. The sub-chapters are divided based on the type of testing methods. In the case of weathering tests storage modulus from DMA and tensile strength is included to study the effect of weathering on the composites.

3.1 TENSILE PROPERTIES OF COMPRESSION MOULDED COMPOSITES

The tensile testing of compression moulded samples were performed to screen the materials and select the best ones in terms of tensile properties. Test results are presented in Figure 6 and Figure 7.

Among the glass fiber reinforced composites, ASA reinforced with 20 wt% fiber shows better tensile strength and elongation than polypropylene reinforced with 30%wt fiber. This result is influenced by the difference in polymer type and fiber content.

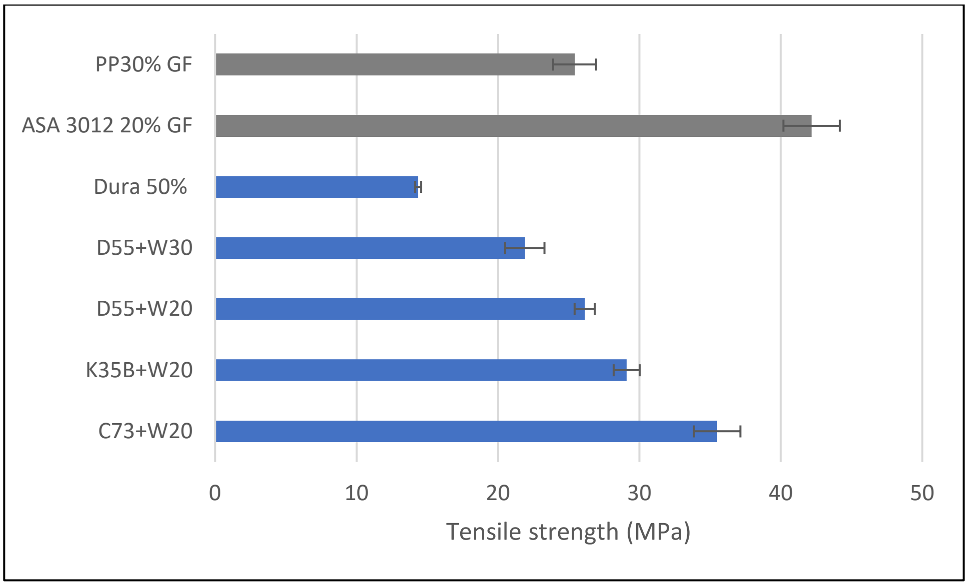


Figure 6. Tensile strength of compression moulded samples

Among the bio-composites, polyester composite reinforced with 20 wt% wood flour, C73+W20 show highest tensile strength and K35B+W20 have highest elongation in tension mode. When comparing D55+W20 and D55+W30, it is understood that increasing the fiber content decreases the tensile strength and increases the composites elongation(Kim, Moon, Kim & Ha 2008). The commercially available Durasense 50 3D (Dura 50%) shows the lowest tensile strength but shows highest elongation at break among all other bio-composites. The increase in elongation of Dura 50% compared to other composites is due to the ductile nature of the polypropylene when compared to the bio-polyesters and ASA.

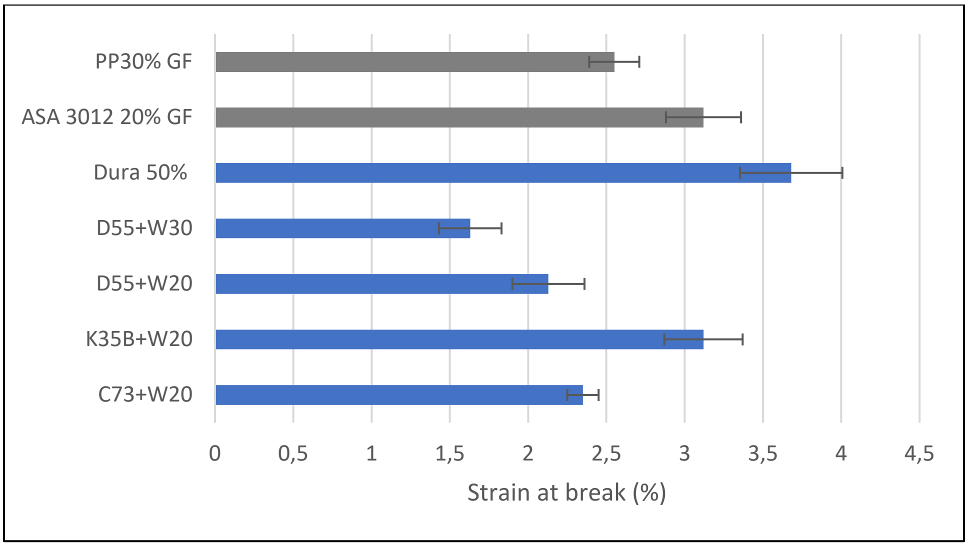


Figure 7. Strain at break of compression moulded samples

Therefore, C73+20 is the best choice in bio-composites, showing the highest tensile strength among wood-flour filled composites. On the other hand, when it comes to elongation properties, polypropylene reinforced with a substantial 50 wt% of wood flour is best among bio-composites, showcasing remarkable flexibility even at higher filler loading. Additionally, in the context of tensile strength, ASA reinforced with a 20% glass fiber content emerges as the best choice among all the composites in the study. These findings underscore the diverse strengths and characteristics of different composite materials considered under study, each excelling in specific mechanical properties, thus offering valuable insights for various end-use applications.

3.2 TENSILE PROPERTIES OF 3D-PRINTED COMPOSITES

The tensile properties of the 3D-printed composites were studied by testing the print direction in parallel and perpendicular to the applied force. The chapter will discuss the effect of printing parameters on the tensile properties of wood plastic composite based on polypropylene. Furthermore, it will present the results from testing other composites.

3.2.1 INFLUENCE OF 3D PRINTING PARAMETERS ON TENSILE PROPERTIES

Printing parameters, such as layer height, printing speed, and cooling influence the mechanical performance of printed composites. Durasense 50 3D (Dura 50%) material was used to print box-shaped products, which were used to prepare samples for tensile tests.

Printing height

The sample plates cut from 3D-printed boxes, fabricated using Dura 50%, were tested by applying force parallel and perpendicular to printing direction. Samples for testing were fabricated using 1.5 mm, 2 mm and 2.5 mm layer heights. The effect of layer height on tensile properties of printed samples are seen in Figure 8 and 9.

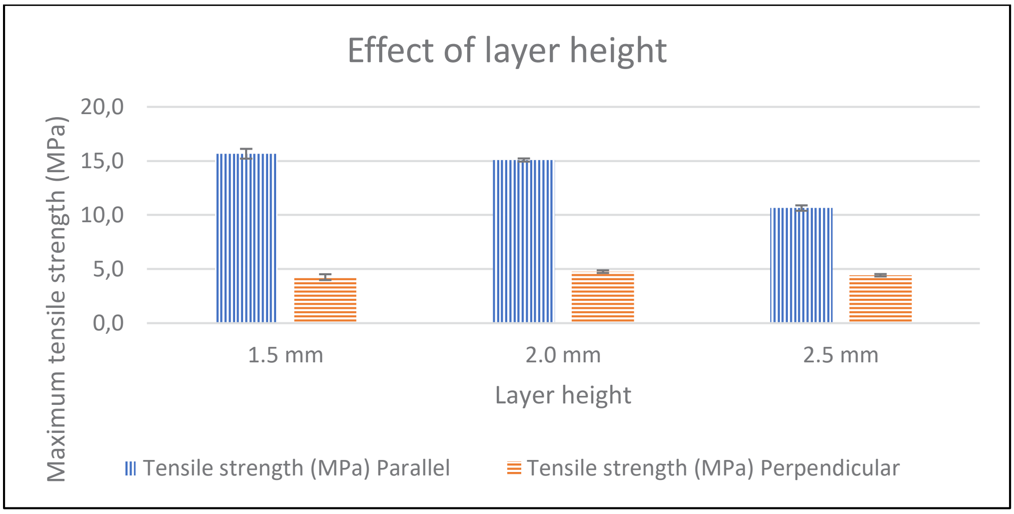


Figure 8. Effect of printing height on the tensile strength (Dura 50%)

The results revealed that in samples tested in parallel direction, those produced using 1.5 mm and 2.0 mm layer height showed similar tensile strength of approx. 15 MPa (Figure 4). The samples tested in perpendicular direction show that the tensile strength is not influenced significantly by change in layer height. While the elongation properties of samples tested in parallel direction show similar trend as in tensile strength, the elongation of samples printed with layer height of 2.5 mm tested in perpendicular direction show the highest value among the three different layer height tested.

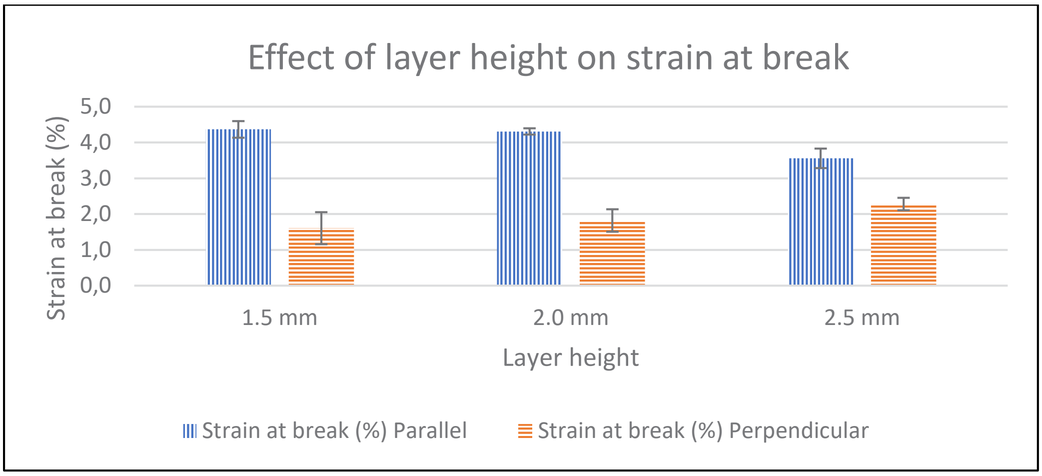


Figure 9. Effect of printing height on the strain at break (Dura 50%)

Printing speed

The effect of printing speed on the tensile properties of composites was tested and results are presented in Figure 10 and 11. The printing speed of 50 mm/s increased the tensile strength. An increase in elongation is also found in samples printed with 50 mm/s speed among the samples tested perpendicular to force.

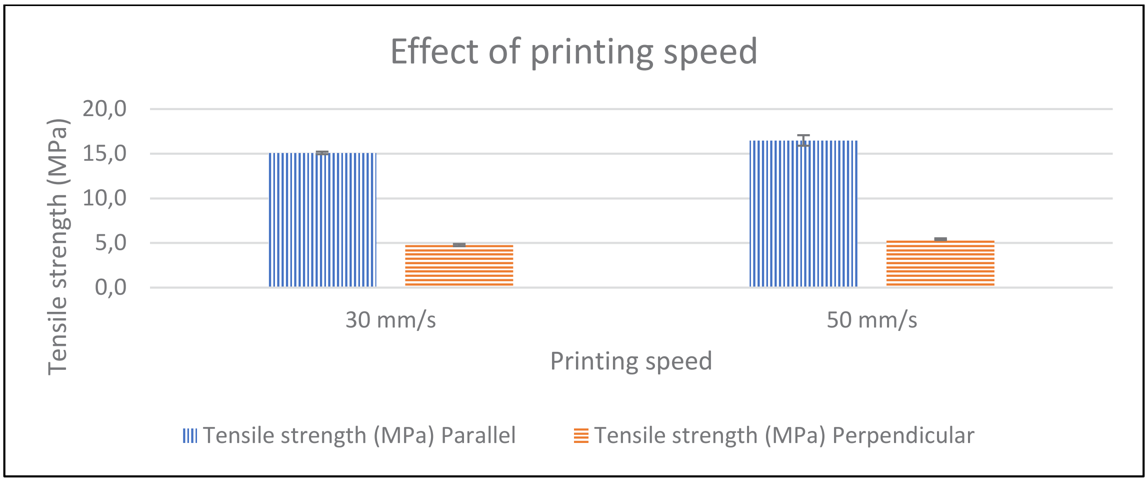


Figure 10. Effect of printing speed on the tensile strength (Dura 50%)

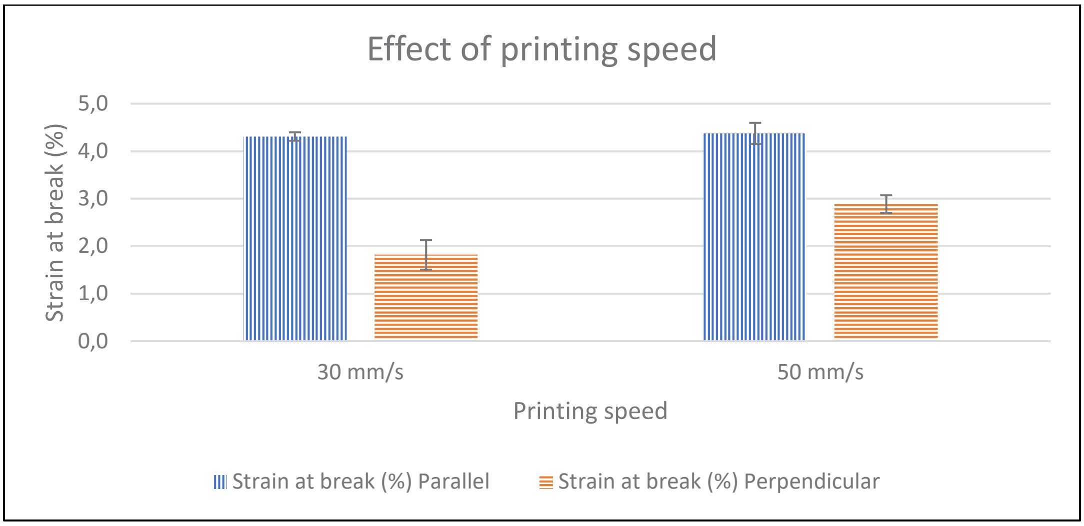


Figure 11. Effect of printing speed on the tensile strength (Dura 50%)

3.2.2 TENSILE PROPERTIES OF BIO-POLYESTERS FILLED WITH WOOD FLOUR

K35B W20 is a composite produced from bio-polyester filled with reclaimed wood flour from plywood industry. The printing parameters for this material was similar to the optimized parameters for Durasense 50 3D. Therefore, the printing temperature was 190°C, printing speed was 30 mm/s and layer height 2 mm.

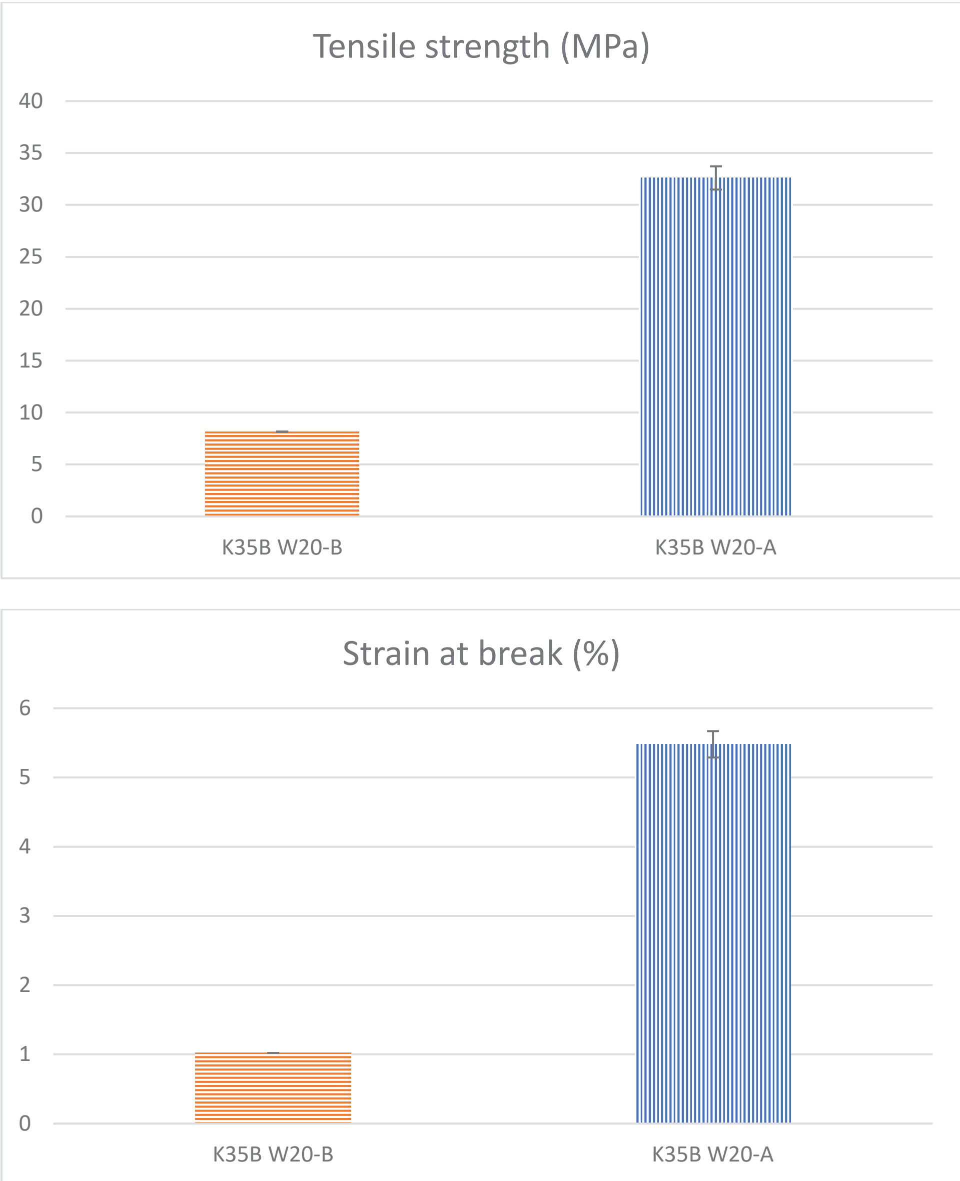


Figure 12. Tensile strength and strain at break of bio-polyester filled with wood flour

A=print direction parallel to tensile force; B=print direction perpendicular to tensile force

The bio-polyester filled wood flour composite exhibit better tensile strength in both A and B directions compared to Durasense 50 3D (Figure 8; 2 mm layer height). The lower tensile properties of the Durasense material is related to the higher wood flour content. Achieving strong bonding between wood flour and the polymer can be challenging, especially as the wood content increases. Poor fibre-matrix bonding can lead to weak interfaces and a reduction in tensile strength and ductility. Moreover, high wood flour content can lead to the non-uniform distribution of fibres within the composite. Agglomeration of wood flour can create stress concentration points, making the material more prone to failure.

3.2.3 GLASS FIBRE REINFORCED POLYMER COMPOSITES

ASA filled with 30 wt% glass fiber and PP filled with 20 wt.% glass fiber was tested for printing parameters. Printing with speed of 30 mm/s and 10 mm/s was tested. It was found that 10 mm/s was best among the chosen parameters for printing both glass fiber reinforced composites. Printing with 30 mm/s was not successful due to high temperature for printing and the drooping effect. The samples printed with 30 mm/s was tested parallel and perpendicular to the tensile force applied. The results are shown in Figure 13.

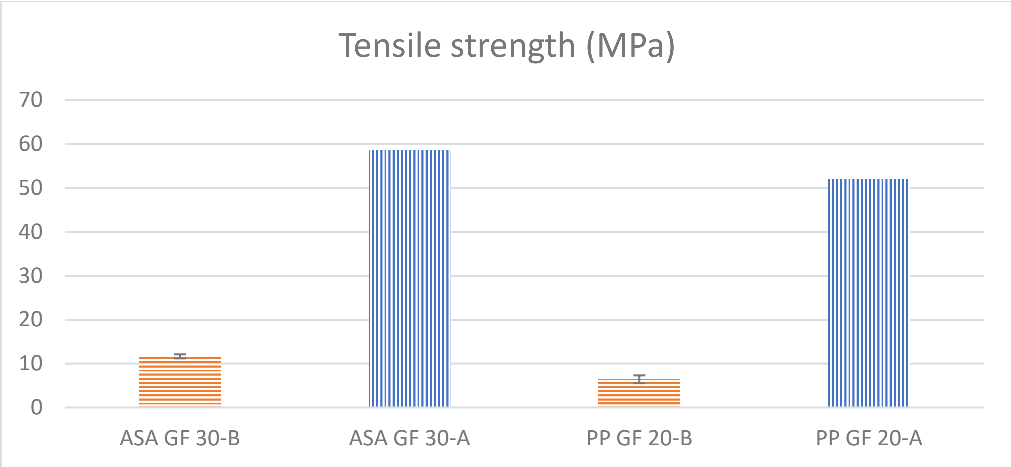


Figure 13. Tensile strength of 3D printed glass fiber filled composites

A=print direction parallel to tensile force; B=print direction perpendicular to tensile force

The printing temperature for ASA GF 30 samples were 230oC and 190oC in the case of PP GF 20. The printing of ASA material is done at optimal and recommended printing temperature. The printing of PP GF 20 material was done at the same temperature as Durasense 50 3D which is PP based composites. The difference in strength between the two-printing layer for these two PP based printing materials might have influenced from the fiber content, fiber length and especially the MFI of the two different polypropylenes used to make the composites. It is worth to note that the results for sample tested in printing direction parallel to the force applied (A) for both ASA GF and PP GF are reported only from one successful test. All other test specimens broke out of the narrow test region.

The main findings from the Chapter 3.2. can be summarized as following. In 3D printing with Durasense 3D 50, finding the right layer height is essential for achieving optimal results. A layer height of 2 mm is a favourable balance, offering a compromise between the lower productivity associated with a 1.5 mm layer and the compromised properties of a 2.5 mm layer. Interestingly, increasing the printing speed can boost tensile strength. This phenomenon occurs because the warmer plastic from the previous layer forms a stronger bond with the new layer. Additionally, comparing materials, K35B+W20 outperforms Dura+50% in tensile strength, owing to its lower filler content. This makes K35B+W20 a promising choice as a printing material, provided it meets other essential test criteria. Moreover, it is worth noting that glass fiber reinforcement enhances the tensile properties of plastic materials to a greater extent than wood-flour, underscoring the significance of material selection in achieving desired performance outcomes in 3D printing.

3.3 COEFFICIENT OF THERMAL EXPANSION

The coefficient of thermal expansion (CTE) is a material property that is indicative of the extent to which a material expands upon heating. CTE will influence both the dimensional accuracy during the printing process, when the material experiences a large decrease in temperature from the print head to the chamber temperature, as well as in end-use applications in heated environments. CTE was measured to understand how both the material (compression moulding samples) and the print parameters (3D-printed samples) affect the thermal expansion. The CTE values are presented in Figure 14.

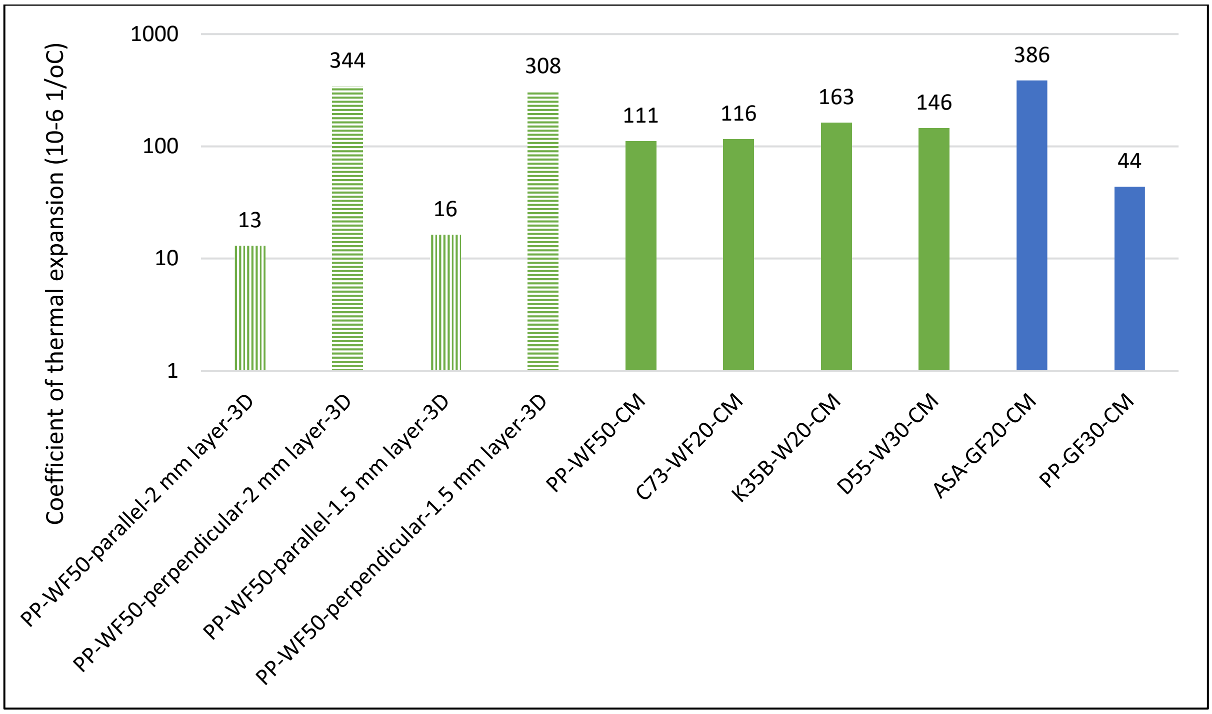


Figure 14. Coefficient of thermal expansion (CTE) of printed and compression molded samples

The 3D-printed samples showed low CTE when tested in print direction (parallel to force) in both layer heights considered (1.5 mm and 2.0 mm). The lower CTE in the print direction is due to the preferential alignment of wood flour in this direction. The samples made from 1.5 mm layer height have lower CTE compared to 2.0 mm in the print direction.

To summarize, glass fiber proves to be more effective than wood-flour in mitigating the Coefficient of Thermal Expansion (CTE), as demonstrated in a study by (Scelsi, Hodzic, Soutis, Hayes, Rajendran, AlMa'adeed & Kahraman 2011). This finding underscores the superior performance of glass fiber as a reinforcement material in controlling the expansion and contraction of composites subjected to temperature variations. Additionally, the results from CTE measurements reveal the advantages of incorporating fillers into materials to manage deformation during the heating and cooling. For instance, in the case of pure polypropylene (PP) with a CTE range of 195 - 200 1/°C at temperatures between 20°C and 134°C, the use of fillers effectively regulates material expansion, leading to a reduction in thermal stresses and subsequent warpage of printed components. This emphasizes fillers pivotal role in enhancing printed parts dimensional stability, particularly in applications where temperature fluctuations are a concern, as noted by (Colón Quintana, Slattery, Pinkham, Keaton, Lopez-Anido & Sharp 2022).

3.4 CYCLIC WEATHERING TEST

As expected, the glass fiber filled composites exhibited better weathering properties compared to bio-composites (Figure 15). All the bio-composites showed a sharp increase in water absorption at the beginning of the test. While all the polyester based bio-composites reached equilibrium in 16 days, the polypropylene based bio-composites did not reach equilibrium in 31 days when the test ended. There was no effect of UV-additives in the moisture absorption behavior of the composites.

The moisture absorption during 31 days of cyclic weathering test resulted in a weak fiber–matrix interface in the case of bio-composites, thus reducing stiffness (storage modulus) after water immersion test (Figure 16). All the polyester-based bio-composites became brittle after the cyclic test, making the sample preparation for DMA analysis impossible.

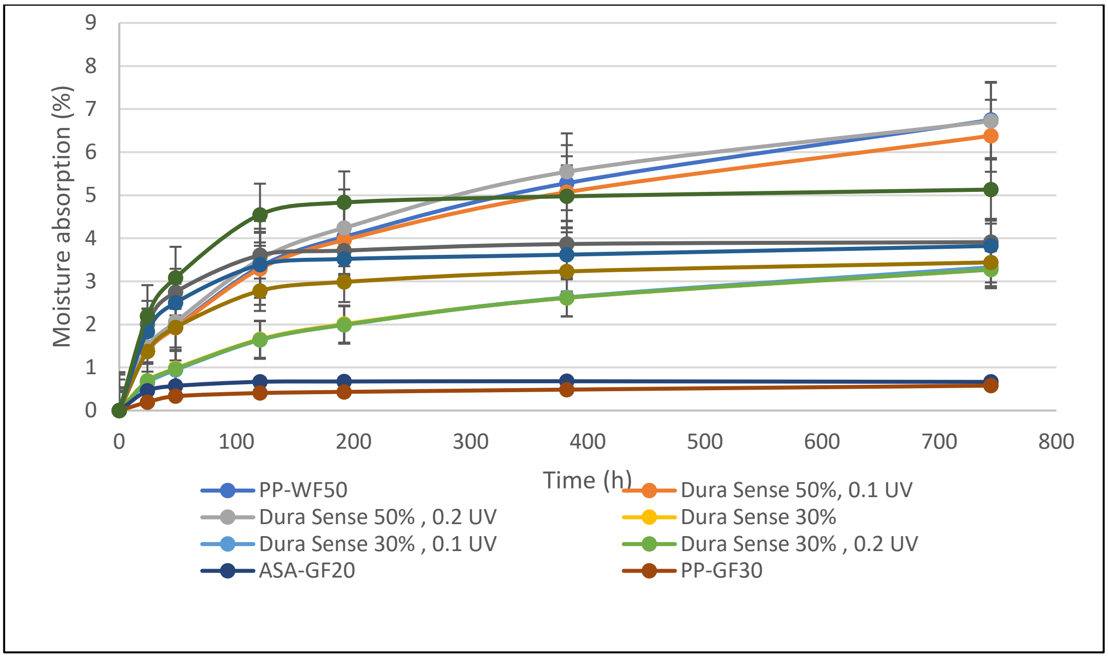


Figure 15: Moisture absorption of the composites considered as 3D printing materials

The moisture absorption in composites also depends on possible defects formed during manufacturing. Through voids, moisture uptake is easily initiated, which negatively influences the properties of the composites. The results from this test should be treated as worst-case scenario since the composites were tested without any protective coating. Our previous study has shown that the gelcoat provides very good protection against water absorption (Rajan, Riihivuori, Rainosalo, Skrifvars & Järvelä 2014). In this study we found that the bio-composites with gelcoat (accelerated test) reached 5% mass gain in 31 days. The same bio-composite reached 5% mass gain within 2 days of water absorption test (ambient conditions). This indeed, point out the importance of using gelcoat on the bio-composites exposed to high moist conditions or direct contact with water.

The cyclic weathering of the test specimens between -10°C and 65°C can induce more damage to the sample. The formation of ice crystals during freezing can cause physical damage to the wood fibre and the polymer matrix. When the temperature rises and the ice within the composite thaws, it can create voids and defects in the composites. These voids can act as stress concentrators, further reducing the storage modulus. The continuous cycling can introduce additional stress, microcracks and defects, decreasing the storage modulus over time.

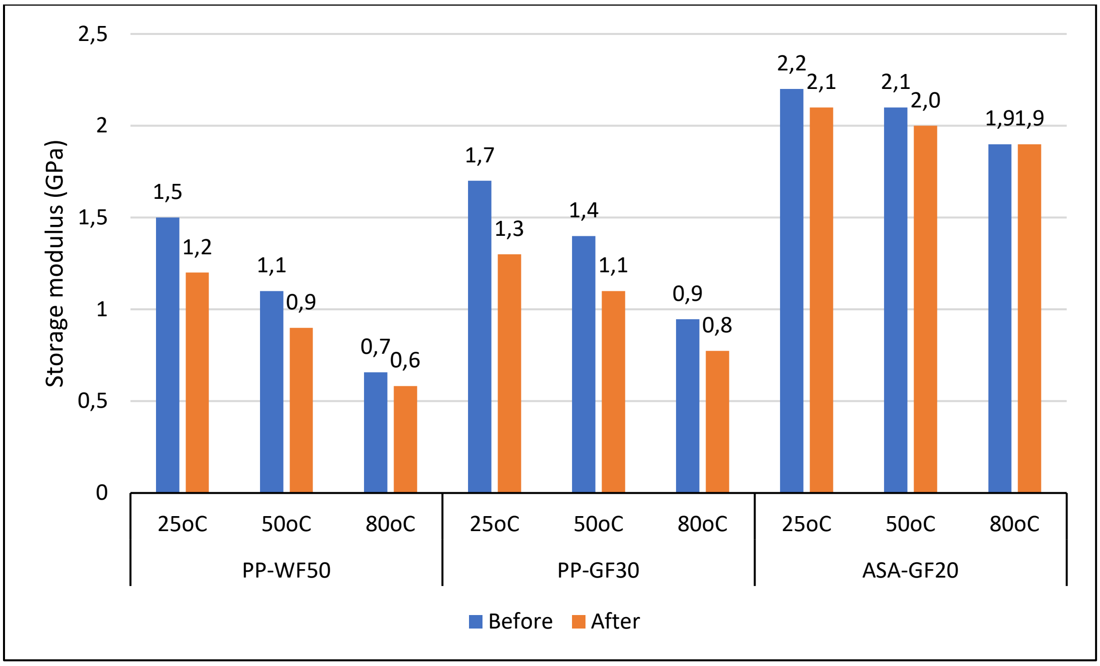
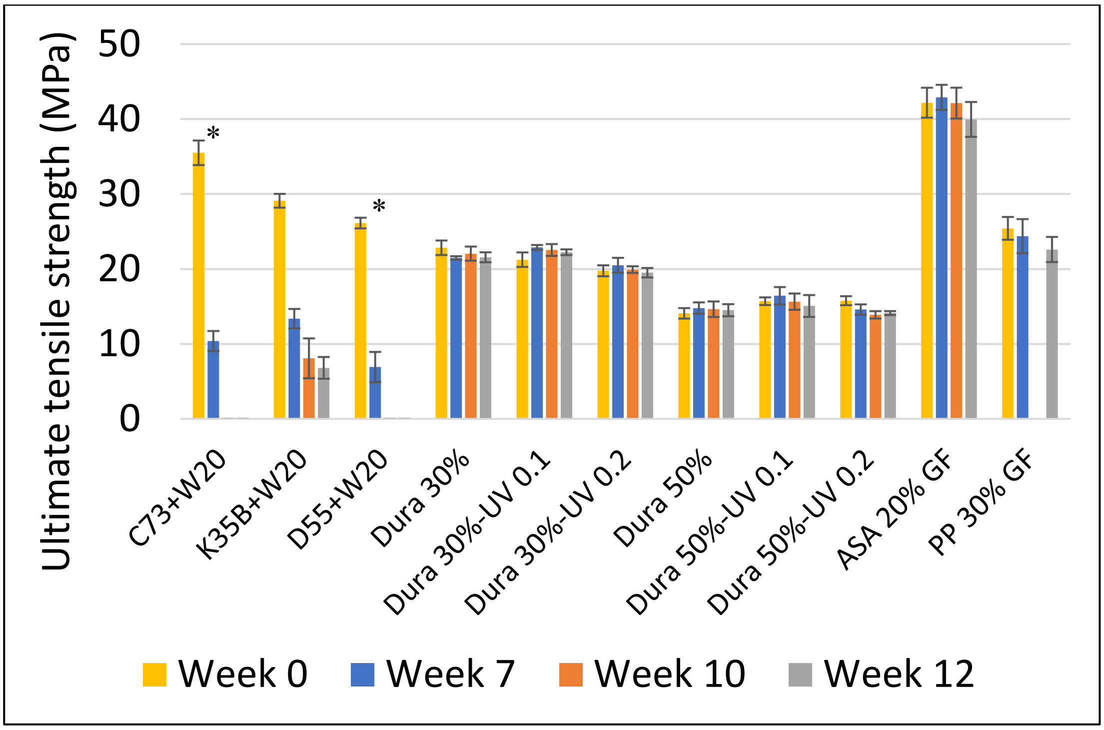


Figure 16. Storage modulus of composites before and after the weathering tests

In summary, the difference in the result among the composites reinforced with glass fibre is due to polymers effectiveness in resisting the cycling weathering conditions. When comparing polypropylene (PP) and Acrylonitrile styrene acrylate (ASA) in the context of weathering conditions, ASA is better resisting compared to polypropylene due to its superior moisture resistance and better performance in colder conditions.

3.5 UV-WEATHERING TEST

Among the wood flour filled composites, Durasense 50 3D (Dura 50%) retains the tensile strength after the total UV exposure of 12 weeks. Bio-polyesters tested show a rapid decrease in the tensile strength due to the polymer degradation after the UV-exposure. The susceptibility of bio-polyester composites to UV and moisture damage can be influenced by the chemical structure of the bio-polyester used in the composite. Specific ester linkages and functional groups in bio-polyesters can be more sensitive to UV radiation and moisture than the hydrocarbon structure of PP. Additionally, the formulation and additives used in bio-polyester composites can impact their UV resistance and overall durability.



*broken during UV-test period

Figure 17 Tensile strength of the composites before and after the UV exposure test

In general, UV-induced aging, known as photo-oxidation, is a well-documented phenomenon in polymers. When exposed to UV light, polymers undergo a complex process involving the formation of radicals within their molecular structure. These radicals originate through various mechanisms, including Norrish-type reactions involving carbonyl groups found in unsaturated and saturated polymer segments. Additionally, external factors such as air pollutants like NOx and the intrinsic alkyl constituents of polymers can contribute to radical formation. Furthermore, the high-temperature processing of polymers can generate alkyl radicals (Yildirim, Sezer Hicyilmaz & Yildirim 2022).

These radicals subsequently react with atmospheric oxygen without requiring additional activation energy, forming peroxides. Peroxides are radicals that need hydrogen atoms to convert into hydroperoxides. The abstraction of hydrogen atoms from polymer macromolecules during this process leads to polymer degradation, resulting in either macromolecule chain scission or crosslinking (Yildirim et al. 2022).

The photodegradation of wood-plastic composites (WPCs) is characterized by the weathering of both principal constituents of WPCs, namely, the wood and the plastic (Matuana, Jin & Stark 2011). Photodegradation in wood primarily arises from the degradation of lignin. Although all wood components are vulnerable to photodegradation, lignin, which is only approx. 30% of wood absorbs the majority, ranging from 80% to 95%, of the total UV light absorbed by wood. In addition, the presence of moisture in wood fibre accelerates the oxidation reaction (Fabiyi, McDonald, Wolcott & Griffiths 2008).

To summarize the chapter, the chemical structure of the polymer matrix is seen as critical factor in explaining the differences in behavior observed in the two types of wood flour filled composites when exposed to UV, with bio-polyesters potentially having more UV-sensitive chemical groups compared to the hydrocarbon structure of PP. The polymer K35B is a bio-based polyester comprising 65% bio-sourced materials and featuring impact modification. Composites derived from polyesters C73 and D55 exhibited a limited UV-weathering endurance of only seven weeks. At this point, they became brittle. The enhanced resilience of K35B-based composites can be attributed to the polyester's modification. It is noteworthy that none of the bio-polyester composite formulations included UV stabilizers. Information regarding UV stabilizers in the Dura 50% formulation was unavailable. The incorporation of UV stabilizers has the potential to enhance the UV resistance of composites based on bio-polyesters.

4 CONCLUSIONS

In conclusion, this comprehensive material test report systematically evaluated materials suitable for 3D printing boat components and molds for composite lamination. Our methodology included a range of testing techniques, including compression molding and CNC machining, to scrutinize various material properties.

Our investigation utilized the selected materials in producing 3D printed boxes, enabling CNC machining sample testing for mechanical properties. The optimization of 3D printing parameters, notably the determination of a 2 mm layer height as an ideal compromise between the limitations of 1.5 mm and 2.5 mm for Durasense 50 3D printing, was a key outcome. The recognition of challenges arising from higher layer heights, particularly in printing sloped wall structures, further underlined the importance of efficient cooling.

Our study continued with applying these parameters to other materials, including critically examining the Coefficient of Thermal Expansion (CTE) to gauge its impact on dimensional accuracy during 3D printing. Additionally, we subjected the materials to rigorous cyclic weathering and UV-weathering tests, enabling us to assess their durability in natural environmental conditions, especially outdoor settings.

The conclusion of our extensive testing revealed interesting insights. Polypropylene and ASA polymers reinforced with glass fiber emerged as the preferred choices for 3D printed products destined for exposure to natural climatic conditions, confirmed by high humidity and UV exposure, based on the robust performance demonstrated in weathering tests. Synthetic polymer-based wood plastic composites also stood out, showcasing their resilience even under severe weathering conditions. Furthermore, it was evident that weathering resistance in bio-composites could be significantly enhanced by applying suitable coatings, rendering them a sustainable option for 3D printing large structures intended for natural weathering environments.

Ultimately, our findings culminated in a resounding recommendation for Durasense 50 3D, especially when combined with weathering-resistant coatings, as the premier choice. This selection offers superior performance in relevant tests. It aligns with environmental considerations, making it an optimal solution for producing 3D-printed products that withstand the harshness of natural weathering conditions.

REFERENCES

Colón Quintana, José Luis, Slattery, Lucinda, Pinkham, Jon, Keaton, Joanna, Lopez-Anido, Roberto A. & Sharp, Keith 2022. Effects of Fiber Orientation on the Coefficient of Thermal Expansion of Fiber-Filled Polymer Systems in Large Format Polymer Extrusion-Based Additive Manufacturing. Materials 2022, Vol. 15, Page 2764. Multidisciplinary Digital Publishing Institute, 15(8), 2764. <https://www.mdpi.com/1996-1944/15/8/2764/htm>. DOI: 10.3390/MA15082764.

Fabiyi, James S., McDonald, Armando G., Wolcott, Michael P. & Griffiths, Peter R. 2008. Wood plastic composites weathering: Visual appearance and chemical changes. Polymer Degradation and Stability. Elsevier, 93(8), 1405–1414. DOI: 10.1016/J.POLYMDEGRADSTAB.2008.05.024.

Interreg Baltic Sea Region n.d. Network of Service Providers for Eco-innovations in Manufacturing SMEs - Interreg Baltic Sea Region. <https://interreg-baltic.eu/project/ecolabnet/> (Accessed 7.9.2023).

Khan, Mohammad Z.R., Srivastava, Sunil Kumar & Gupta, M. K. 2020. A state-of-the-art review on particulate wood polymer composites: Processing, properties and applications. Polymer Testing. Elsevier, 89, 106721. DOI: 10.1016/J.POLYMERTESTING.2020.106721.

Kim, Sam Jung, Moon, Jin Bok, Kim, Gue Hyun & Ha, Chang Sik 2008. Mechanical properties of polypropylene/natural fiber composites: Comparison of wood fiber and cotton fiber. Polymer Testing. Elsevier, 27(7), 801–806. DOI: 10.1016/J.POLYMERTESTING.2008.06.002.

Matuana, Laurent M., Jin, Shan & Stark, Nicole M. 2011. Ultraviolet weathering of HDPE/wood-flour composites coextruded with a clear HDPE cap layer. Polymer Degradation and Stability. Elsevier, 96(1), 97–106. DOI: 10.1016/J.POLYMDEGRADSTAB.2010.10.003.

Poletto, Matheus, Zattera, Ademir J., Forte, Maria M.C. & Santana, Ruth M.C. 2012. Thermal decomposition of wood: Influence of wood components and cellulose crystallite size. Bioresource Technology. Elsevier, 109, 148–153. DOI: 10.1016/J.BIORTECH.2011.11.122.

Rajan, R., Riihivuori, J., Rainosalo, E., Skrifvars, M. & Järvelä, P. 2014. Effect of viscose fabric modification on the mechanical and water absorption properties of composites prepared through vacuum infusion. Journal of Reinforced Plastics and Composites. SAGE Publications Ltd, 33(15), 1416–1429. <https://journals.sagepub.com/doi/full/10.1177/0731684414534748>. DOI: 10.1177/0731684414534748/ASSET/IMAGES/LARGE/10.1177_0731684414534748-FIG11.JPEG.

Scelsi, L., Hodzic, A., Soutis, C., Hayes, S. A., Rajendran, S., AlMa'adeed, M. A. & Kahraman, R. 2011. A review on composite materials based on recycled thermoplastics and glass fibres. Plastics, Rubber and Composites. Taylor & Francis, 40(1), 1–10. <https://www.tandfonline.com/doi/abs/10.1179/174328911X12940139029121>. DOI: 10.1179/174328911X12940139029121.

Yildirim, Fatma Filiz, Sezer Hicyilmaz, Ayse & Yildirim, Kenan 2022. The effects of the weathering methods on the properties of the ABS, ASA and PMMA polymers. Polymer Testing. Elsevier, 107, 107484. DOI: 10.1016/J.POLYMERTESTING.2022.107484.

ABSTRACT

Fused granular fabrication (FGF), an innovative 3D-printing method, utilizes thermoplastic granules (pellets) as the printing material, offering the distinct advantage of producing large components for various applications. This report explores the potential of FGF, particularly in the context of wood plastic composites (WPCs) comprised of bio-based materials for manufacturing boat components and composite tooling. While WPCs demonstrate environmental sustainability and reduced carbon footprint, they are limited to specific thermoplastic polymers due to the thermal degradation of wood-flour at elevated temperatures.

The report highlights a recent development at Centria University of Applied Sciences (Centria), Finland, involving robot-assisted FGF to create recyclable WPC-based composite tooling. Traditional tooling methods are labor-intensive and produce substantial waste, posing challenges in disassembly and recycling. Centria's approach introduces a sustainable solution, showcasing the possibility of producing recyclable composite tooling and direct 3D printing of boat components.

The project VENEPRINT underlines the potential of FGF in the boat-building industry, which traditionally relies on non-recyclable thermoset composites. The boat industry could transition towards sustainability by adopting thermoplastic raw materials compatible with FGF. However, this transition requires ensuring that 3D-printed components meet requisite mechanical, thermal, and weathering resistance properties compared to conventional materials.

The report focuses on material selection for boat components and composite tooling, encompassing testing methods to evaluate wood-filled thermoplastic composites and glass fiber-reinforced thermoplastic composites. Specific attention is given to properties crucial for the service life of 3D-printed products. This comprehensive examination is a foundation for advancing sustainable manufacturing practices in industries reliant on composite materials.

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