3D printing of spray dried CNFs reinforced polypropylene composites

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ABSTRACT

Spray-dried cellulose nanofibrils exhibit excellent dispersion and distribution in a polymer matrix attributable to their µm size and spherical shape of individual particles. The tensile and flexural properties of PP increased after adding 10 wt.% SDCNFs, and the impact strength of SDCNFs-filled PP was 136% higher than that of 10 wt.% wood flour-filled PP. The storage modulus of SDCNFs-filled PP was higher than wood flour addition. Furthermore, the addition of SDCNFs to the PP matrix resulted in faster crystallization and a 12% reduction in crystallinity level of PP, and CTE of PP was reduced by 20%. After the SDCNFs-reinforced PP composites were used for 3D printing, the shrinkage rate of PP was reduced by 39%, and the printability of PP was significantly improved because of the presence of SDCNFs. The improvements in the performance of PP are expected to be helpful in automotive components.

INTRODUCTION

THE PROBLEM

- Reinforcing materials, such as glass fibers, enhance the performance of plastic matrix composites (PMCs) including thermoplastics such as polypropylene
- Inorganic reinforcing fillers including glass, carbon, aramid, and boron fibers cause environmental pollution during manufacturing and do not decompose naturally
- Highly ordered crystal structure with high crystallinity in PP causes shrinkage/warping during 3D printing, limiting its use in FLM technology

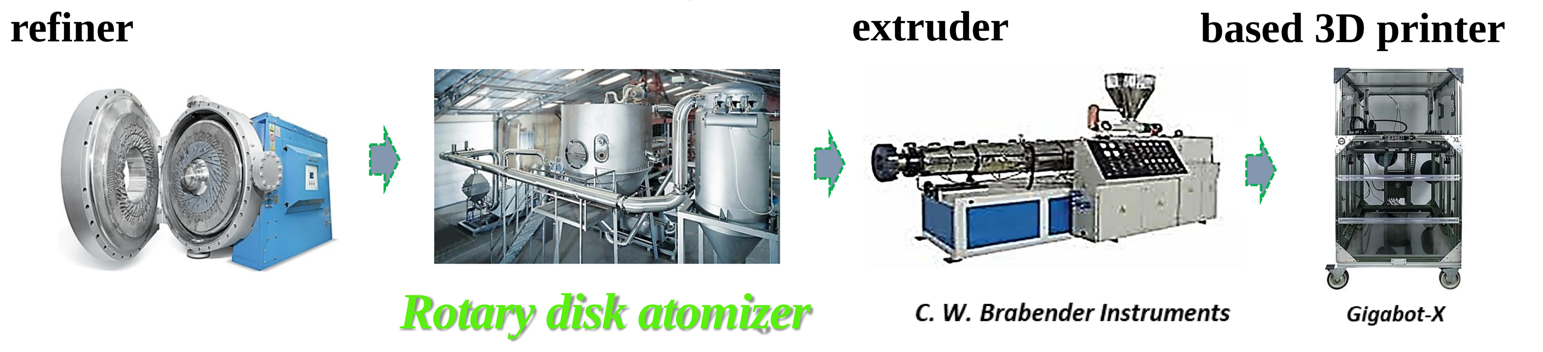
THE SOLUTION

- Cellulose nanofibrils (CNFs) are environmentally friendly materials that can be used as a replacement for inorganic fillers in polymer matrices
- **Pros**: compared to larger-sized fillers, the use of nano-fillers can provide further improvements in the printability of PP
- **Cons**: conventional CNF drying techniques leads to fibril agglomeration and loss of nanoscale properties. High cost and low yields also concerns
- **Solution**: spray-dried cellulose nanofibrils (SDCNFs) dried by a pilot-scale rotary disk atomizer

MATERIALS & METHODS

RESEARCH PLAN

Thermomechanical refiner → Spray drying → Co-rotating twin extruder → Pellet fed extrusion-based 3D printer



TESTING

Size and shape of particles | Mechanical properties of composites | Physical and thermal behavior of composites

EXPERIMENTAL SECTION

- Bleached kraft pulp (BKP), unbleached kraft pulp (UKP), and old corrugated cardboard pulp (OCC) were fibrillated to over 90% fines level. Wood flour (WF) was used as a control

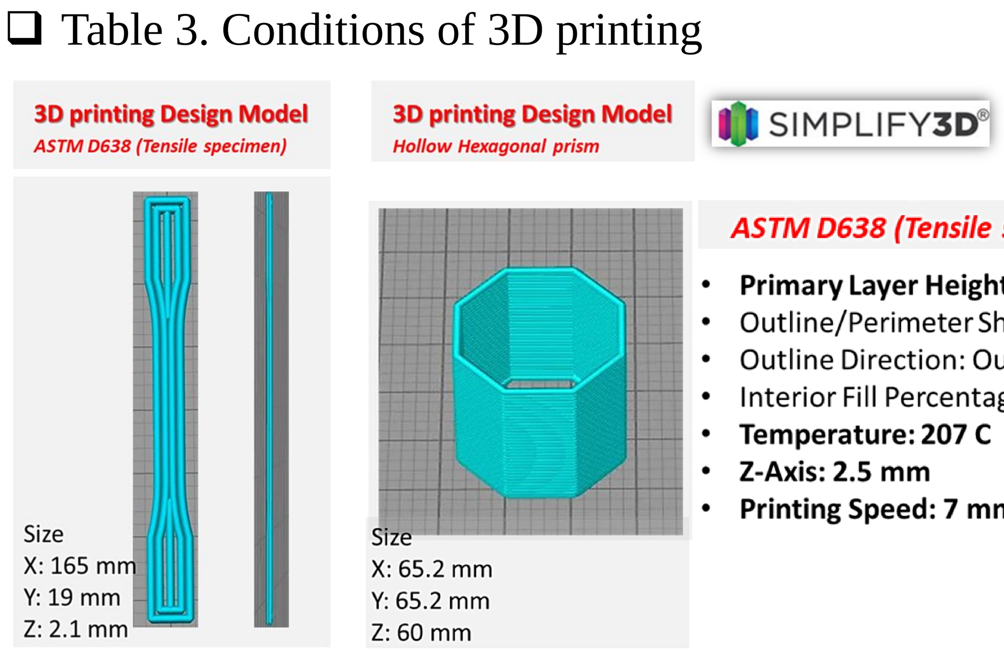
- Table 1. Conditions of spray drying

	Inlet Temp, ℃	Outlet Temp, ℃	Bag house Temp, ℃	Spinning disk, RPM	Feeding rate, Kg/hr	Air speed, %
Conditions	248	123	117	30,000	17	85

- Table 2. Compounding formulations

	Composite	Pulp Fine level, wt.%	Filler, wt.%	MAPP, wt.%	PP, wt.%
1	Neat PP	-	0	0	100
2	10% WF	100 mesh wood flour	10	5	85
3	10% BKP SDCNFs	90% fines level	10	5	85
4	10% UKP SDCNFs	90% fines level	10	5	85
5	10% OCC SDCNFs	90% fines level	10	5	85

- Table 3. Conditions of 3D printing



ASTM D638 (Tensile specimen)

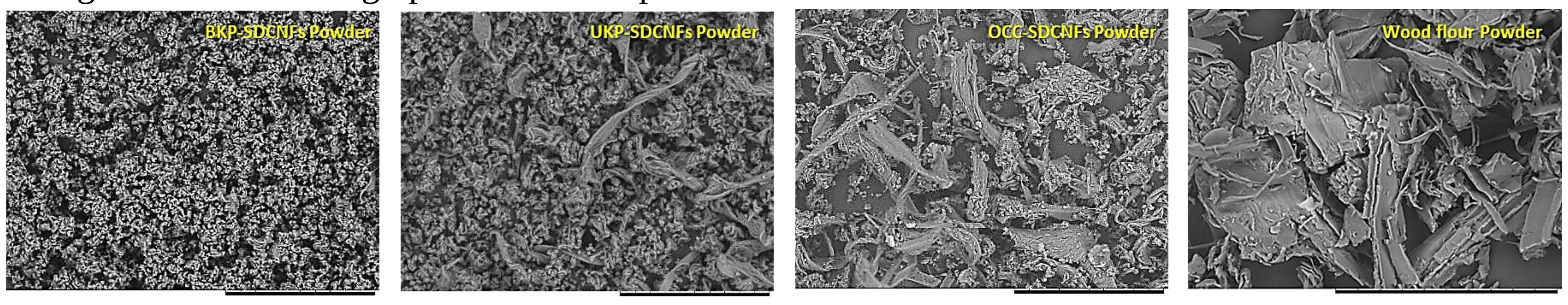
- Primary Layer Height: 1.7 mm
- Outline/Perimeter Shells: 1
- Outline Direction: Outside-In
- Interior Fill Percentage: 0%
- Temperature: 207 C
- Z-Axis: 2.5 mm
- Printing Speed: 7 mm/s

Hollow Hexagonal prism

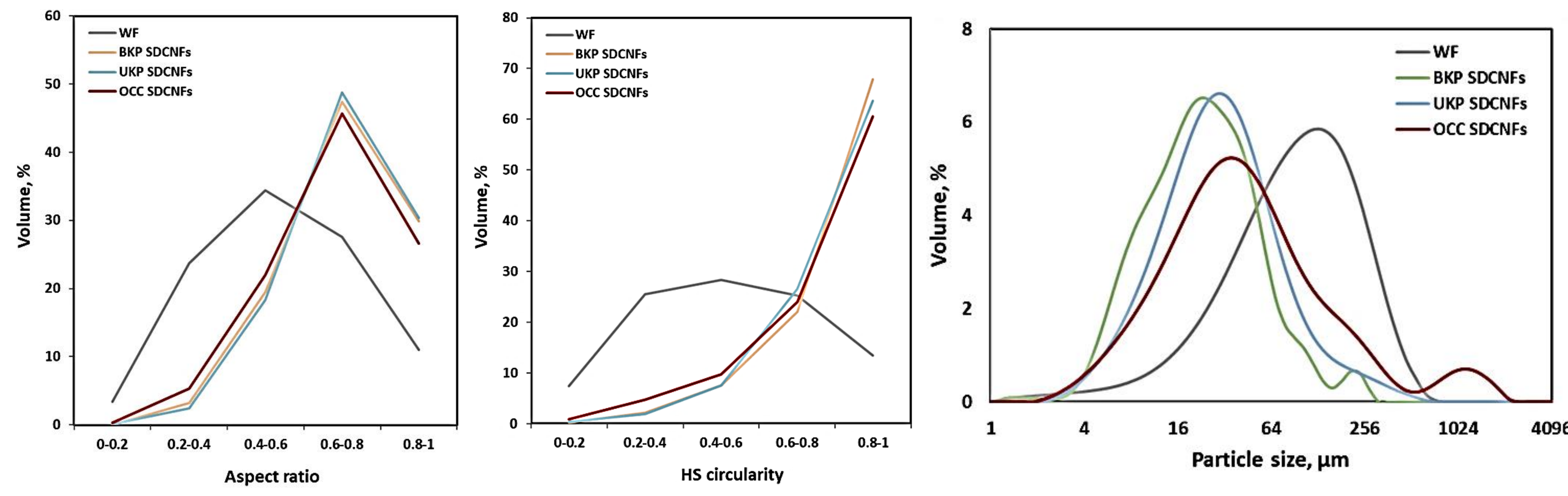
- Primary Layer Height: 1 mm
- Outline/Perimeter Shells: 2
- Outline Direction: Outside-In
- Interior Fill Percentage: 100%
- Temperature: 212 C
- Z-Axis: 2.6 mm
- Printing Speed: 6 mm/s

RESULTS & DISCUSSIONS

- Figure 1. SEM micrographs of SDCNF powders

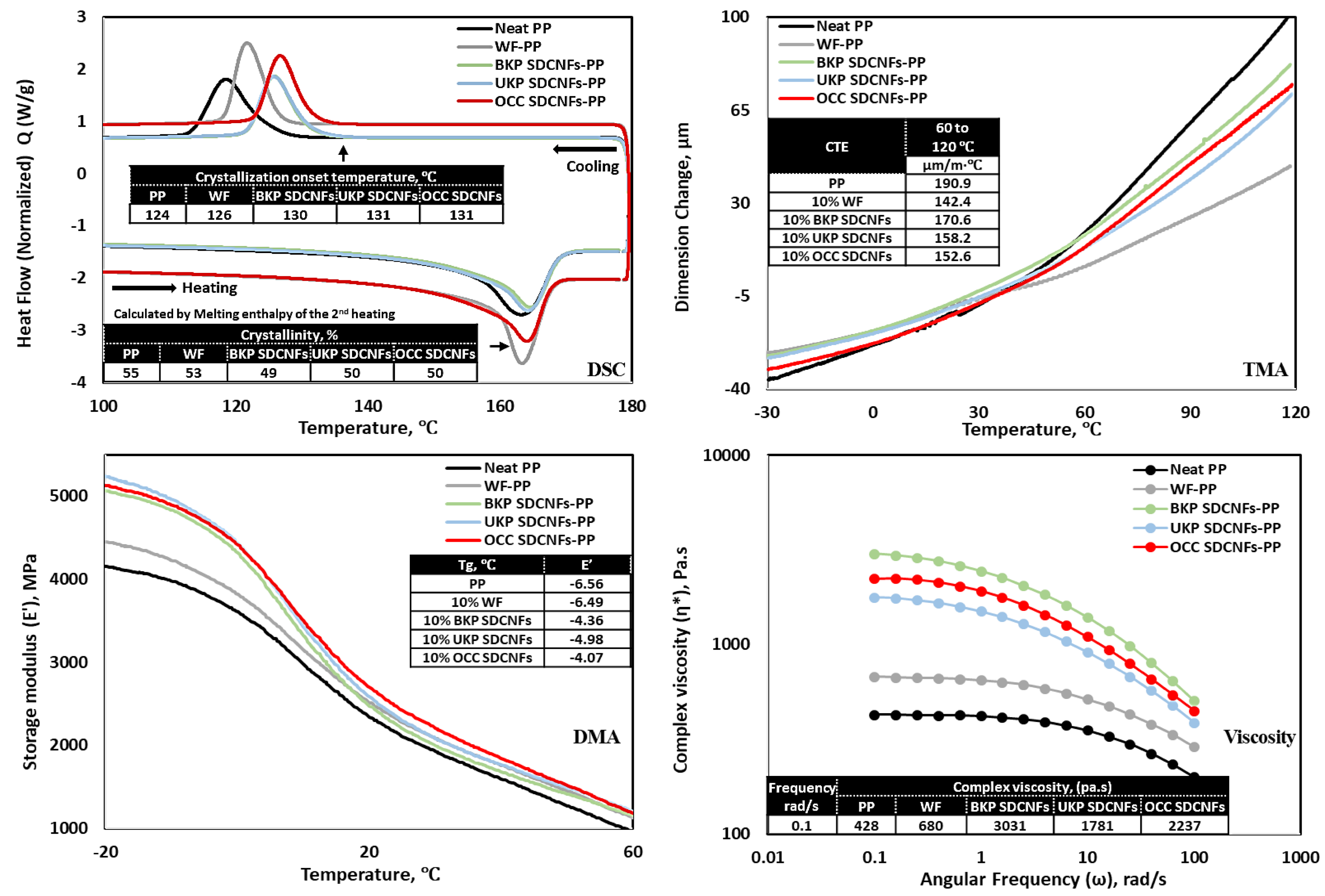


- Figure 2. Morphological, and particle size distribution of SDCNF powders



Average Particle Size, µm	
D[3,2]	
WF	38
BKP SDCNFs	15
UKP SDCNFs	19
OCC SDCNFs	21

- Figure 3. Thermal analysis and viscosity of SDCNFs-reinforced PP composites



Crystallization onset temperature, ℃				
PP	WF	BKP SDCNFs	UKP SDCNFs	OCC SDCNFs
124	126	130	131	131

Crystallinity, %				
PP	WF	BKP SDCNFs	UKP SDCNFs	OCC SDCNFs
55	53	49	50	50

CTE	60 to 120 ℃
	µm/m·℃
PP	190.9
10% WF	142.4
10% BKP SDCNFs	170.6
10% UKP SDCNFs	158.2
10% OCC SDCNFs	152.6

Tg, ℃	E'
PP	-6.56
10% WF	-6.49
10% BKP SDCNFs	-4.36
10% UKP SDCNFs	-4.98
10% OCC SDCNFs	-4.07

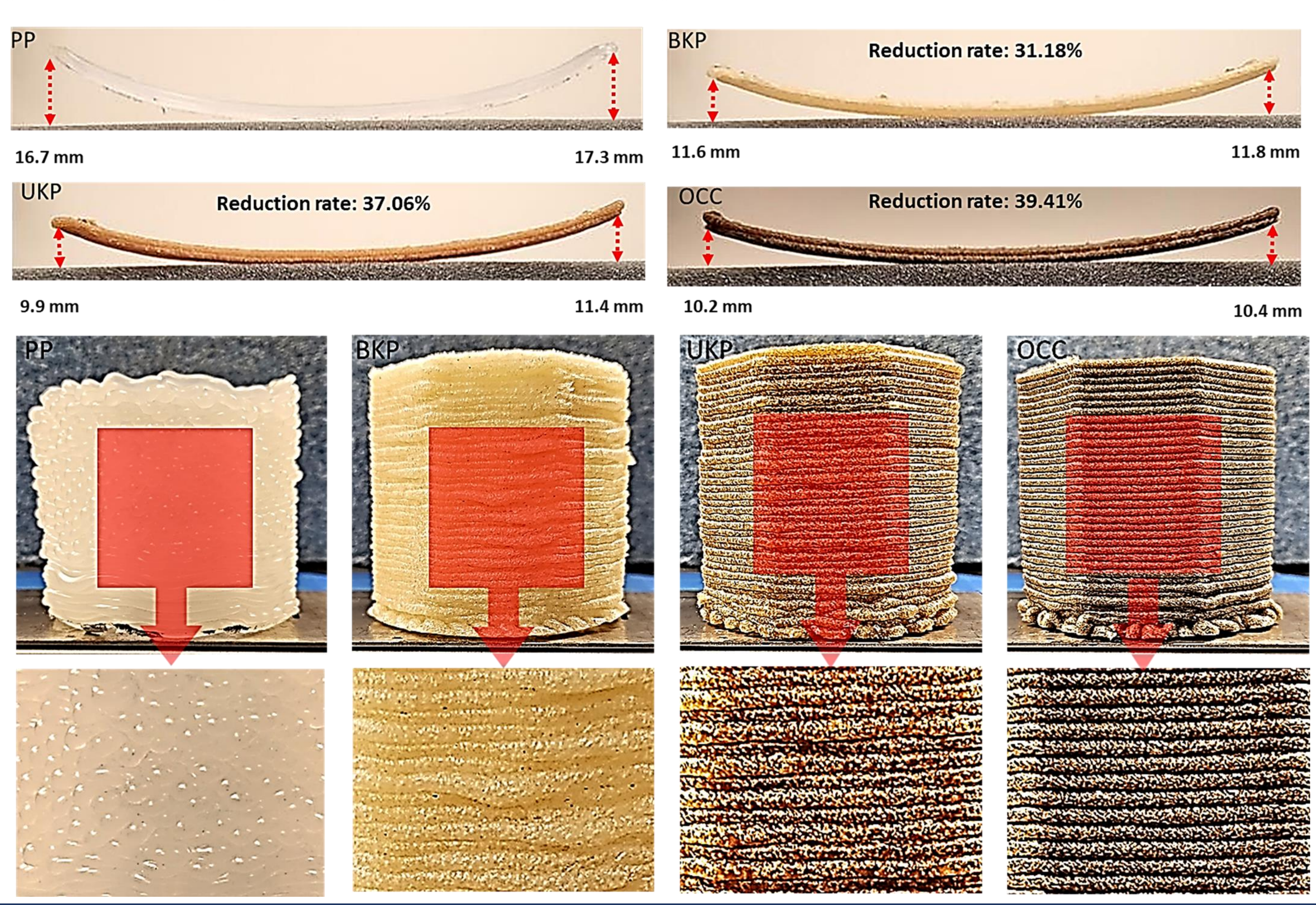
Frequency rad/s	Complex viscosity, (pa.s)				
	PP	WF	BKP SDCNFs	UKP SDCNFs	OCC SDCNFs
0.1	428	680	3031	1781	2237

- Figure 4. Mechanical properties of SDCNFs-reinforced PP composites

Maximum increase rate of SDCNFs-PP compared to the PP matrix					
SDCNFs	Tensile STR	Tensile MOE	Flexural STR	Flexural MOE	Impact STR
	29%	66%	15%	27%	10%

Maximum increase rate of SDCNFs-PP compared to WF-PP					
SDCNFs	Tensile STR	Tensile MOE	Flexural STR	Flexural MOE	Impact STR
	6%	13%	5%	0%	141%

- Figure 5. Shrinkage reduction rates and printability of 3D printed parts



CONCLUSION

- SDCNFs, which are micrometer spherical-shaped particles with a high specific surface area, interact effectively with MAPP, resulting in improved interfacial bonding between filler and matrix. SDCNFs also improved the distribution and dispersion of filler in the matrix
- The addition of SDCNFs in PP resulted in earlier crystallization, decreased crystallinity and CTE, and increased viscosity and stiffness
- The improved physical and mechanical properties of PP by SDCNFs make 3D printed PP a promising material in the automobile industry