

# Optimization of 3D Printing in Delta Systems: Parameterization and Rheological Characterization for Fiber-Cement Composites Incorporating Oyster Shell Powder

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## IIBCC 2024

International Inorganic-Bonded  
Fiber Composite Conference ■



# University of São Paulo (FZEA-USP)







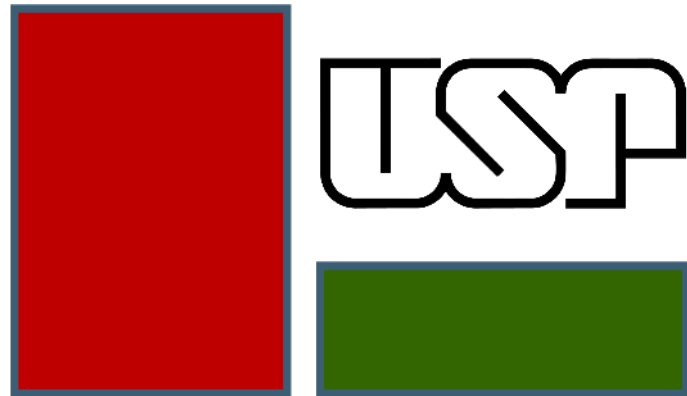
# Graduate Program in Materials Science and Engineering

# NAP BioSMat - USP

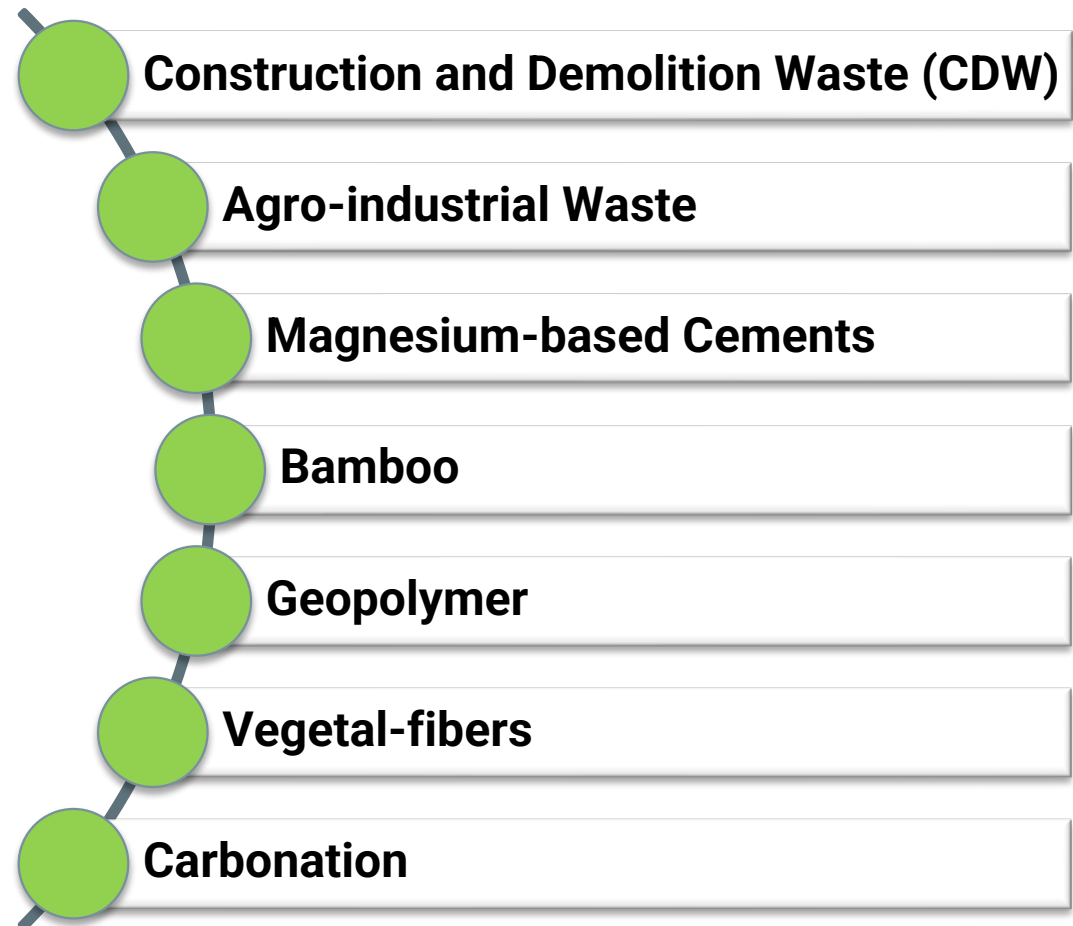


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**BioSMat**  
Materials for Biosystems



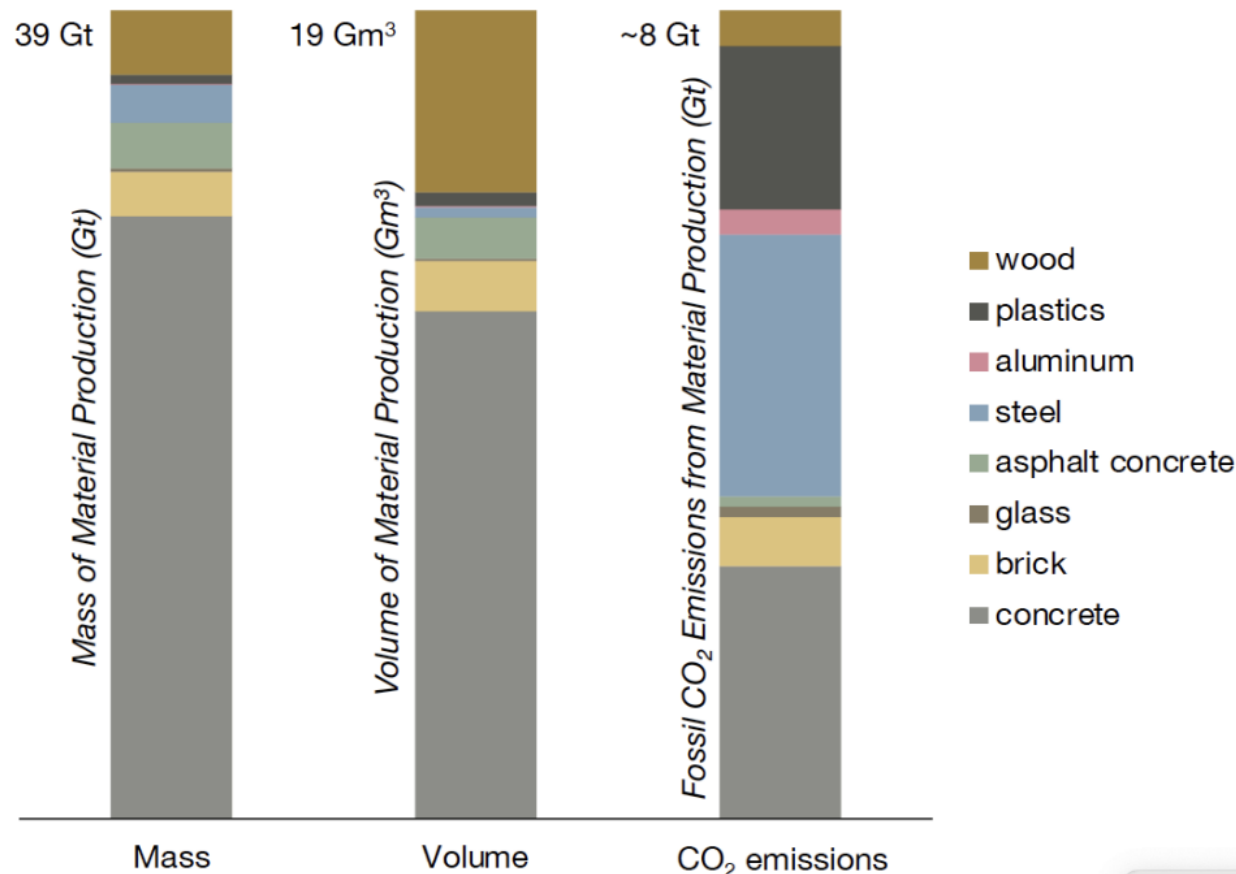
# Highlights

- Introduction
  - The sustainability in the construction sector
  - The use of residues, printable mortars,
- Materials and methods
  - Raw materials preparation and characterization
  - Mixing formulation, rheology assessment
- Experimental results
  - Physical, mechanical and rheology properties
- Conclusions

# INTRODUCTION



# Construction materials emissions

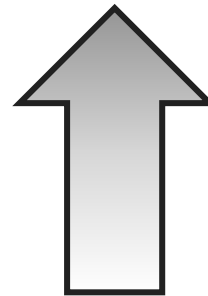


Karen Scrivener: LC3 / LC2 opportunities for fast and large scale decarbonisation and cost reduction of cement and concrete. (2024) Congreso Cemento y concreto verde 2050.

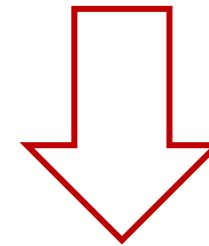
# Oyster shell waste



(%w.t.) Oyster shell  
waste



~93% CaCO<sub>3</sub>



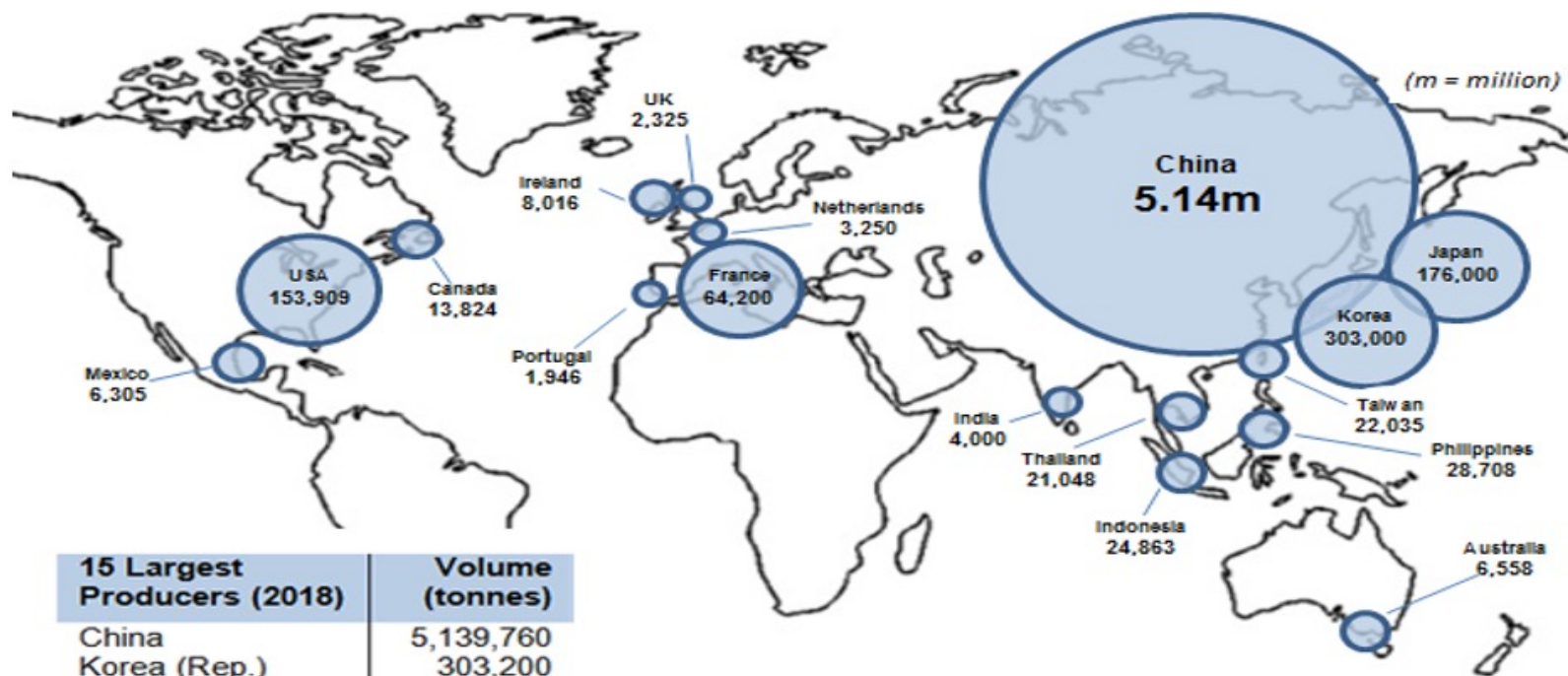
**Reducing the carbon  
footprint of  
production of PC**

(Gonçalves et al., 2019)



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## 15 Largest Producers (2018)

## Volume (tonnes)

China	5,139,760
Korea (Rep.)	303,200
Japan	176,000
USA	153,909
France	84,910
Philippines	28,708
Indonesia	24,863
Taiwan	22,035
Thailand	21,048
Canada	14,614
Ireland	10,369
Australia	6,558
Mexico	6,305
India	4,000
UK	2,325

**China** dominates global oyster production,

Countries with significant oyster production:

- France,
- United States
- South Korea,
- Japan, and
- Philippines



Food and Agriculture Organization  
of the United Nations

(2018)

# 3D cement printing

The **rheological** analysis of printing materials, which includes:

- **Viscosity;**
- **Thixotropy;**
- Behavior under different **shear conditions,**

Is essential to ensure proper extrusion and accurate deposition of layers during printing (Barnes, 2000).



# OBJECTIVES

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To evaluate the potential of waste oyster shell powder as a **rheological modifier** for cementitious materials.

To **enhance the extrusion process** of cement-based composites through the incorporation of oyster shell powder.

To develop **fiber-cement** composites with **reduced clinker content**, promoting more sustainable construction materials.

# **MATERIALS AND METHODS**

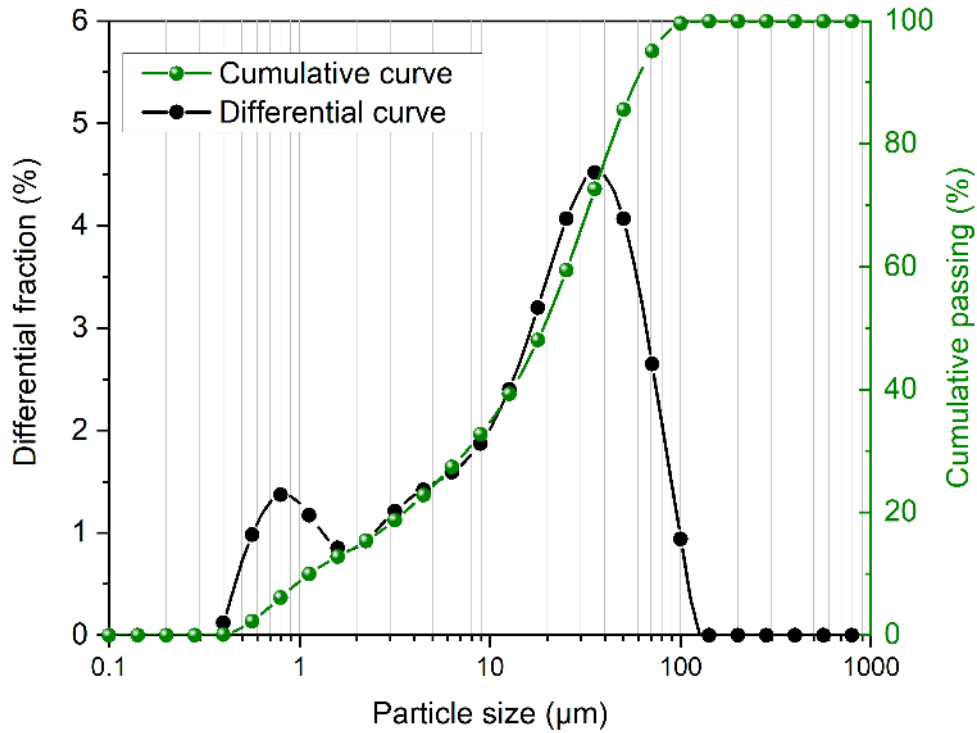


# Materials

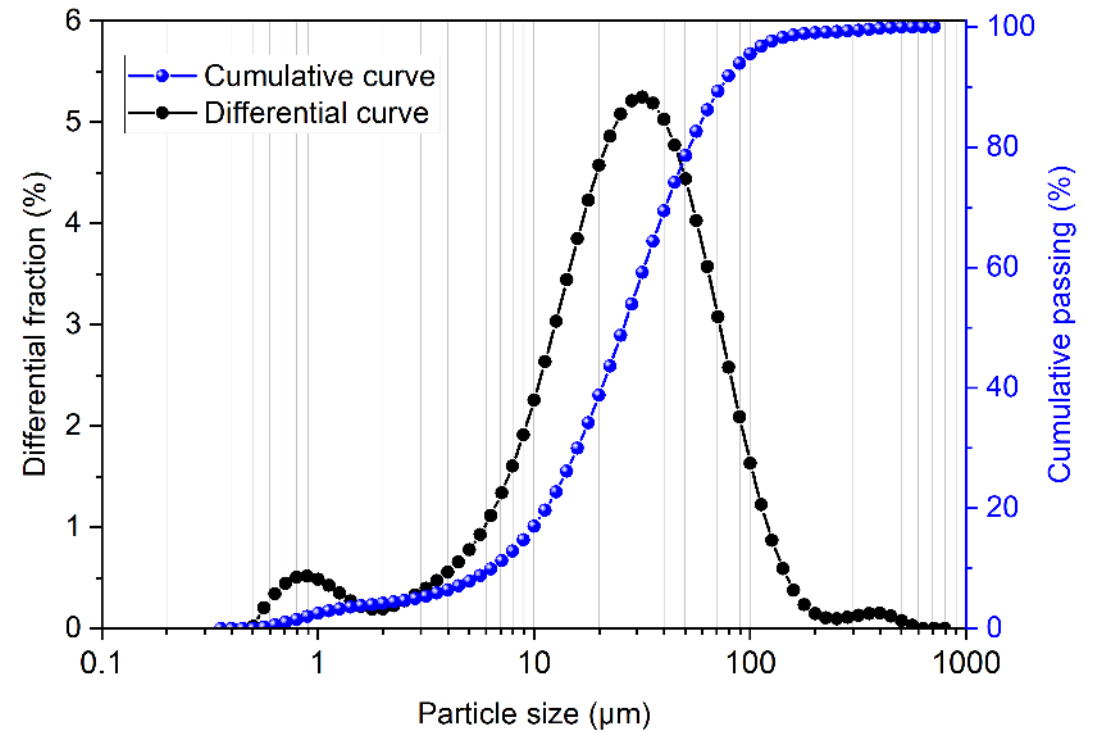
Material	Type/source
Pozzolanic Portland cement	ASTM C105
Shell powder waste	CYSY Mining (Jaguaruna/SC, Brazil)
Bleached eucalyptus cellulose pulp	Suzano Paper & Cellulose (Brazil)
Polycarboxylate-based superplasticizer	ADVA 527
Viscosity and water retention modifier	HPMC-CELOTEX K15 Premium

# Particle size distributions

### Oyster Shell Powder Waste (after grinding <75 μm)



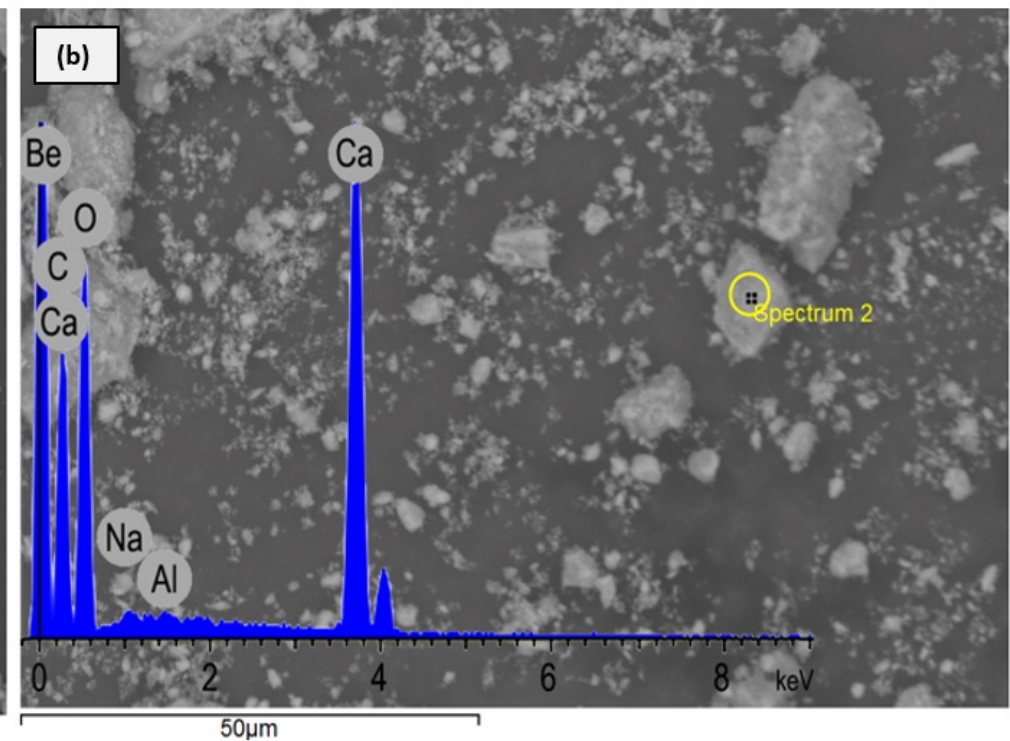
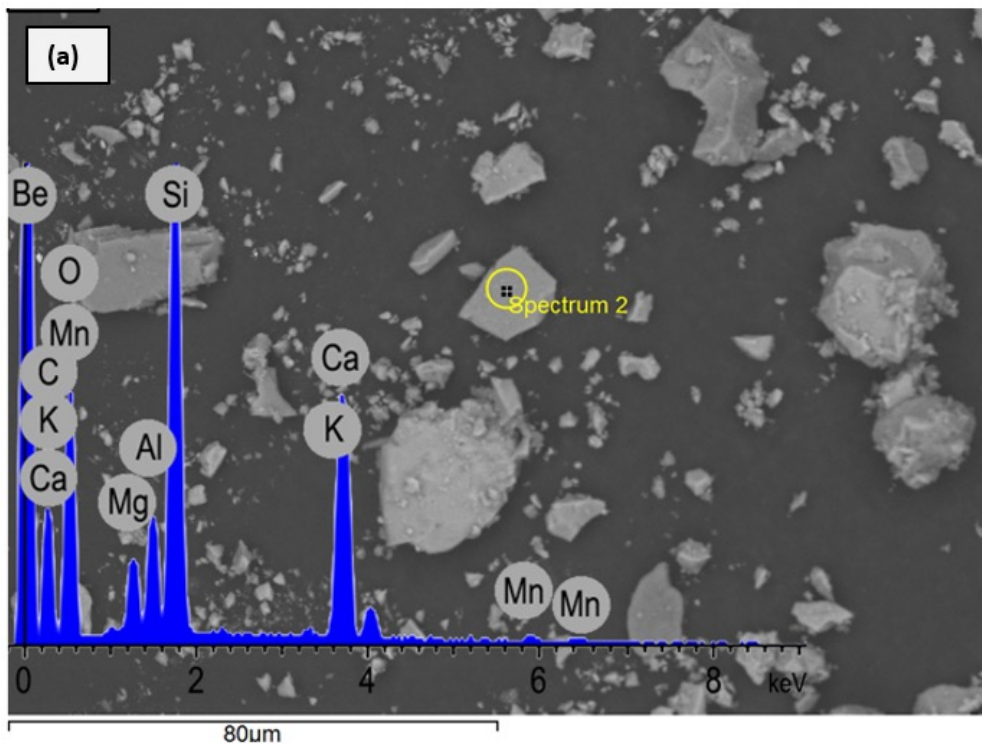
### Pozzolanic Portland Cement



# SEM analysis

(a) Pozzolan Portland Cement

(b) Oyster Shell Powder Waste



# Chemical composition

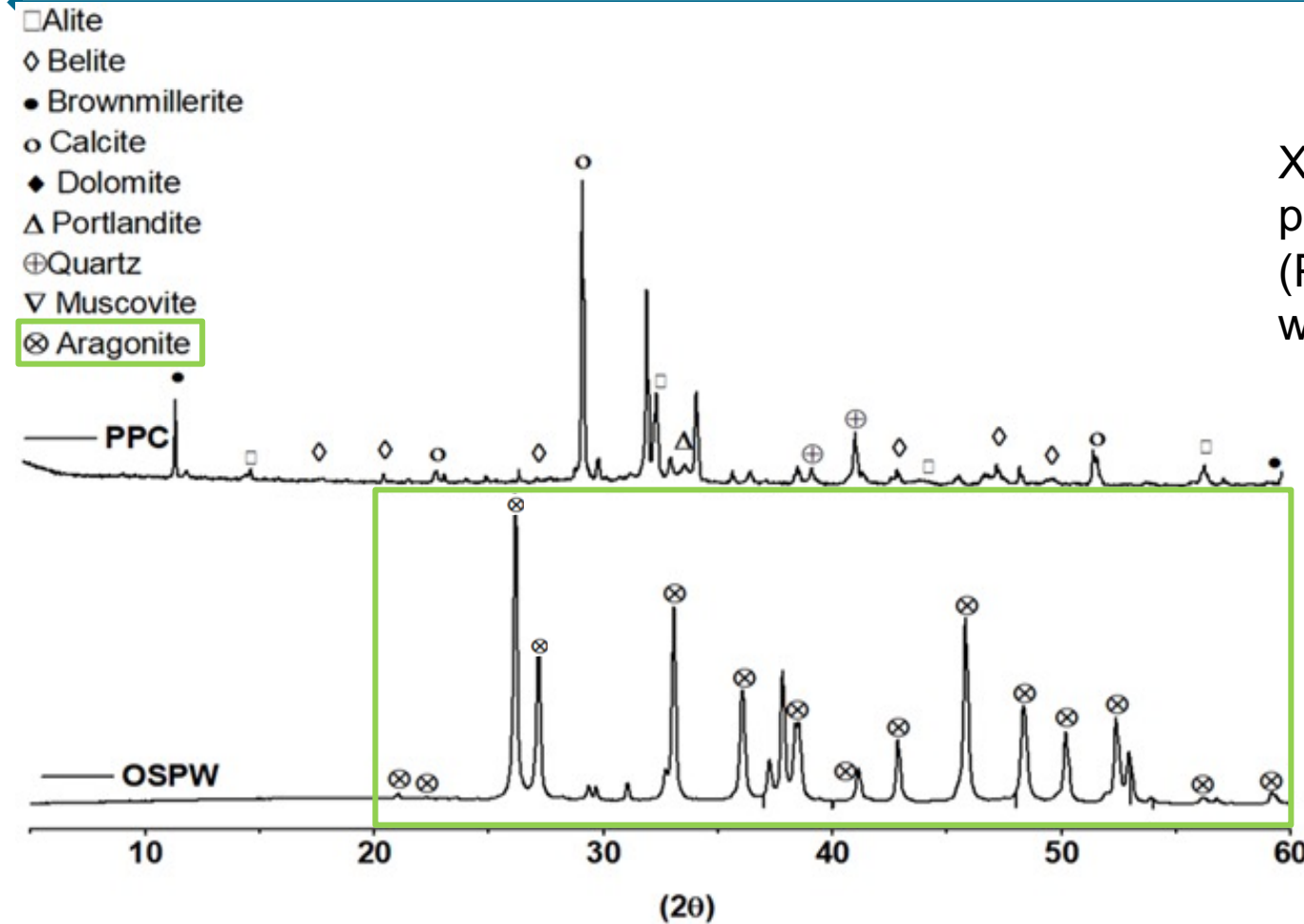
## X-ray fluorescence (XRF)

Samples	Mass Fraction (wt. %)												
	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub>	SrO	LOI*
PPC	1.15	2.21	6.05	15.73	1.05	7.81	1.43	61.18	0.29	0.43	0.43	0.23	6.20
OSPW	-	0.51	0.49	0.88	1.43	2.49	0.14	93.54	0.01	-	0.01	0.41	49.00

\* Loss on ignition at 1020°C.

Samples	Density (g/cm <sup>3</sup> )	Specific surface area (m <sup>2</sup> /g)
PPC	3.06	1.11
OSPW	2.82	7.34

# Mineralogical composition

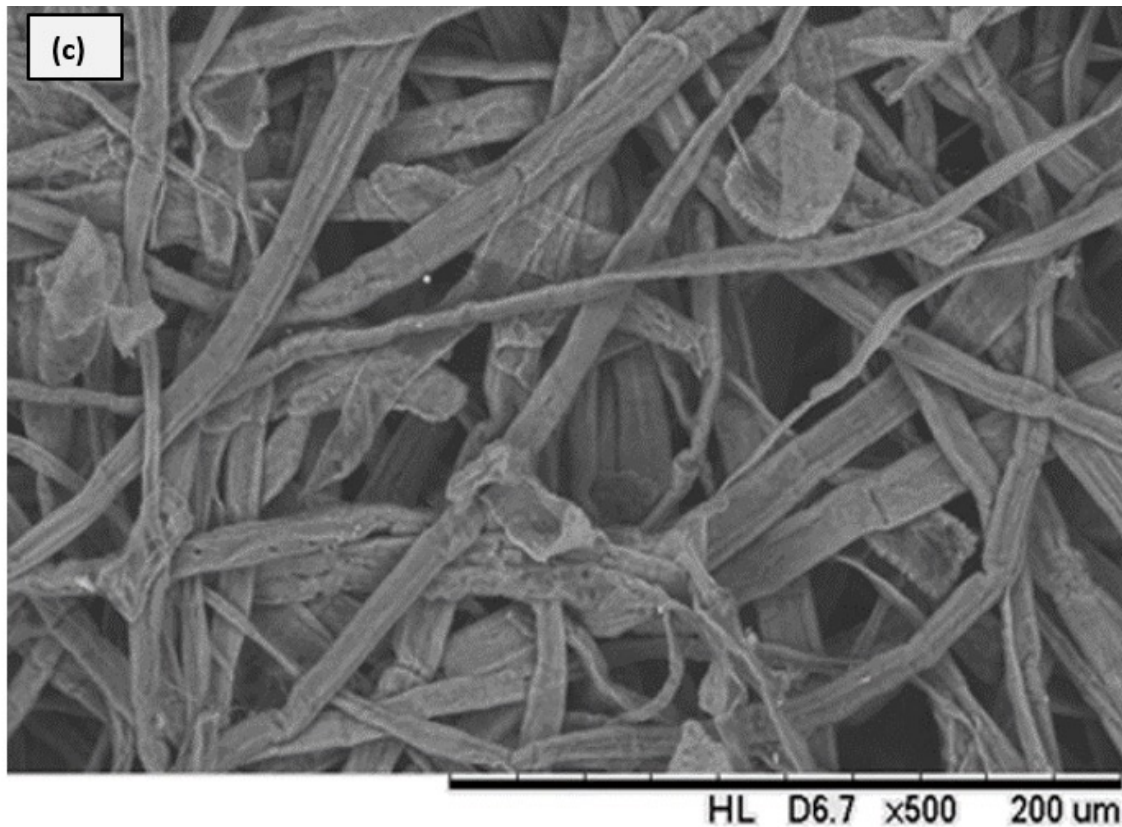


XRD of raw materials, pozzolanic Portland cement (PPC) and oyster shell powder waste (OSPW).



# SEM analysis

## Eucalyptus bleached pulp



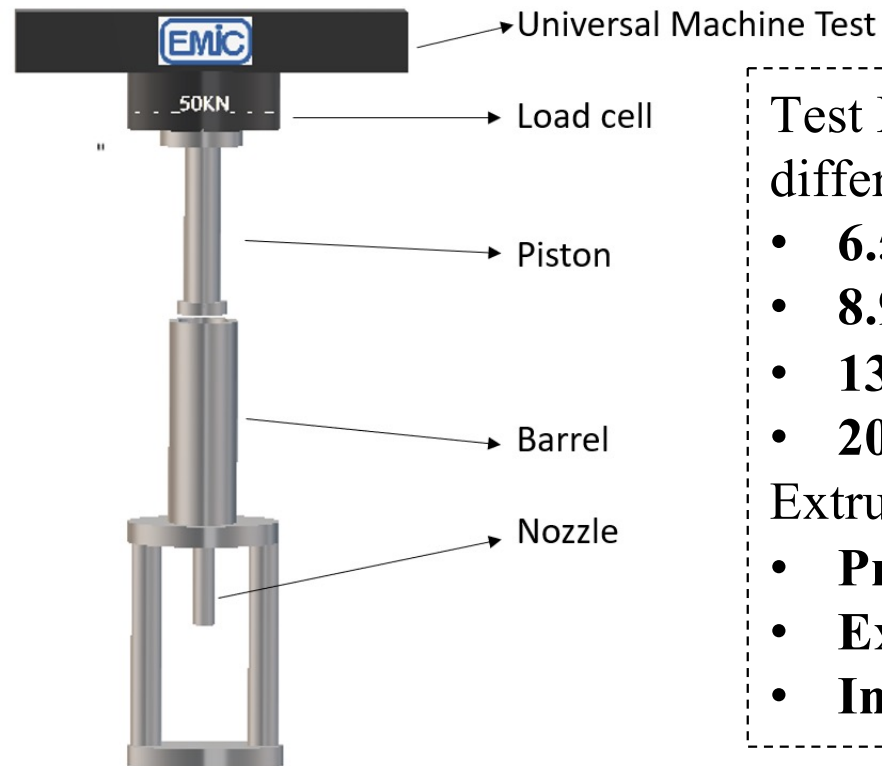
Properties	
Average fiber length	791 μm
Average fiber width	18 μm

# Mix compositions

	PPC 70% OSP 30%	PPC 40% OSP 60 %	PPC 20% OSP 80 %
Pozzolanic Portland cement (PPC)	70	40	20
Oyster shell powder waste (OSP)	27	57	77
Bleached eucalyptus cellulose pulp	3	3	3

- Water/Solids= 0,3
- Superplasticizer= 1%
- Viscosity Modifier= 1%

# Rheology test: Extruder rheometer



Test Procedure: Compression at different speeds (**mm/s**)

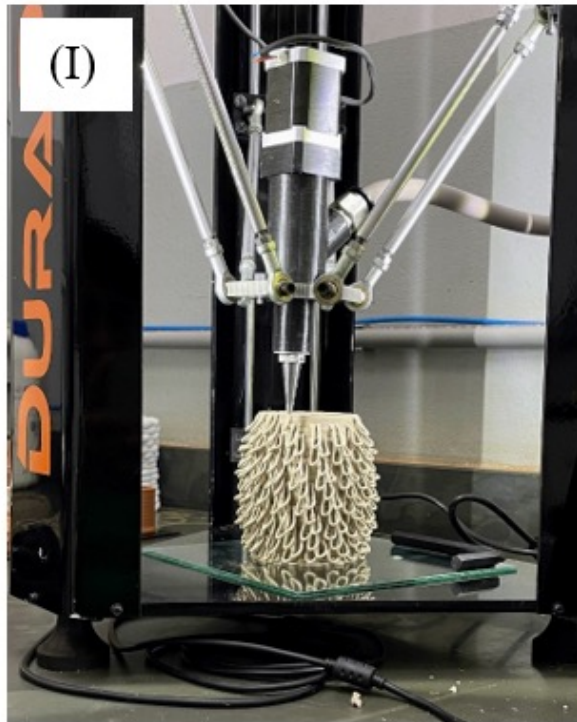
- **6.5;**
- **8.9;**
- **13.3;**
- **20.**

Extrusion parameters:

- **Pressure**
- **Extrusion deformation**
- **Initial yield strength**

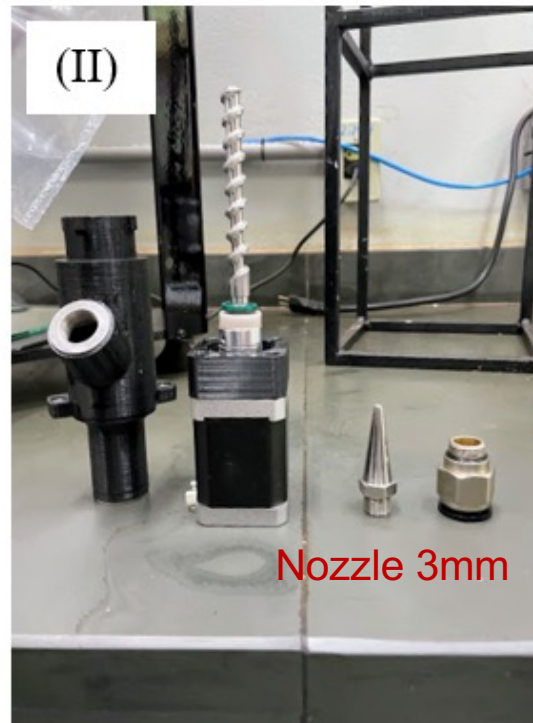
# 3D PRINTER

I. Delta system;



DuraPrinter E02, model

II. Mini extruder;



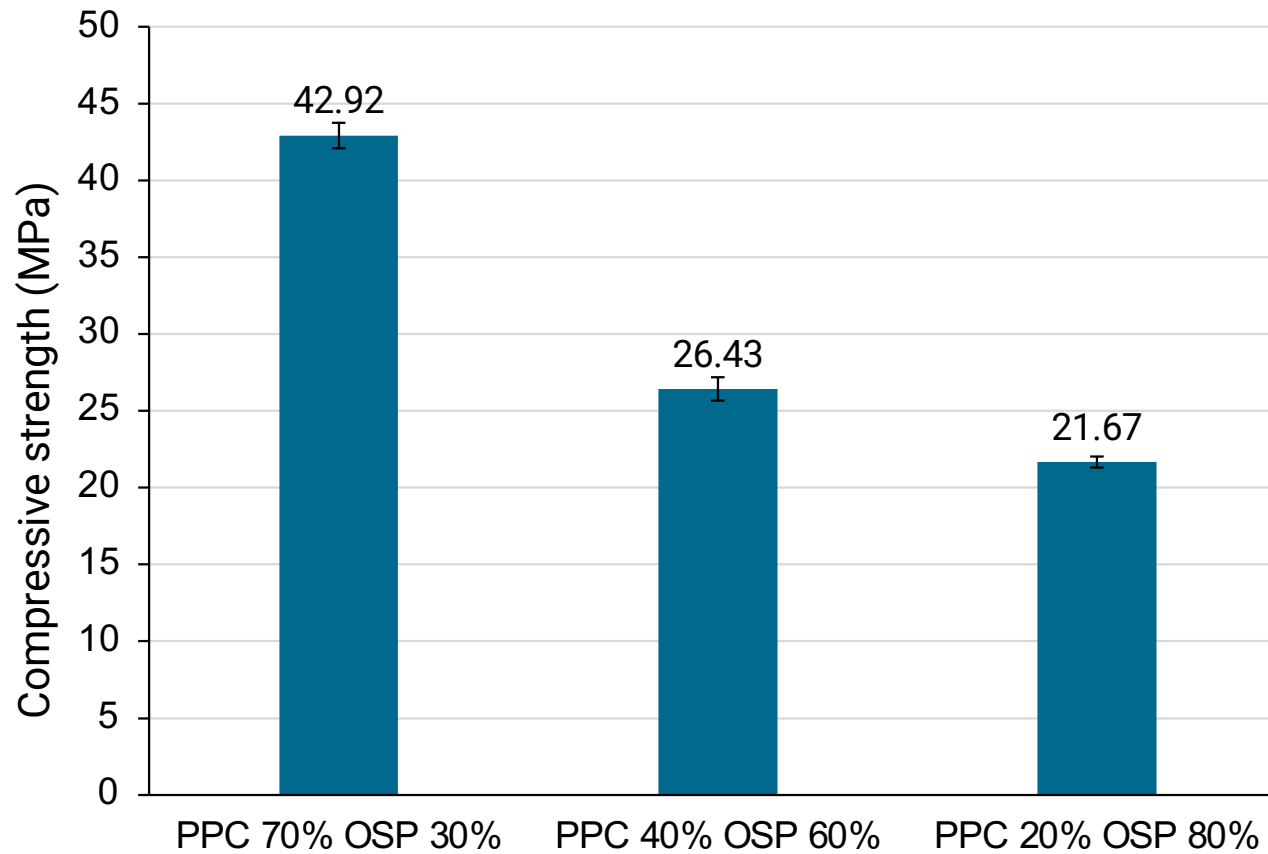
III. Reservoir.



# RESULTS



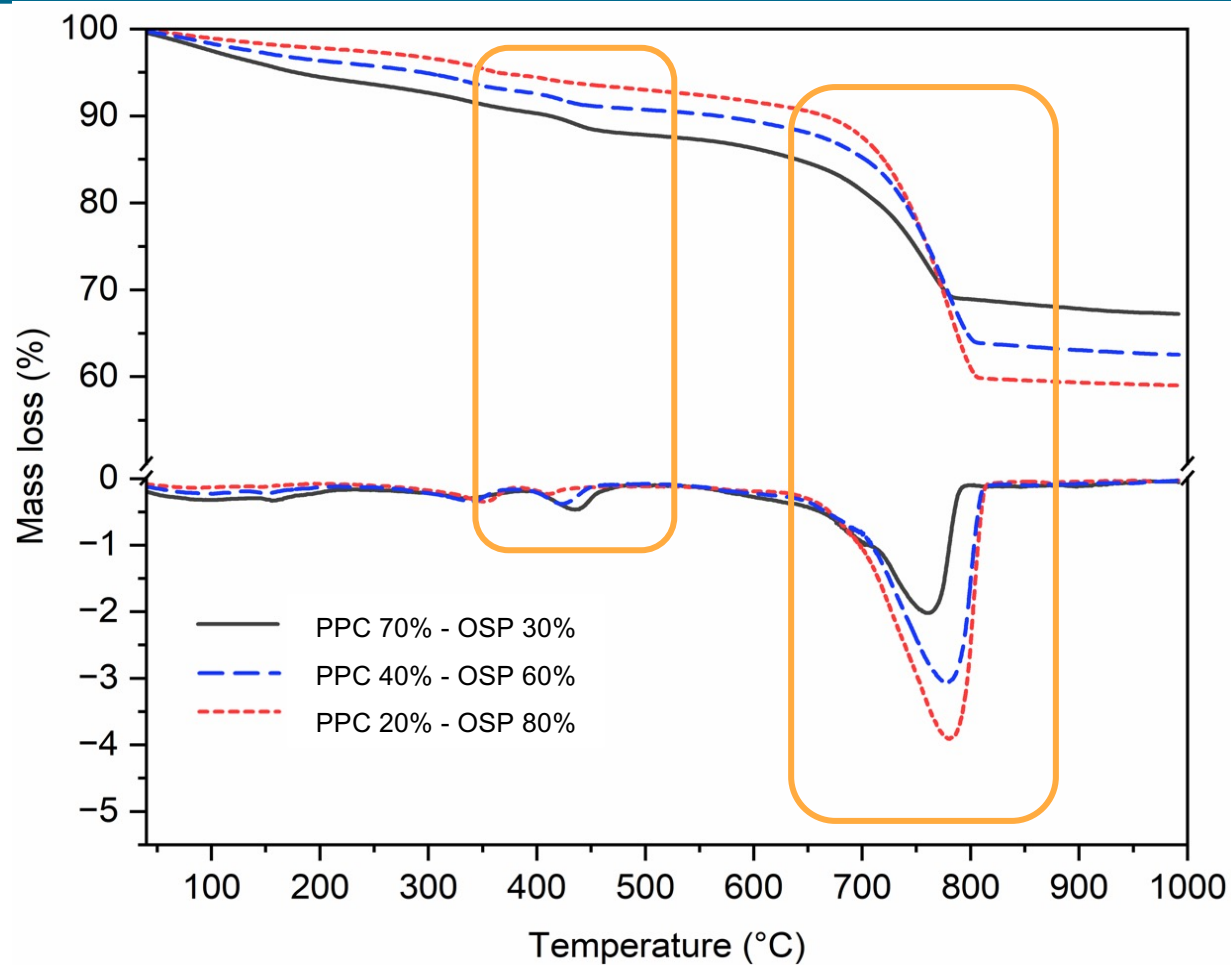
# Compressive strength of composites



# Compressive strength and physical properties of composites

Compositions	Water absorption (%)	Porosity (%)	Bulk density (g/cm <sup>3</sup> )
PPC 70% - OSP 30%	12.69 ± 0.19	22.71 ± 0.39	1.78 ± 0.02
PPC 40% - OSP 60%	15.58 ± 0.10	30.04 ± 0.13	1.68 ± 0.01
PPC 20% - OSP 80%	19.15 ± 0.23	32.19 ± 0.29	1.66 ± 0.01

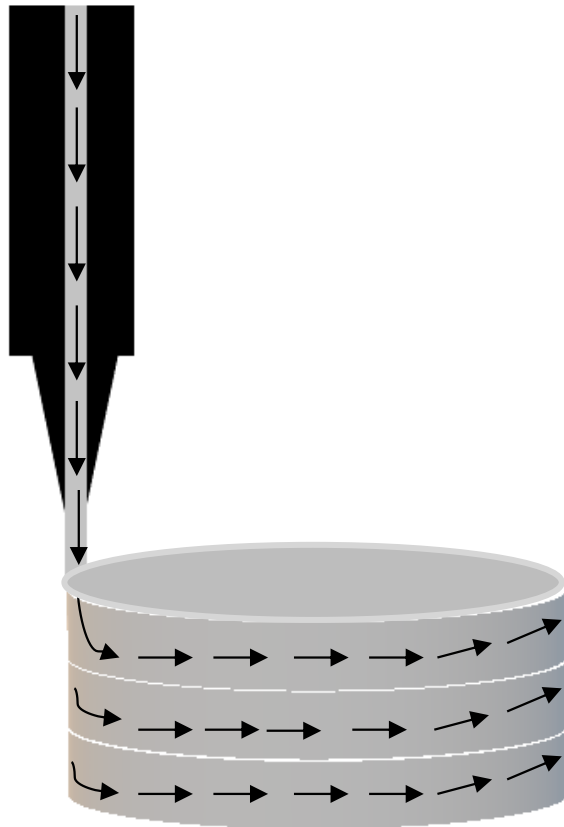
# Thermogravimetric curves (TGA/DTG)



# Rheological parameter values

Compositions	Yield stress	Yield strength	Initial shear stress	Strain rate	Pressure
	$\sigma_0$	$\alpha$	$\tau_0$	$\beta$	$p$
	(kPa)	(kPa/mm.s <sup>-1</sup> )	(kPa)	(kPa/mm.s <sup>-1</sup> )	(kPa)
PPC 70% - OSP 30%	222.22 ± 30.51	13.07 ± 2.23	4.70 ± 3.19	0.42 ± 0.20	900 ± 42
PPC 40% - OSP 60%	68.14 ± 10.22	0.56 ± 0.28	2.59 ± 0.93	0.35 ± 0.06	517 ± 21
PPC 20% - OSP 80%	30.68 ± 7.95	0.29 ± 0.53	1.18 ± 0.48	0.12 ± 0.04	205 ± 10

# The role of cellulose Pulp









During extrusion, the fibers present in the eucalyptus pulp **oriented the flow direction** of the printed material;

Improves **stability** during extrusion;

More uniform and controlled deposition;

Greater **cohesion** and control of material fluidity

Printing speed Layer height	1 mm	1.5 mm	2 mm
15 mm/s			
20 mm/s			

3D printed samples using PPC20 formulation.



# CONCLUSIONS

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Despite reduced mechanical properties, the **increased porosity** could benefit applications like additive manufacturing, positioning it as an alternative to CO<sub>2</sub>-intensive Portland cement.

**Fiber Role:** Fibers enhance cohesion and stability, preventing collapse during 3D printing.

**Oyster shell powder** promotes low-clinker fiber-cements.

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