Effect of selected additives on mechanical properties of Poly(L-lactide) and Poly(L-lactide-*co*-ε-caprolactone)

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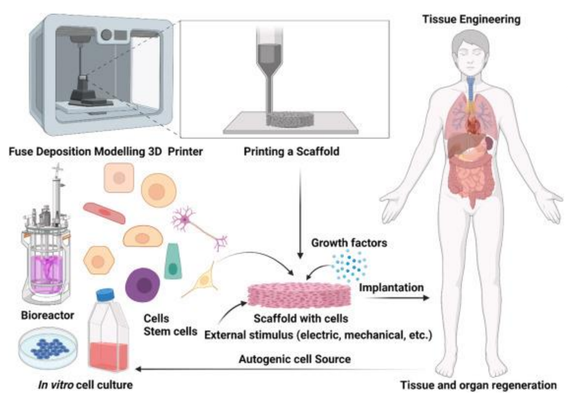
Abstract

Three-dimensional (3D) printing, especially Fused Deposition Modeling (FDM), has made significant advancements in the fields of tissue engineering and medical use. Poly(L-lactide) (PLA) and Poly(L-lactide-*co*-ε-caprolactone (PLC) are commonly used materials for filament manufacturing in medical applications. However, both PLA and PLC have limitations in their mechanical properties for producing the FDM filament: PLA is rigid but brittle, while PLC lacks sufficient strength. In this work, the effects of various additives on the mechanical properties of PLA and PLC were studied to enhance their appropriateness. The addition of different additives, including poly(ethylene glycol) (PEG), glycerol, zinc phenylphosphonate (TMC-200), dimethyl 5-sulfoisophthalic acid potassium salt (TMC-301), zirconium oxide (ZrO_2), and Tween 80, at amount 0.5% w/w were blended *via* the internal mixer. The mechanical properties of polymers blended with different additives were evaluated using tensile testing, thermal properties analysis, and dilute solution viscosity analysis. The results showed the mechanical properties of PLA/Tween 80 were improved compared to other samples. The tensile strength and Young's modulus of PLA/Tween 80 were 18.704 ± 1.265 MPa and 845.475 ± 96.817 MPa, respectively, resulting in stronger materials with better tensile resistance. This was consistent with the DSC analysis, which showed a decrease in glass transition temperature (Tg). In the case of PLC/ZrO_2, the tensile strength and Young's modulus were 17.647 ± 1.575 MPa and 417.205 ± 67.086 MPa, respectively, making the material stronger and more ductile when compared with the other sample, which was further confirmed by an increase in Tg from DSC results. This study demonstrated the addition of different additives into PLA and PLC are the potential for improving the mechanical performance of the of the polymers.

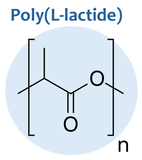
Introduction



The Fused Deposition Modeling (FDM) technique for tissue engineering

Biodegradable polymer used for filament materials

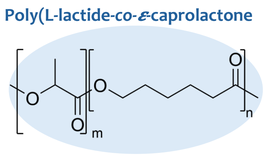
Poly(L-lactide)



Advantages
- High biocompatibility
- Biodegradability

Disadvantages
- Brittle
- Rigid
- Low temperature resistance

Poly(L-lactide-co-ε-caprolactone



Advantages
- High biocompatibility
- Flexible
- Biodegradability

Disadvantages
- Lower mechanical strength

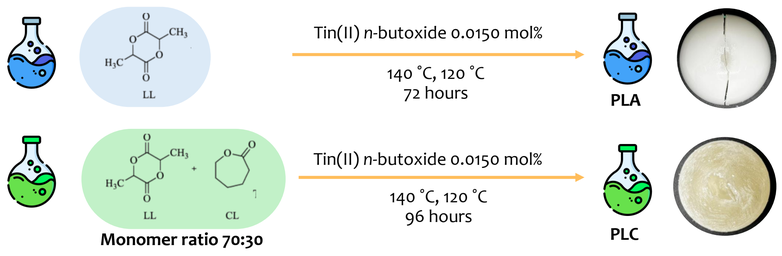
Blending PLA and PLC with additives to enhance the mechanical properties.

Research Objectives

- To study the effects of various additives on the mechanical properties of PLA and PLC
- To enhance the properties of PLA and PLC to achieve the optimal mechanical characteristics for filament preparation in fused deposition modeling (FDM) 3D printing.

Methodology

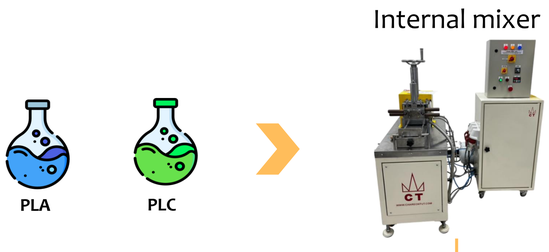
Synthesis PLA and PLC



Characterizations of the pure polymers

Viscosity | DSC | NMR

PLA and PLC Blended with additives



Characterizations of the polymer blended

Viscosity | DSC | NMR | Tensile testing

Additives
- Poly(ethylene glycol) 6000 (PEG)
- Glycerol
- Tween 80
- Zirconium oxide (ZrO_2)
- Zinc phenylphosphonate (TMC-200)
- Dimethyl 5-sulfoisophthalic acid potassium salt (TMC-301)

Conclusion

PLA and PLC blended with various additives at a concentration of 0.5% w/w. In PLA, the optimal additive was Tween 80, which enhances mechanical and thermal properties. From tensile testing and DSC, respectively, tensile strength, % strain at break, and Young's modulus were increased, and then Tg of PLA/Tween 80 was decreased from 57.14 to 55.74°C. Additionally, stress-strain curves showed PLA/Tween 80 was optimal for the mechanical properties when compared with other samples. In the PLC case, the optimal additive was ZrO_2, which improved mechanical and thermal properties. From tensile testing, respectively, tensile strength, % strain at break, and Young's modulus were increased and DSC showed Tg of PLA/ZrO_2 was increasing from 31.60 to 38.86°C. Therefore, the stress–strain curves showed PLA/ZrO_2 was optimal for the mechanical properties when compared with other samples.

Acknowledgement

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Result and Discussion

Physical and Thermal properties

Table 1 : DSC results and physical results of PLA, PLC, PLA/additives and PLC/additives blends.

Samples	LL : CL ratio [a]	Intrinsic viscosity (dl/g) [b]	T_g (°C) [c]	T_m (°C) [c]	Tensile Strength (MPa) [d]	Percentage Strain at break [d]	Young's Modulus (MPa) [d]
PLA	-	2.1895±0.035	57.14	159.33	15.228±0.661	5.367±0.579	769.307±156.922
PLA/PEG	-	1.7054±0.034	59.57	162.00	15.923±1.008	15.083±0.457	825.534±98.285
PLA/Glycerol	-	1.0615±0.007	57.53	162.00	16.226±0.445	8.614±0.591	759.916±41.443
PLA/Tween 80	-	1.6393±0.016	55.74	161.33	18.704±1.265	12.231±3.211	845.475±96.817
PLA/ZrO_2	-	1.4340±0.031	56.65	162.00	13.540±0.167	7.664±0.835	668.355±22.595
PLA/TMC-200	-	0.9434±0.004	56.40	158.00	14.547±0.238	6.070±0.827	686.490±12.279
PLA/TMC-301	-	1.2733±0.008	56.35	157.17	19.583±1.315	7.321±0.609	739.956±83.775
PLC	71 : 29	1.5473±0.028	31.60	-	12.206±1.508	257.656±44.765	145.401±28.073
PLC/PEG	77 : 23	1.3828±0.023	34.95	141.67	17.055±3.644	261.002±105.239	478.325±39.697
PLC/Glycerol	77 : 23	1.2744±0.033	38.15	142.67	14.153±0.653	295.172±65.060	344.706±54.401
PLC/Tween 80	74 : 26	1.2886±0.031	33.18	141.33	15.972±2.687	220.362±39.367	418.070±49.096
PLC/ZrO_2	76 : 24	1.3171±0.030	38.86	141.33	17.647±1.575	308.454±44.485	417.205±67.086
PLC/TMC-200	76 : 24	1.1074±0.034	31.26	140.83	14.508±0.579	153.711±25.456	454.780±27.977
PLC/TMC-301	78 : 22	1.0586±0.006	34.16	141.67	15.207±0.997	211.497±51.104	520.558±61.119

[a] calculated by ^{1}H-NMR ,[b] calculated by viscometer, [c] calculated by DSC and [d] calculated by Tensile strength tester

Thermal properties

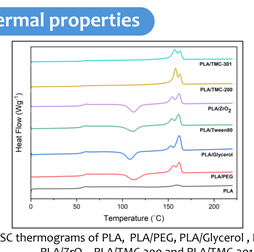

Fig 1. DSC thermograms of PLA, PLA/PEG, PLA/Glycerol , PLA/Tween80 , PLA/ZrO_2 , PLA/TMC-200 and PLA/TMC-301

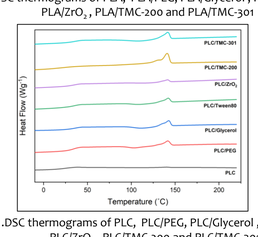

Fig 2 .DSC thermograms of PLC, PLC/PEG, PLC/Glycerol ,PLC/Tween80 , PLC/ZrO_2 , PLC/TMC-200 and PLC/TMC-301

- The T_g of **PLA** decreased after being **blended with Glycerol, Tween80, ZrO2, TMC-200,** and **TMC-301**, but the **PEG** increased.
- In **PLC**, after being blended with **PEG, Glycerol , Tween80, ZrO_2 ,** and **TMC-301**, T_g were increased but the **TMC-200** decreased.

Characterization : NMR

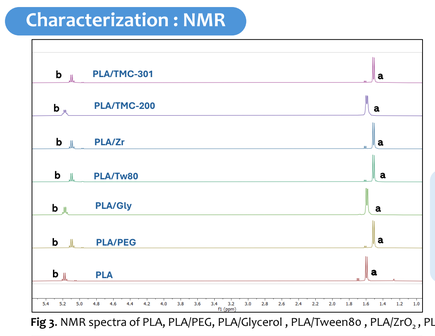

Fig 3. NMR spectra of PLA, PLA/PEG, PLA/Glycerol , PLA/Tween80 , PLA/ZrO_2 , PLA/TMC-200 and PLA/TMC-301

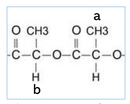

Fig 5. Structure of PLA

NMR spectra confirmed of PLA structure. The characteristic peak shifts at 5.0-5.3 ppm (CH, LL ; peak b) and 1.5-1.7 ppm (CH_3 ,LL ; peak a)

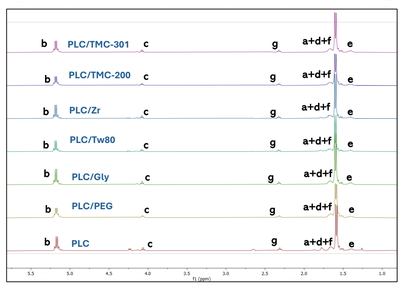

Fig 4. NMR spectra of PLC, PLC/PEG, PLC/Glycerol ,PLC/Tween80 , PLC/ZrO_2 , PLC/TMC-200 and PLC/TMC-301

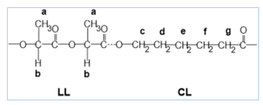

Fig 6. Structure of PLC

NMR spectra confirmed of PLC structure. The characteristic peak shifts at 5.0-5.2 ppm (CH, LL ; peak b), 4.0-4.3 ppm and 2.2-2.5 ppm (CH_2,CL ; peak c and g) and 1.5-1.7 ppm (CH_3 ,LL ; peak a)

Physical appearances : Film casting

Fig 7. Physical appearances of PLA, PLA/PEG, PLA/Glycerol , PLA/Tween80 , PLA/ZrO_2 , PLA/TMC-200 and PLA/TMC-301

Fig 8. Physical appearances of PLC, PLC/PEG, PLC/Glycerol ,PLC/Tween80 , PLC/ZrO_2 , PLC/TMC-200 and PLC/TMC-301

Mechanical Properties

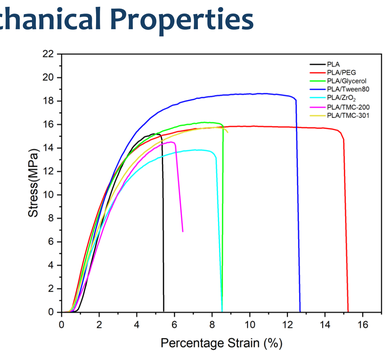

Fig 9. Stress-percentage strain curves of PLA, PLA/PEG, PLA/Glycerol , PLA/Tween80 , PLA/ZrO_2 , PLA/TMC-200 and PLA/TMC-301

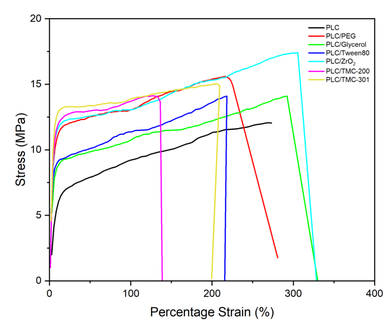

Fig 10. Stress-percentage strain curves of PLC, PLC/PEG, PLC/Glycerol , PLC/Tween80 , PLC/ZrO_2 , PLC/TMC-200 and PLC/TMC-301

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