Research article

Comparison of the Mechanical Properties of PCL-Based Fiber Composites Fabricated by Fused Deposition Modeling and Injection Molding

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Abstract Polycaprolactone (PCL), a synthetic aliphatic polyester, has gained prominence in the realm of biocomposites due to its biodegradability, biocompatibility, and relatively low melting point. To further enhance the mechanical properties of PCL, natural fibers like bleached kraft eucalyptus pulp (BKEP) have been incorporated with PCL. This study measures and presents a comparative analysis of the mechanical properties of PCL/BKEP samples fabricated by fused deposition modeling (FDM) and injection molding (IM). Commercial BKEP was compounded with PCL at varying fiber contents ranging from 0 to 30 weight percentage (wt%). The resulting composites were characterized in terms of tensile strength, elongation at break, and Young's modulus comparing FDM and IM techniques. The findings demonstrate that IM yielded superior tensile strength values for PCL/BKEP with fiber contents exceeding 20 wt% compared to FDM. At 30 wt% fiber content, IM exhibited a 17% and a 50% increase in tensile strength compared to their FDM counterparts. At 10 wt% fiber content, FDM biocomposites demonstrated a 21% and 9% enhancement in tensile strength and Young's modulus, respectively, compared to IM counterparts. The choice between FDM and IM for fabricating PCL/BKEP depends on the desired fiber content and mechanical properties. IM is more suitable for producing high-fiber-content composites, while FDM excels for low-fiber-content composites with improved tensile strength and Young's modulus.

Keywords tensile strength, elongation at break, young's modulus, biodegradability, biocompatibility

INTRODUCTION

Fused Deposition Modeling (FDM), including 3D printing technology, has been rapidly gaining popularity over the past decade. FDM builds objects layer-by-layer through the controlled deposition of melted material. A continuous filament, typically a thermoplastic polymer, is fed through a heated nozzle, transforming it from a solid to a semi-liquid state (Dizon et al., 2018; Mitchell et al., 2018). The rapid growth of FDM is driving shift from Injection Molding (IM) to FDM and is driven by numerous advantages such as the ability to fabricate complex and accurate geometries as a single unit or part without joints and with little waste, lower material and labor costs, better surface finish, and reduced energy demand. FDM has simpler processing requirements, i.e., CAD model-Print-Install, compared to IM, near-net shape finish, faster production time, shorter lead time, and the ability to manufacture complex structures with satisfactory sizes (Lay et al., 2019). Consequently, FDM systems are now utilized in diverse settings, from personal use by hobbyists in their homes to industrial applications for prototyping and even small-batch production. (Abeykoon et al., 2020; Brian, 2012).

A mainstay in plastics processing, IM excels at mass-producing complex shapes. This technique allows for the creation of intricate parts at a high-volume (Agrawal et al., 1987; Piotter et al., 2001). Creating a mold is the foundation of the IM process, and it begins with meticulously designing the mold to match the final product's shape. Because molds need customization for each unique component and a vast array of shapes are achievable, this technique is most cost-effective for producing large quantities of identical items (Khosravani and Nasiri, 2020).

Researchers are increasingly using 3D printing to integrate Polycaprolactone (PCL), a versatile polymer, into structures with precisely controlled porosity and interconnectivity. This allows for fine-tuning of the material's internal architecture, opening doors for applications in tissue engineering, drug delivery, and filtration (Amni et al., 2021; Carrow et al., 2015). PCL is a pioneer among commercially available synthetic polymers, distinguished by its remarkable biodegradation and mechanical properties, which can be precisely modulated by tailoring the surrounding environmental factors (e.g., microorganisms, enzymes, hydrolysis). Due to its faster resorption rate and prolonged degradation in aqueous environments of up to 3-4 years, PCL has garnered significant attention as a biomimetic material capable of orchestrating selective cellular responses through controlled intracellular resorption pathways. Compared to other aliphatic polyesters, PCL's exceptional rheological and viscoelastic properties facilitate its fabrication and manipulation into a diverse array of three-dimensional platforms, e.g., porous scaffolds, micro and nanocarriers, and implantable devices (Guarino et al., 2017). Due to its excellent biocompatibility and processability, PCL has emerged as a leading choice for 3D porous scaffolds in tissue engineering.

OBJECTIVE

This research undertakes a comprehensive comparative investigation of the mechanical properties exhibited by PCL/BKEP biocomposites manufactured through the more recent development of FDM and the more conventional process of IM.

MATERIALS AND METHODS

Materials

Polycaprolactone (PCL) CapaTM 6500 was generously supplied by Perstorp Specialty Chemicals AB (Perstorp, Sweden). Bleached kraft Eucalyptus pulp (BKEP) was generously provided by Torraspapel S.A.(Spain), originally with 16 µm of diameter and 700 µm of length.

Process of Sample Preparation

The eucalyptus fiber was prepared from bleached kraft eucalyptus pulp. A laboratory pulper was employed to process 60 grams of BKEP and 5 liters of water. The mixture was vigorously agitated for approximately one hour at a pulper rotation speed of 1000 rpm. Subsequently, the resulting pulp was dried at room temperature for 24 hours and then pulverized by a knife mill to refine and soften the texture of the resultant fibers. The pulverized fiber was then dried in an oven at 80°C before blending with the PCL matrix.

PCL and eucalyptus fibers were manually mixed to ensure uniform distribution. These uniformly mixed batches were then melt-blended using a Brabender with concentrations ranging from 10wt% to 30wt% of eucalyptus fiber. The blended composites were manually removed from the mixing chamber. Before blending, the Brabender mixer was set to the appropriate temperature based on the material requirements and thoroughly cleaned to remove any residual polymer material. All subsequent batches of composites were prepared following the same experimental procedure. The Brabender chamber temperature was set to 120°C, and the blending process continued for 8 minutes. The melt-blended composites were then removed from the Brabender chamber and allowed to cool at room temperature. This process was repeated to produce additional batches. Next, the composites were milled using a blade mill (Retsch SM 100) to obtain pellet form. The resulting pellets were stored in appropriately labeled plastic bags.

Table 1 Parameter of injection molding for PCL-based composite

Material PCL/BKEP (wt%)	Feed Zone (^{0}C)	Transition Zone (^{0}C)	Transition Zone (^{0}C)	Transition Zone (^{0}C)	Metering Zone (^{0}C)	Cooling Time (s)	Pressure (Bar)	Value (mm)
90/10	125	135	140	145	150	60	700	28.5
80/20	135	140	145	150	155	50	860	30
70/30	140	150	155	160	165	50	1025	30

Table 2 Parameter of FDM Nx 3D printer

Printing parameters	PCL/10%BKEP	PCL/10%BKEP	PCL/10%BKEP
Bed temperature (^{0}C)	60	60	60
Nozzle diameter (mm)	0.4	0.4	0.4
Nozzle temperature (^{0}C)	95	105	115
Printing speed	100	100	100
Layer height (mm)	0.15	0.15	0.15
Filament flow (%)	100	100	100
Infill line direction	0^0	0^0	0^0
Infill density (%)	100	100	100
Layer height (mm)	1	1	1
Enable print cooling	Yes	Yes	Yes
Brim width (mm)	3	3	3

Injection Molding

The injection molding process was conducted using an Arburg/Allrouder 220M/350-90 injection molding machine, manufactured in Germany, with a clamping force of 40 tons. The material was introduced into the injection molding machine with a dog bone-shaped mold with dimension of 165 mm x 19 mm x 13 mm for tensile strength test and a dimension of 64 mm x 13 mm x 3 mm for impact strength test. The injection molding parameters in Table 1, including temperature, screw speed, back pressure, and cooling time, were optimized based on the characteristics of the raw materials employed.

Fused Deposition Modeling

Filament makers 3devo (Precision 450) lead the industry in extrusion quality materials, such as PEEK, PETG, PEKK, etc. The filament making machine can handle temperatures up to 450°C and has a simple interface and presets to make it accessible. There are 4 heating zones and a USB connection. A 3D printer manufactured by Voladora NX, (Spain) with the related to specifications and detailed noted as following: Software: Repetier, Cura, File types: Stereolithography (Stl), Connectivity: Wi-Fi, Cable USB, Ethernet, Operating systems: Window, Mac, Linux.

The specimens D638-type IV dog bone were printed by the Voladora NX 3D printer following the methodology experiment detailed in Table 2. The FDM printer's plate was preheated to a temperature of 60°C before filament feeding. The printing nozzle temperatures were set at 95°C for 10wt% eucalyptus fibers, 105ºC for 20 wt% eucalyptus fibers and 115°C for the 30 wt% one, Manual bed leveling was performed by measuring the Z-offsets parallel to the printing bed. The printer was connected to a smartphone or laptop computer to set up all fabrication parameters, including 90°C and 0°C, as well as other parameters listed in Table 2. PCL/BKEP biocomposites were fabricated using D638-type IV dog bone specimens for mechanical property testing.

Tensile Test

Tensile testing was performed using a 10 kN Universal Testing Machine (UTM) manufactured by Pol, Belartza (San Sebastian, Spain) to assess the mechanical properties of the samples. Dumbbell-shaped specimens, gripped at a distance of 50 mm, were subjected to a crosshead speed of 10 mm/min during the test at 25°C, adhering to the ASTM D638 standard. Five specimens per sample were tested to ensure statistically robust results. Average values of tensile strength, Young's modulus, and elongation at break were then calculated and used to construct graphs for further analysis and comparison.

RESULTS AND DISCUSSION

Tensile Strength

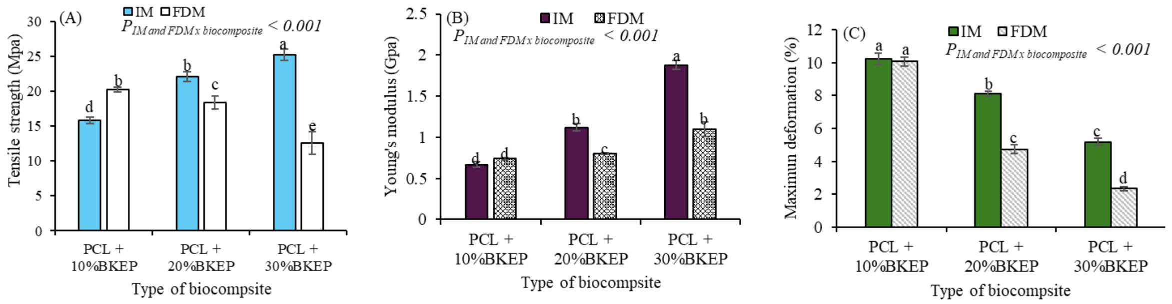
Fig. 1A, demonstrates the tensile properties of the different types of biocomposites fabricated using FDM and injection molding. The tensile strength of FDM printed PCL+20%BKEP and PCL+30%BKEP are found to be 16%, and 49% lower compared to those fabricated using IM. There is a statistically significant difference between the tensile strength of IM and FDM (p-value < 0.001). During IM, high-pressure forces molten polymer into the mold cavity, leading to a significant intertwining of chains. This intertwining can significantly impact the final material's properties. In fact, studies have shown that incorporating PCL into a PLA (polylactic acid) matrix using this process can result in materials with a tensile strength ranging from 18.25 to 63.13 megapascals (MPa), (Delgado-Aguilar et al., 2020). This increased chain entanglement translates to enhanced stiffness and strength in the final product (Lay et al., 2019; Weng et al., 2016). Additionally, the FDM printing process itself might introduce defects or voids into the material, further compromising its mechanical properties.

Maximum Deformation

In Fig. 1C, it is shown that the Maximum deformation of PCL+10%BKEP, PCL+20%BKEP, and PCL+30%BKEP fabricated using FDM are comparable with the IM samples with percentage differences of 1.56%, 41.58% and 54.91%, respectively with a p-value <0.001. The data suggests that adding BKEP to PCL increases the maximum deformation of the material, with a higher content of BKEP leading to a greater increase. Additionally, IM samples appear to deform slightly more than FDM samples.

Young's Modulus

The observed decrease in Young's modulus with increasing BKEP content demonstrated in Fig. 1B suggests that the BKEP incorporation weakens the stiffness and load-bearing capacity of the PCL matrix. The Young's modulus exhibited a linear increase with rising PCL content, suggesting well-dispersed constituents within the blend (Delgado-Aguilar et al., 2020) This could be attributed to the inherent flexibility of cellulose fibers within the BKEP, reducing the overall rigidity of the composite material. PCL+20%BKEP and PCL+30%BKEP fabricated using FDM are comparable with the IM samples with percentage differences of 28% and 41%, respectively. There is a statistically significant difference between Young's modulus of IM and FDM (p-value < 0.001). While adding more fibers makes the material stronger, it also makes it stiffer and less able to stretch (Tarrés et al., 2018). The PCL + 10% BKEP samples exhibited the lowest Young's modulus in all groups with values of 0.67 Gigapascals (GPa) for IM and 0.73 GPa for FDM. In all BKEP content, IM samples had higher Young's modulus than FDM samples and the difference ranged from 0.1 GPa to 0.3 GPa.



(A) tensile strength (B) Young's modulus (C) maximum deformation

Note: Different alphabetical letters denote significant differences among means at the error level of 5%

Fig. 1 Comparing the effects of mechanical properties of composites under IM and FDM

Table 3 Elongation at break of composites from FDM and IM

Composites	IM	FDM
PCL/10%BKEP	Not break (under 100 mm) (%)	Not break (under 100 mm) (%)
PCL/20%BKEP	8.637±2.215	5.302±0.138
PCL/30%BKEP	5.237±0.219	2.445±0.13

Elongation at Break

Samples containing 30% BKEP in Table3 exhibited the highest elongation at break for both IM and FDM, reaching 8% for IM and 5% for FDM. The PCL + 10% BKEP samples exhibited the lowest elongation at break in all groups. The values were 7.4% for IM and 5.9% for FDM. In all BKEP concentrations, IM samples had a slightly higher elongation at break compared to FDM samples. The difference ranged from 0.6% to 2.6%. The data suggests that adding BKEP to PCL decreases the elongation at the break of the material, with a higher concentration of BKEP leading to a greater decrease. Additionally, IM samples appear to have a slightly higher ductility compared to FDM samples.

CONCLUSION

For high-fiber-content composites (>20% BKEP), IM proved more suitable, leading to enhanced tensile strength (12-25% higher than FDM) and improved elongation at break (6-16% higher). In contrast, FDM was more effective for low-fiber-content composites (≤10% BKEP), exhibiting higher Young's modulus (4-11% greater than IM) while maintaining acceptable tensile strength. This suggests that IM facilitates better fiber dispersion and alignment at higher concentrations, leading to superior load-bearing capacity and ductility. Conversely, FDM may introduce localized defects or weaker inter-layer bonding at higher fiber loadings, impacting stiffness and strength. From the results of this study, both IM and FDM offer viable approaches for fabricating PCL/BKEP bio-composites with distinct advantages depending on the desired fiber content and targeted mechanical properties. For best strength, 3D-printed parts should have their fibers and molecular chains aligned with the pulling force (Liu et al., 2019). By tailoring the fabrication method to the specific application requirements, these biocomposites can be effectively utilized in various fields requiring strong, lightweight, and bio-compatible materials. Beyond their use in bioprinting, PCL-based bio-composites can be used in the medical field such as drug delivery devices, medical devices, and tissue engineering (Hivechi et al., 2019; Zander et al., 2010) and to make film for food packaging (Gutiérrez et al., 2021)

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