Wet and Spray-dried Cellulose Nanofibrils as Nucleating Agent for Biopolymer Composites

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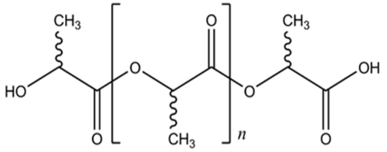
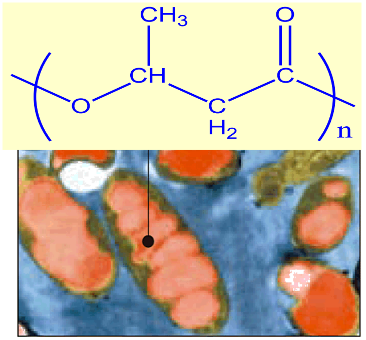
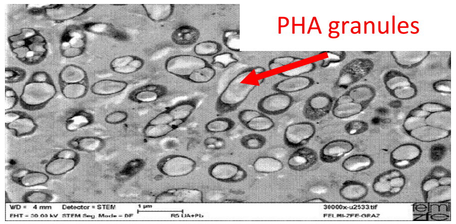
BIOPOLYMERS

Biopolymers are polymers produced from natural sources either chemically synthesized from a biological material or entirely biosynthesized by living organisms (Smith et al., 2016)







Electron micrograph of PHA granules in *Cupriavidus necator*. Source: Koller *et al.*, 2012

Polylactic acid (PLA)

Polyhydroxyalkanoates (PHA)

PLA: bio-based and compostable polymer which can be mass produced from renewable bioresources through fermentation of lactic acid followed by synthetic polymerization.

PHA: bio-based and biodegradable polymer produced by microorganisms through fermentation as carbon and energy storage. Different fermentation strategy and type of substrate determine the characteristics of the PHA produced (homopolymer / copolymer)

GENERAL CHARACTERISTICS

Table. General properties of PLA, PHA and PP

Properties	PLA (Naser et al., 2021)	PHA (Naser et al., 2021)	PP (Pavlík et al., 2019)	LDPE (Favaro et al., 2017)	HDPE (Favaro et al., 2017)
Density (g/cm^3)	1.21 – 1.25	1.25	0.9 – 0.91	0.92 – 0.94	0.94 – 0.97
Glass transition temperature, T (˚C)	45 - 60	2	-20		
Melting temperature, T_m (˚C)	150 – 162	160 - 175	160	106 - 112	130 - 133
Young's modulus (GPa)	0.35 – 3.5	1 – 2	1.0 – 1.6	0.1 – 0.24	0.96 - 1
Tensile strength (MPa)	21 – 60	15 – 40	25 – 40	7 - 17	18
Elongation at break (%)	2.5 – 6	1 - 15	100 - 1000	100 - 700	20 - 100

- Naser, A.Z.., Deiab, I., Darras, B.M. *RSC Adv.*, 2021, **11**, 17151-17196
- Pavlík, Z., Pavlíková, M., Záleská, M. Properties of concrete with plastic polypropylene aggregates, In: Woodhead Publishing Series in Civil and Structural Engineering, 2019. 189-213,\
- Favaro, S.L., Pereira, A.G.B., Fernandes, J.R., Baron, O., da Silva, C.T.P., Moisés, M.P. and Radovanovic, E. (2017) Outstanding Impact Resistance of Post-Consumer HDPE/Multilayer Packaging Composites. Materials Sciences and Applications, 8, 15-25

SHORTCOMINGS OF BIOPOLYMERS:

1) **Expensive** (USD 2.40 – 5.50) **vs USD 1.20 of synthetic plastics**

2) **Slow crystallization rate**

Polymer	Tensile strength, MPa	Elongation at break, %	Crystallization half time *($t^{1/2}$)*, min
PHBHHx (6-12% HHx)	25-28	26-331	7.45
Polylactic acid	52	5	23.5
Low density polyethylene	32	70	1.93
Polystyrene	39.7	1.33	-
Polypropylene	28.7	17.8	1.4

- Crystallization is part of the material and component design process. The mechanical and optical performance of plastic products will be affected by crystallization.
- PLA requires slow cooling for achieving a higher degree of crystallinity (Mileva et al., 2018)
- The low level of PLA crystallinity leads to a low quality and inconsistent polymer product (Lynch, 2014).
- In industrial processing, **nucleating agent** is used to increase the crystallization temperature, leading to **faster nucleation and shorter production cycles** (Mileva et al., 2018).

1. Akbari, B. and Bagheri, R. (2016) 'Deformation behavior and mechanical properties of polystyrene/organoclay/SEBS', *Mechanics of Materials*. Elsevier Ltd, 103, pp. 11–17.
2. Kaneka Corporation (2016) 'Aonilex-Biobased Biodegradable Polymer', p. 2.
3. Kakroodi, A. R. *et al.* (2015) 'Poly(lactic acid)-Based in Situ Microfibrillar Composites with Enhanced Crystallization Kinetics, Mechanical Properties, Rheological Behavior, and Foaming Ability', *Biomacromolecules*, 16(12), pp. 3925–3935. doi: 10.1021/acs.biomac.5b01253.
4. Guschl, P. C. and Otaigbe, J. U. (2003) 'Crystallization Kinetics of Low-Density Polyethylene and Polypropylene Melt-Blended with a Low Tg Tin-Based Phosphate Glass', *Journal of Applied Polymer Science*, 90(12), pp. 3445–3456. doi: 10.1002/app.13084.
5. Crutchik et al., 2020. https://www.mdpi.com/2073-4441/12/4/1118/htm

Nucleating agents facilitate the crystallization process by providing a surface on which the "host" polymer molecules can orientate and organize themselves (Mileva et al., 2018)

Addition of nucleating agents help in improving the crystallization rate of polymer

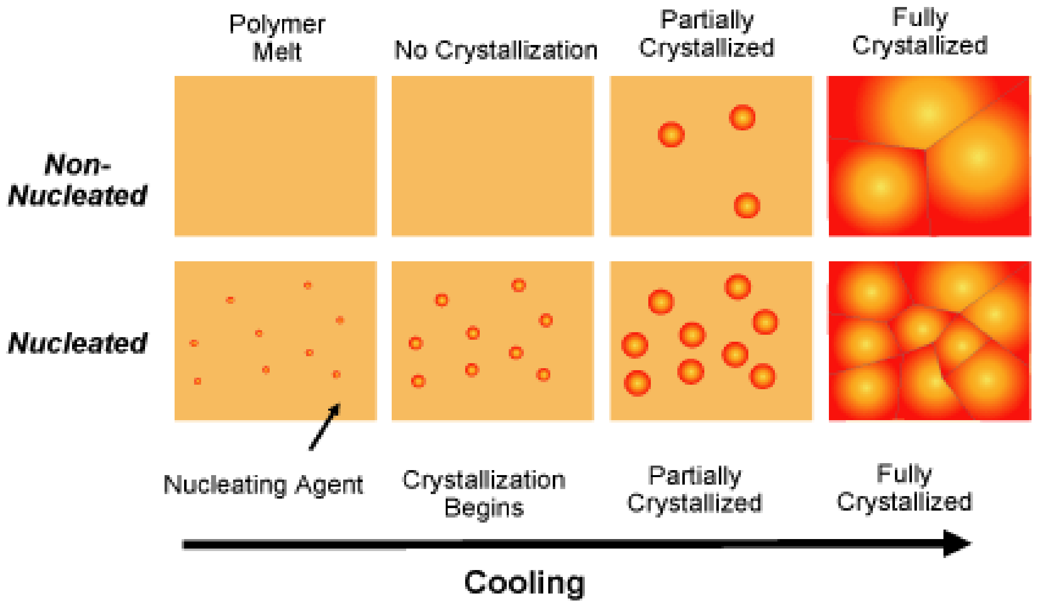


Figure. Mechanism of crystallization via nucleating agents

NA: Provides a disturbance in the polymer matrix and a surface area for the crystals to grow[1]

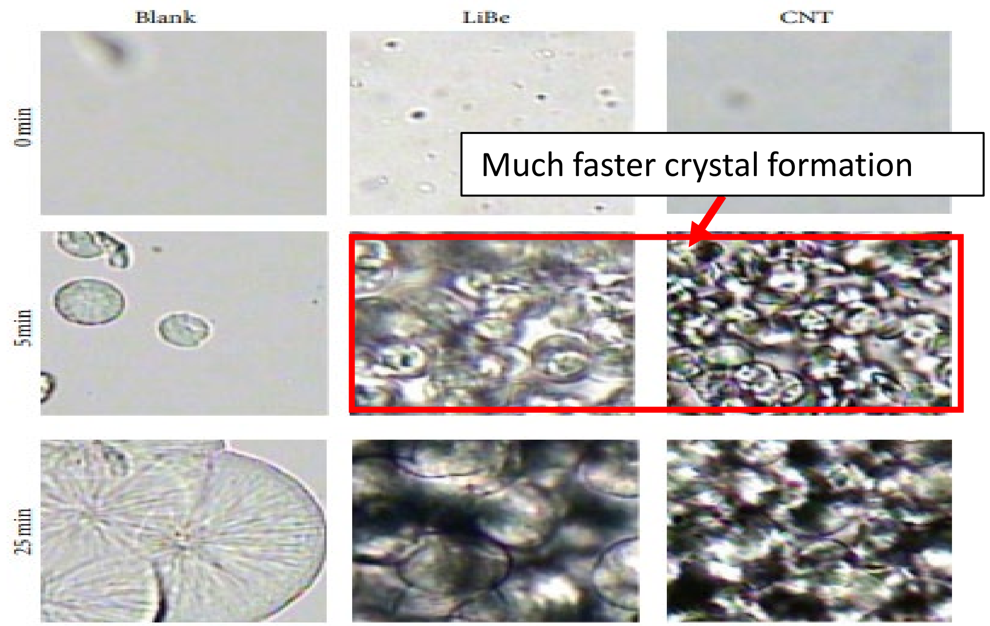


Figure: Examples of previously studied nucleating agents (lithium benzoate (LiBe), carbon nanotube (CNT). (Abdel-hamid *et al., 2012)*

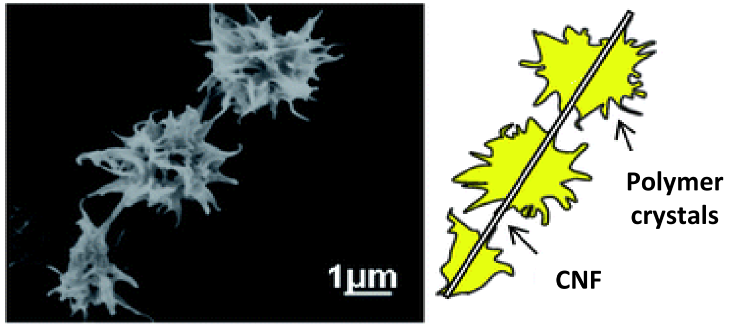


Figure: Nucleating ability of Cellulose Nanofiber (Uchida *et al., 2017)*

[1] Abdel-Hameed, S. A. M. *et al.* (2012) 'Effect of different nucleating agents on the crystallization of leucite', *InterCeram: International Ceramic Review*, 61(3), pp. 127–133.

Nucleating agent → An additive that promotes nucleation and eventually facilitating crystal growth and increasing the crystallization rate

(Kučerová, 2008)

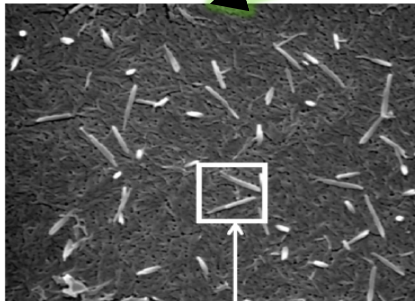
Talc
Cipriano *et al.* (2014)

Phosphorus-based
Meliva *et al.* (2018)

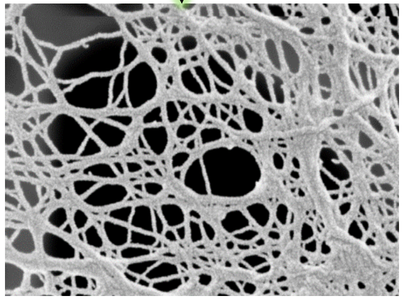
Graphene
Yang *et al.* (2019)

Nanomaterials
Song *et al.* (2013)

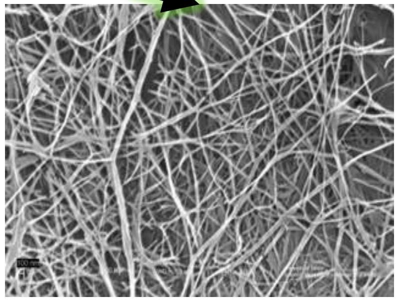
Nanocellulose: size range from 1-100 nm (Klemnn., 2011)



Cellulose nanocrystal (CNC)



Cellulose nanofibers (CNF)



Bacterial nanocellulose (BNC)

A promising bio-based, biodegradable nucleating agent for biopolymers

PREPARATION OF WET AND DRY CELLULOSE NANOFIBRIL FROM OIL PALM BIOMASS

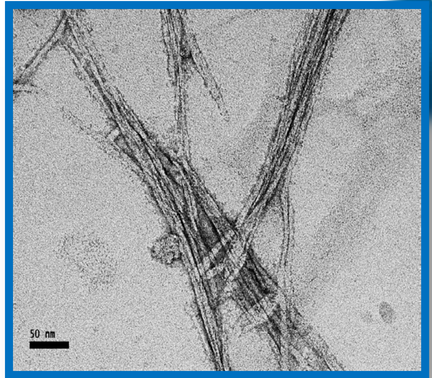
Oil palm biomass

Pretreatment (pulping and bleaching)

Cellulose fiber (pulp)

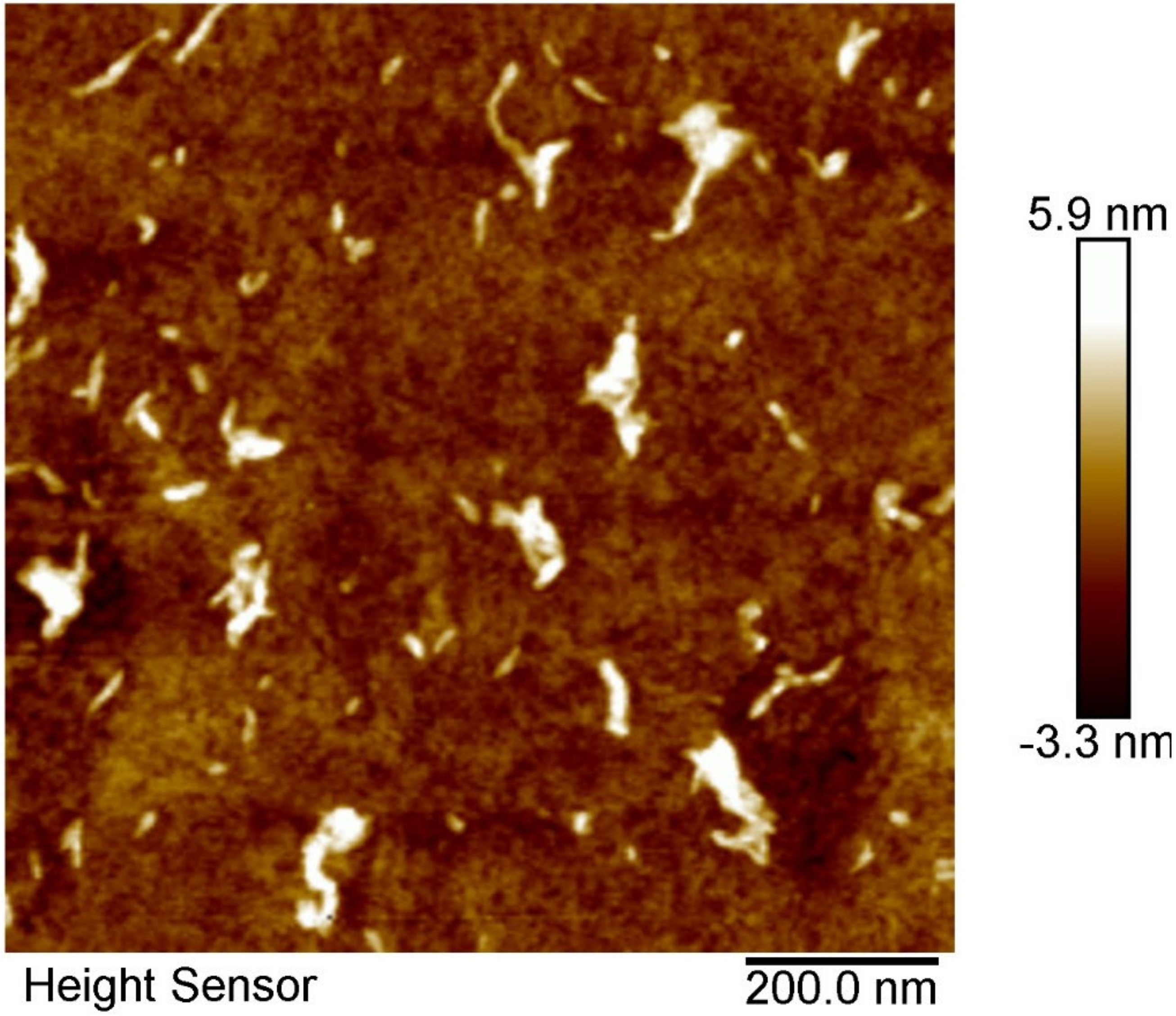
Nanofibrillation by WDM (wet process)

Cellulose nanofibril (CNF) suspension



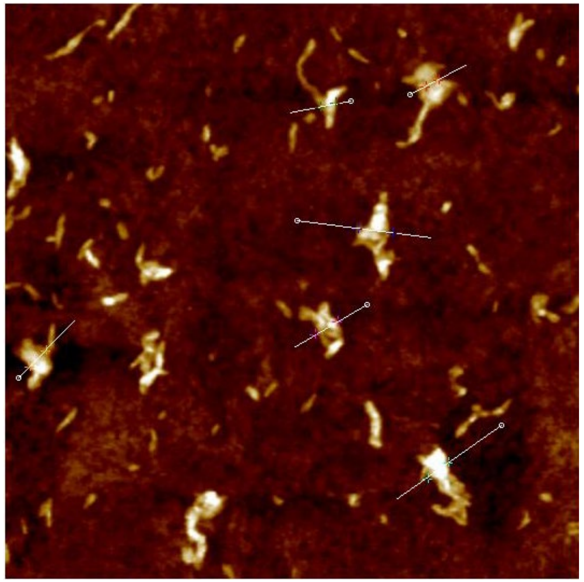
Spray-dried CNF

Characterization of Spray-dried CNF: Atomic Force Microscopy



Left Figure: Spray dried CNF (SDCNF) under AFM.
Average size: 30 – 40 nm
Largest size: 60 nm

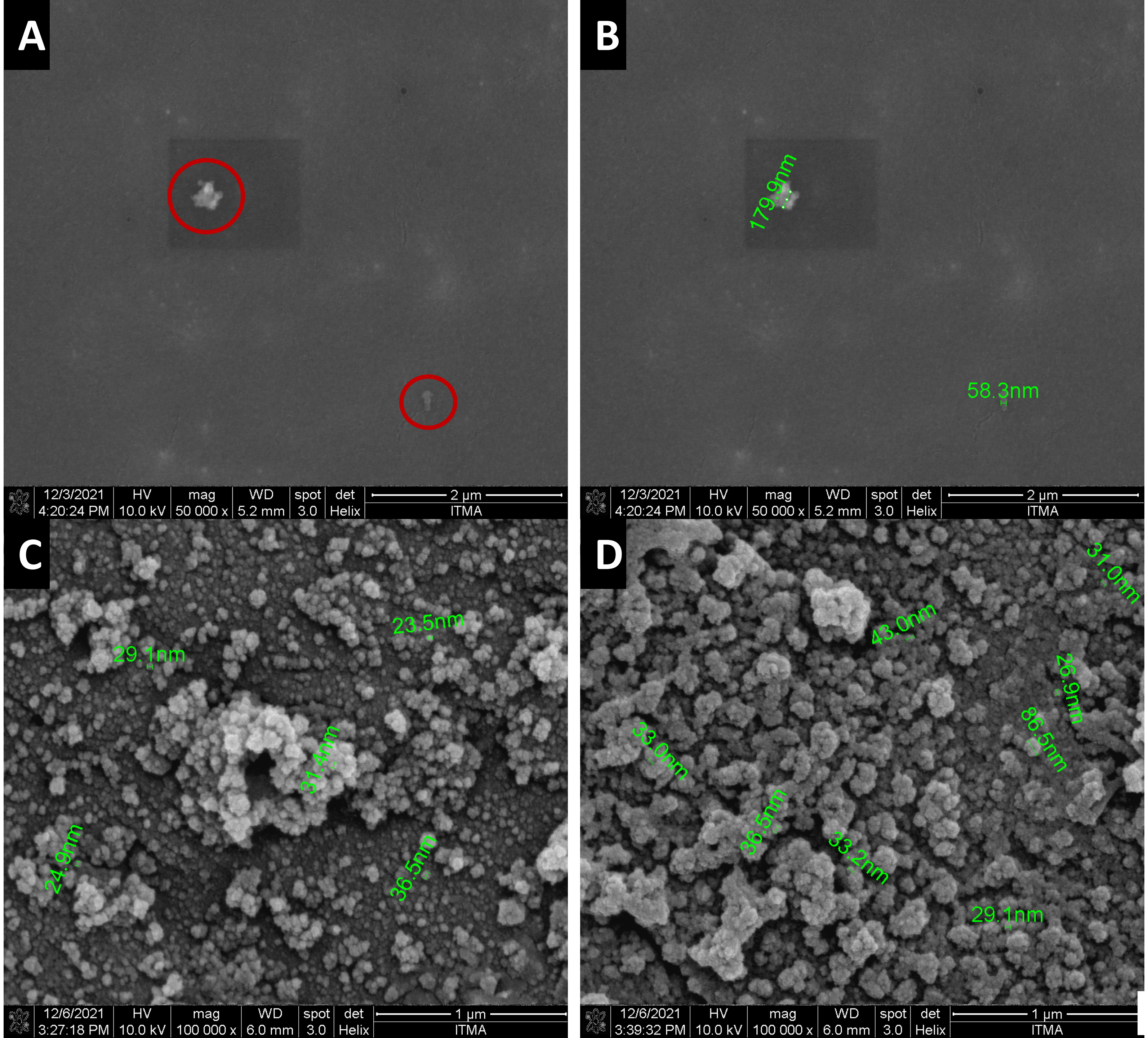
*CNF size was measured using the Nanoscope analysis software (Bruker).



Fiber dimension measured by AFM

Spray Dried CNF

Characterization of Spray-dried CNF: FESEM



A,B – SDCNF powder

C,D – SDCNF in water (0.05% w/v)

PLA/CNF BIONANOCOMPOSITES

PREPARATION OF PLA/CNF BIONANOCOMPOSITES

Polylactid Acid
(PLA2003D, NatureWorks)

Cellulose Nanofibrils (CNF)
DP ~1400, width size 10-20 nm

0 – 6 wt%

Melt-compounding & compression moulding

Crystallization kinetic study (non-isothermal and isothermal – Avrami equation)

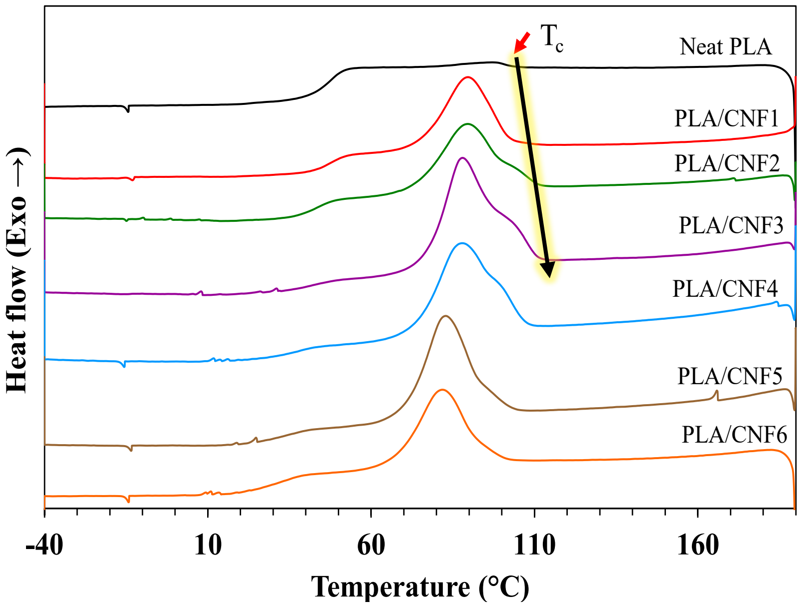
Characterization

- Mechanical properties
- Crystallite size
- Morphology
- Thermal stability

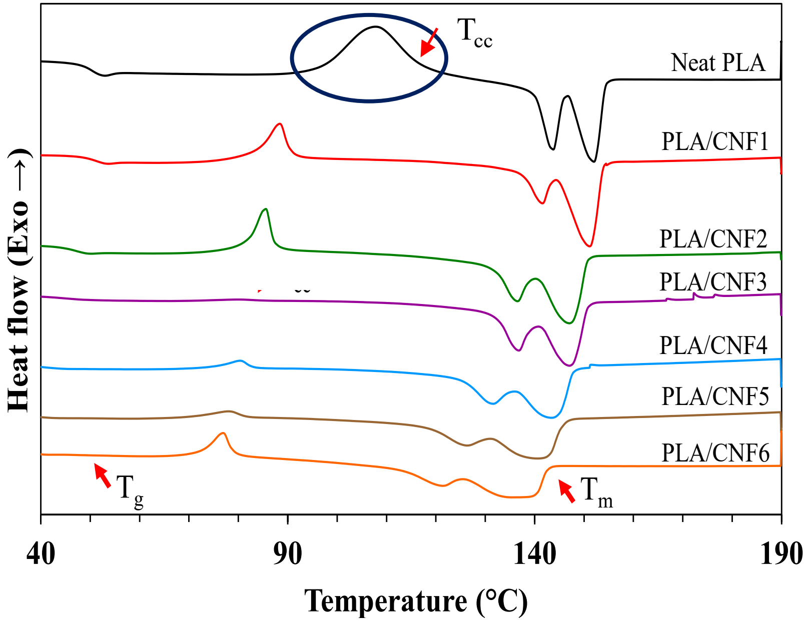
PLA/CNF BIONANOCOMPOSITES

1 (a) NON-ISOTHERMAL CRYSTALLIZATION

COOLING CYCLE



2nd HEATING CYCLE



Sample	T_g (°C)	T_c (°C)	T_{cc} (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔH_c (J/g)	ΔH_m (J/g)	ΔH_{cc} (J/g)	X_c (%)
Neat PLA	50.4	106.1	91.3	143.5	152.1	1.31	35.6	33.4	2.3
PLA/CNF1	51.4	111.2	80.1	141.4	151.1	19.5	37.7	11.1	28.4
PLA/CNF2	47.1	114.1	74.9	136.4	147.0	22.2	40.8	11.5	31.2
PLA/CNF3	43.9	114.6	71.0	136.7	147.1	33.6	42.3	0.9	44.2
PLA/CNF4	40.9	110.1	75.2	131.4	143.5	29.7	43.0	2.6	43.1
PLA/CNF5	37.3	106.4	73.6	126.4	140.8	28.1	37.2	3.6	35.9
PLA/CNF6	36.8	102.7	70.3	121.4	135.4	21.4	30.9	6.4	26.1

1 (b). ISOTHERMAL CRYSTALLIZATION

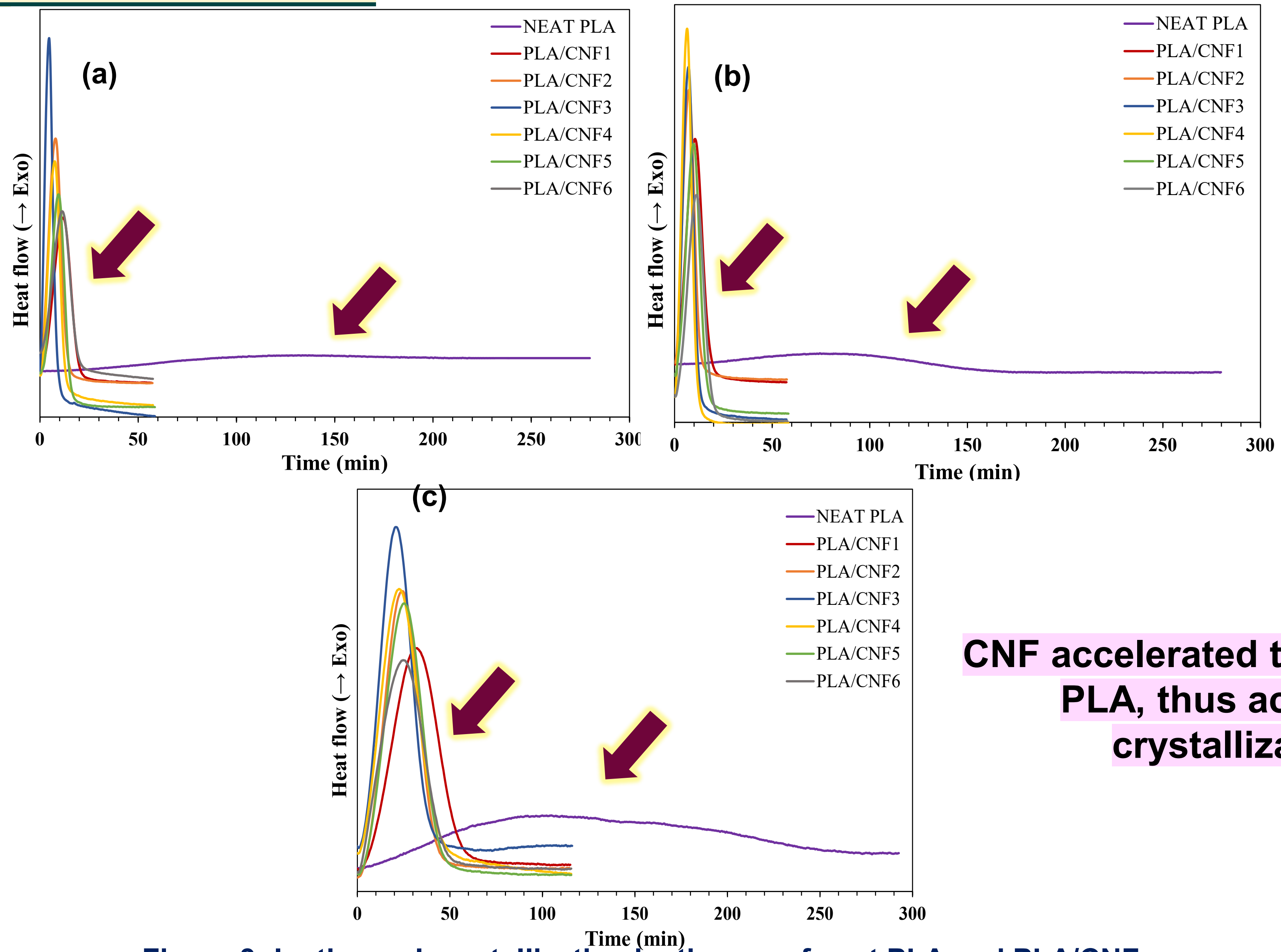


Figure 3: Isothermal crystallization isotherms of neat PLA and PLA/CNF nanocomposites at (a) 90, (b) 100 and (c) 110°C.

CNF accelerated the crystallization in PLA, thus accelerating the crystallization speed

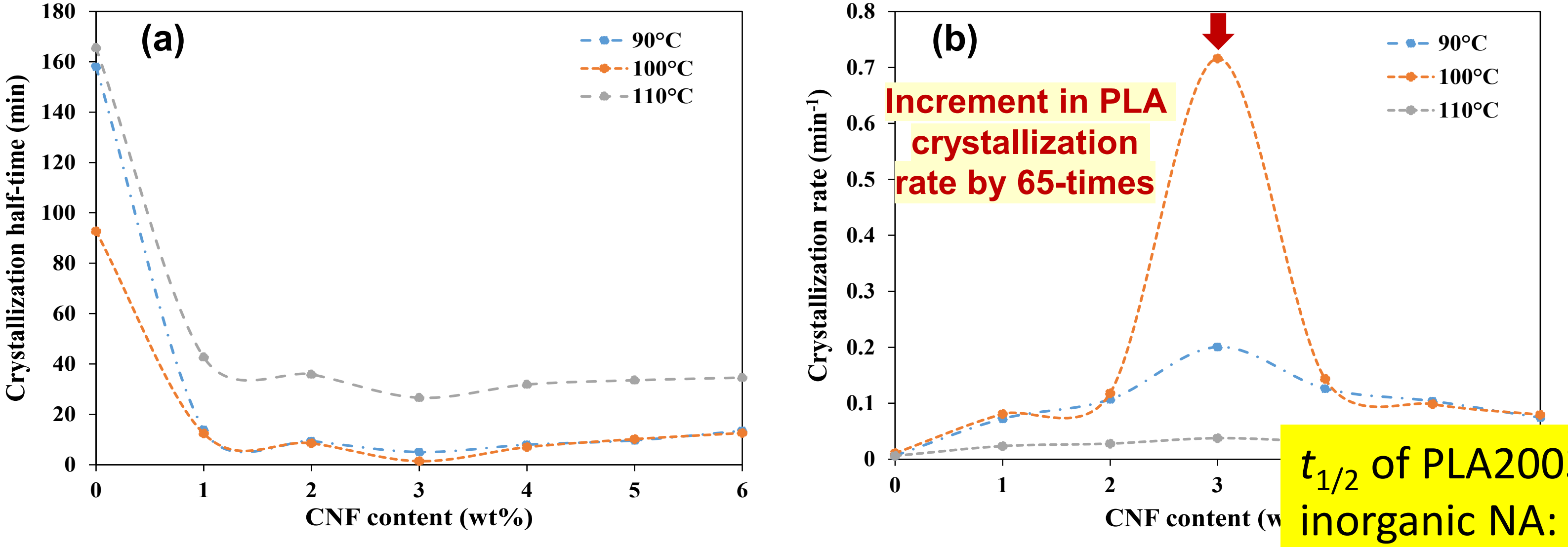


Figure: Dependence of (a) crystallization half-time and (b) crystallization ra
for PLA melt-crystallized isothermally at 90, 100 and 110°

$t_{1/2}$ of PLA2003D incorporated with inorganic NA:

PLA/talc: 5.7 min
PLA/nanoclay: 2 min

Table: Avrami parameters for isothermal crystallization of PLA/CNF nanocomposites.

Sample	90°C				100°C				110°C			
	n	k (min^{-n})	$t_{1/2}$ (min)	$1/t_{1/2}$ (min^{-1})	n	k (min^{-n})	$t_{1/2}$ (min)	$1/t_{1/2}$ (min^{-1})	n	k (min^{-n})	$t_{1/2}$ (min)	$1/t_{1/2}$ (min^{-1})
Neat PLA	3.22	5.72×10^{-8}	158.01	0.006	2.74	2.83×10^{-6}	92.72	0.011	2.46	2.46×10^{-6}	165.59	0.006
PLA/CNF1	3.25	1.35×10^{-4}	13.85	0.072	3.13	2.60×10^{-4}	12.38	0.081	3.14	5.26×10^{-6}	42.72	0.023
PLA/CNF2	3.10	6.80×10^{-4}	9.35	0.107	3.26	6.51×10^{-4}	8.49	0.118	2.78	3.35×10^{-5}	35.87	0.028
PLA/CNF3	2.59	1.09×10^{-2}	4.99	0.200	3.11	2.45×10^{-1}	1.40	0.716	3.34	1.20×10^{-5}	26.63	0.038
PLA/CNF4	3.53	4.69×10^{-4}	7.92	0.126	3.20	1.39×10^{-3}	6.97	0.144	2.89	3.09×10^{-5}	31.85	0.031
PLA/CNF5	3.44	2.88×10^{-4}	9.64	0.104	3.36	2.88×10^{-4}	10.16	0.098	3.15	1.09×10^{-5}	33.54	0.030
PLA/CNF6	2.94	3.31×10^{-4}	13.45	0.074	3.31	1.55×10^{-4}	12.59	0.079	2.64	5.97×10^{-5}	34.60	0.029

*n = avrami constant, k = crystallization rate constant, $t_{1/2}$ = crystallization half-time, $1/t_{1/2}$ = crystallization rate

Optimum temperature for isothermal crystallization → 100°C

Comparison of PLA/CNF with neat PLA

Sample	Crystallinity (%)	Crystallization half time (min)*	Crystallization rate (min^{-1})	Tensile strength (MPa)	Young's modulus (GPa)
Neat PLA	2.3	92.72	0.011	70.6 ± 0.3	2.9 ± 0.0
PLA/CNF3	44.2	1.40	**0.716**	**74.1 ± 0.5**	**3.3 ± 0.1**

Note: Isothermal melt crystallization was conducted at 100°C

The best!

CONCLUSION

- **Increment in PLA crystallization rate by 65-times** when 3 wt% CNF was added and isothermally melt crystallized at 100°C suggests the **effectiveness of CNF as a nucleating agent for PLA**
- Increased crystallinity of the polymer led to the **increment in mechanical properties.**
- **Dual role of CNF:**

i) **Nucleating agent**

ii) **Reinforcement material**

PHBHHx BIONANOCOMPOSITES

PREPARATION OF PHBHHx/CNF BIONANOCOMPOSITES

Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHHx, Kaneka Corp.)

- **Spray-dried CNF**
- **Nanobiochar**

Melt-compounding & compression moulding

↓

Crystallization kinetic study (non-isothermal and isothermal – Avrami equation)

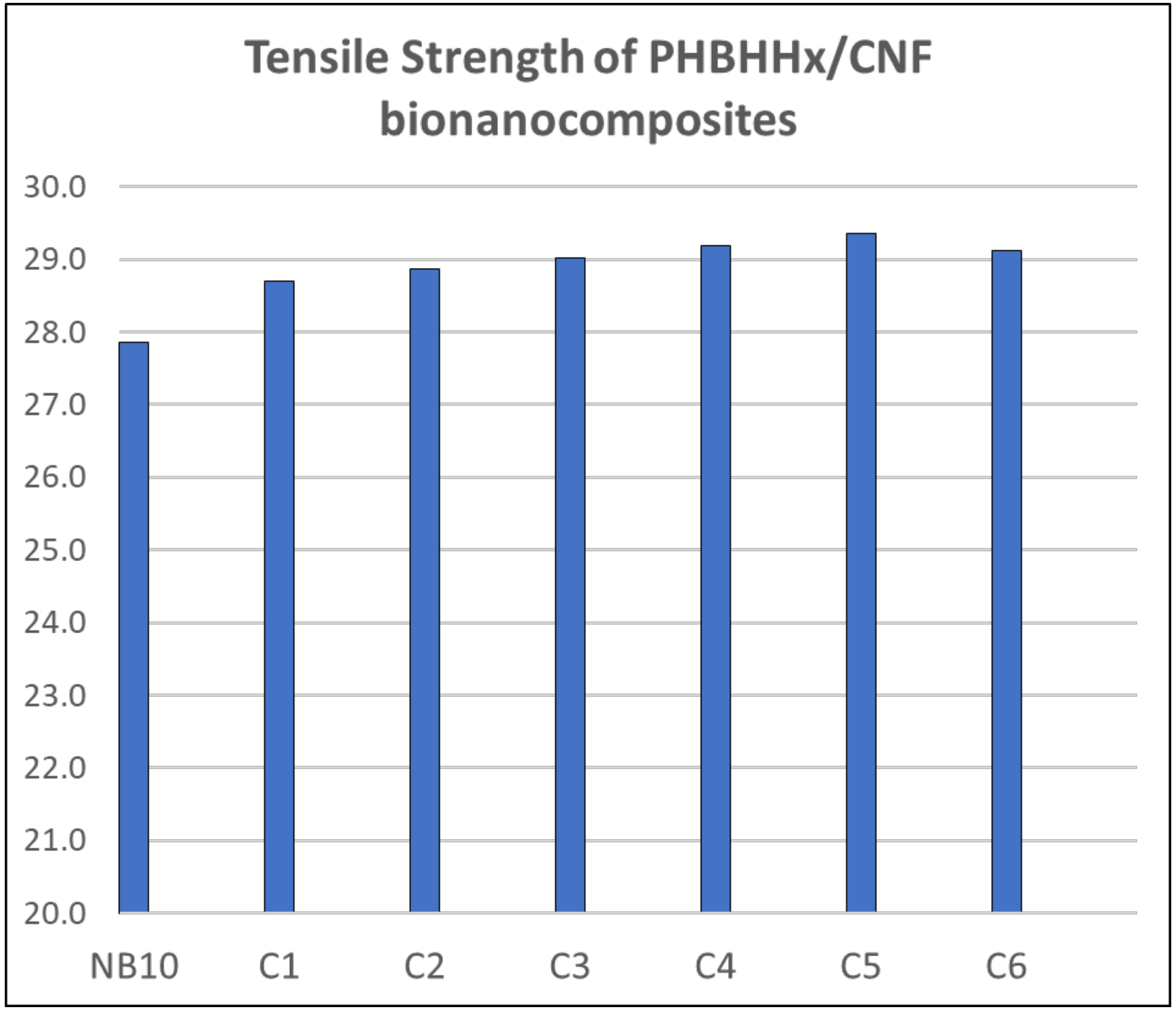
↓

Characterization

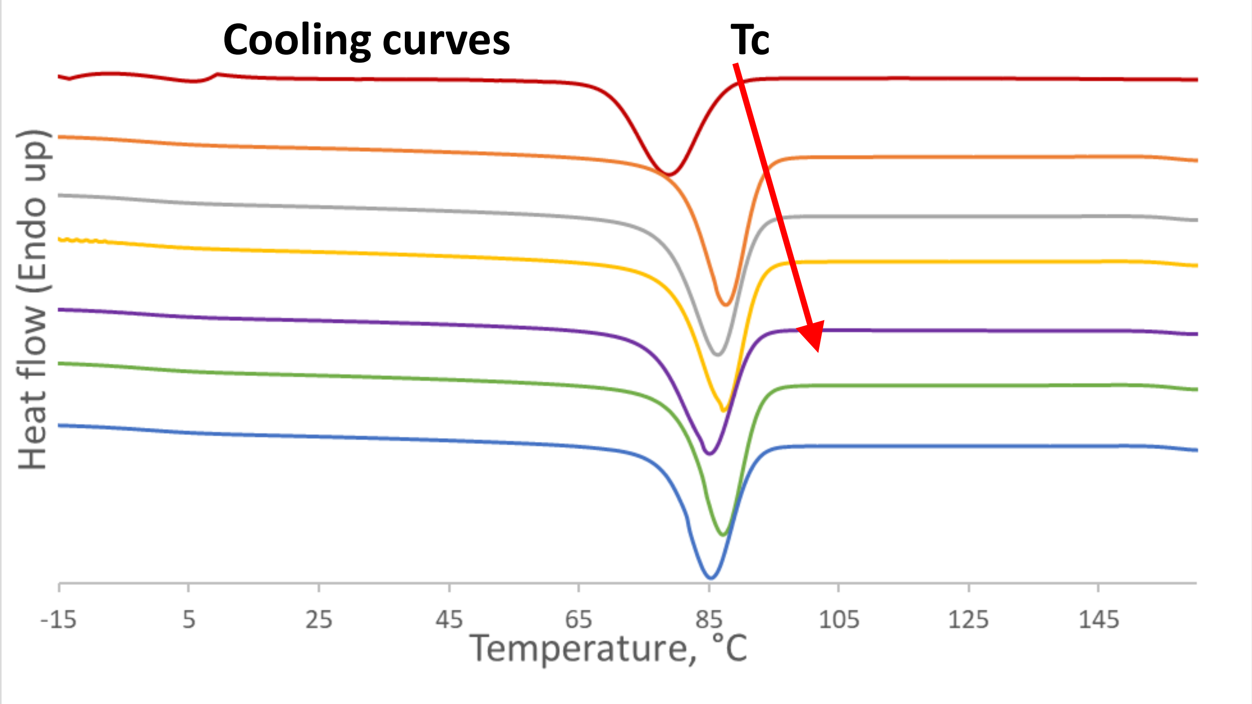
- Mechanical properties
- Crystallite size
- Morphology
- Thermal stability

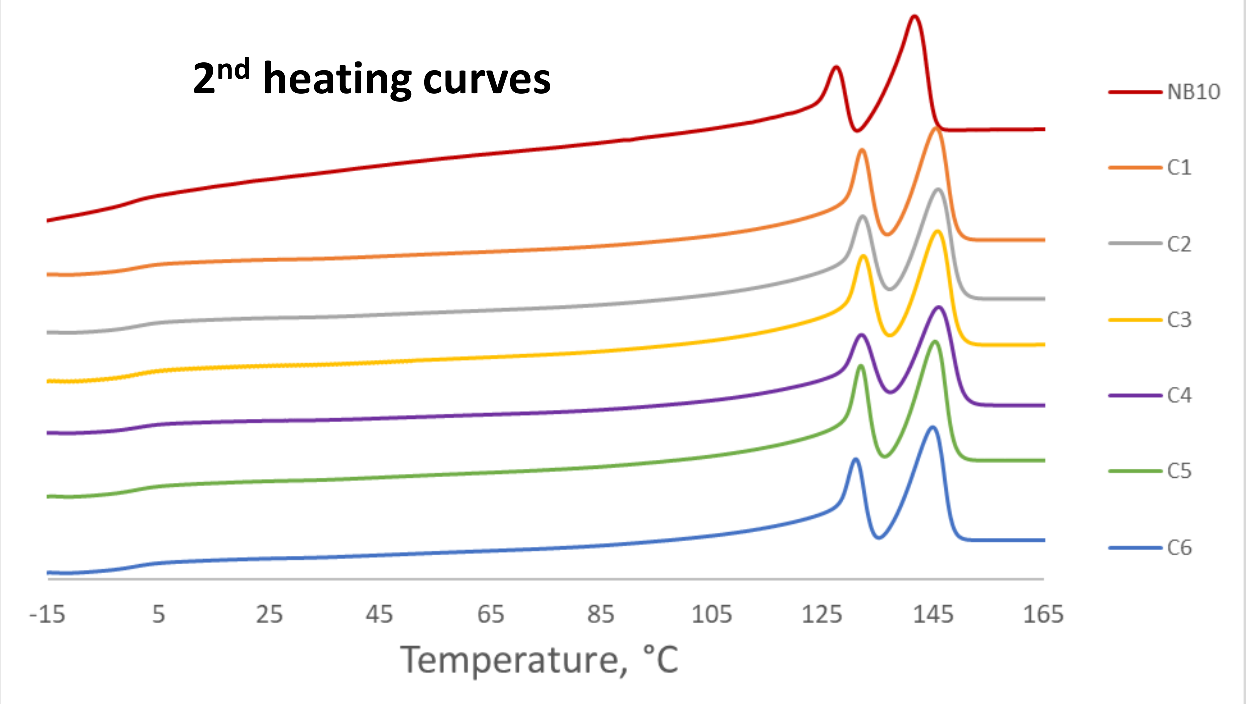
PHBHHx/CNF BIONANOCOMPOSITES: TENSILE PROPERTIES

Sample	Tensile stress at max load (MPa)	Tensile modulus (GPa)	Elongation at break (%)
NB10	27.9 ±0.33	4.8	4.1
C1	28.7 ±0.25	4.8	6.6
C2	28.9 ±0.37	4.8	5.8
C3	29.0 ±0.27	5.0	6.3
C4	29.2 ±0.33	5.1	5.2
C5	29.4 ±0.16	5.3	4.6
C6	29.1 ±0.21	5.4	2.0



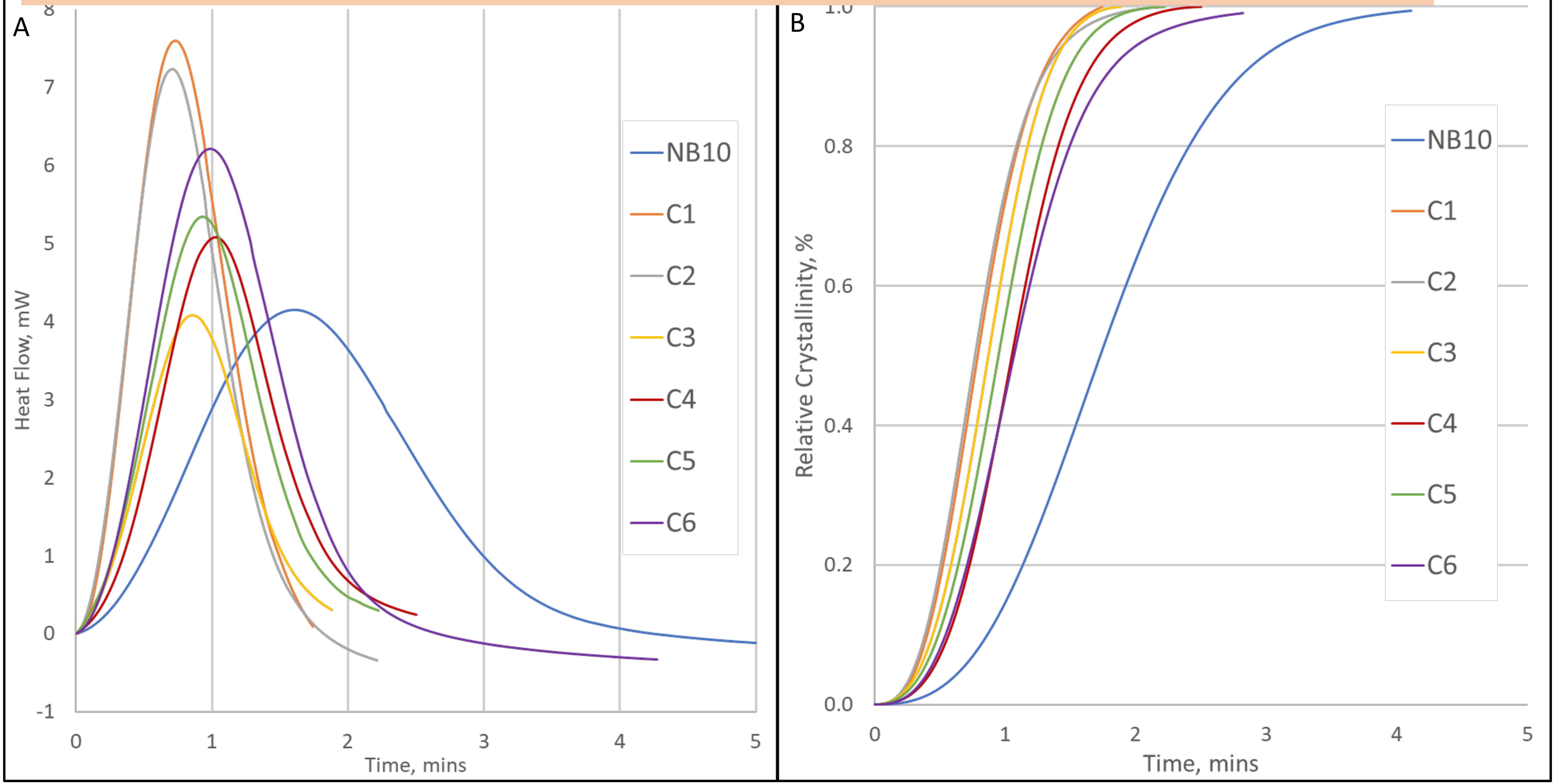
PHBHHx/CNF BIONANOCOMPOSITES: NON-ISOTHERMAL CRYSTALLIZATION





Sample			Neat	C1	C2	C3	C4	C5	C6
Cooling	Tc Onset		95	**98**	97	98	97	98	97
	Peak/°C		79	88	86	87	85	87	85
	ΔH/J/g		38	45	47	46	43	45	41
Heating	Peak 1	Peak/°C	128	132	132	132	132	132	131
		ΔH/J/g	10	19	16	16	12	15	15
	Peak 2	Peak/°C	142	145	146	146	146	145	145
		ΔH/J/g	26	23	23	24	21	25	26
	Total ΔH/J/g		36	42	39	40	34	40	40
	X_c /%		25	29	27	27	23	28	28

PHBHHx/CNF BIONANOCOMPOSITES: ISOTHERMAL CRYSTALLIZATION



PHBHHx/CNF BIONANOCOMPOSITES: ISOTHERMAL CRYSTALLIZATION

Sample	n	k (min^{-n})	$t_{1/2}$(min)	Crystallization rate(min^{-1})
NB10	2.53	0.16	1.79	0.56
C1	2.80	1.24	0.81	1.23
C2	2.52	1.14	0.82	1.22
C3	2.56	1.05	0.85	1.17
C4	2.66	0.59	1.06	0.94
C5	2.56	0.82	0.94	1.07
C6	2.37	0.43	1.23	0.81
C7	2.54	0.18	1.69	0.59
C10	2.68	0.25	1.47	0.68

+120%

+91%

ISOTHERMAL CRYSTALLIZATION: PHBHHX/NBC vs PHBHHX/CNF

PHBHHX/NBC

Sample	n	k (min^{-n})	$t_{1/2}$(min)	Crystallization rate (min^{-1})
NB10	2.53	0.16	1.79	0.56
N1	2.58	0.27	1.44	0.70
N2	2.60	0.47	1.16	0.86
N3	2.67	0.28	1.40	0.72
N4	2.42	0.25	1.52	0.66
N5	2.54	0.28	1.44	0.70

+54%

PHBHHX/CNF

Sample	n	k (min^{-n})	$t_{1/2}$(min)	Crystallization rate (min^{-1})
NB10	2.53	0.16	1.79	0.56
C1	2.80	1.24	0.81	1.23
C2	2.52	1.14	0.82	1.22
C3	2.56	1.05	0.85	1.17
C4	2.66	0.59	1.06	0.94
C5	2.56	0.82	0.94	1.07
C6	2.37	0.43	1.23	0.81
C7	2.54	0.18	1.69	0.59
C10	2.68	0.25	1.47	0.68

+120%

+91%

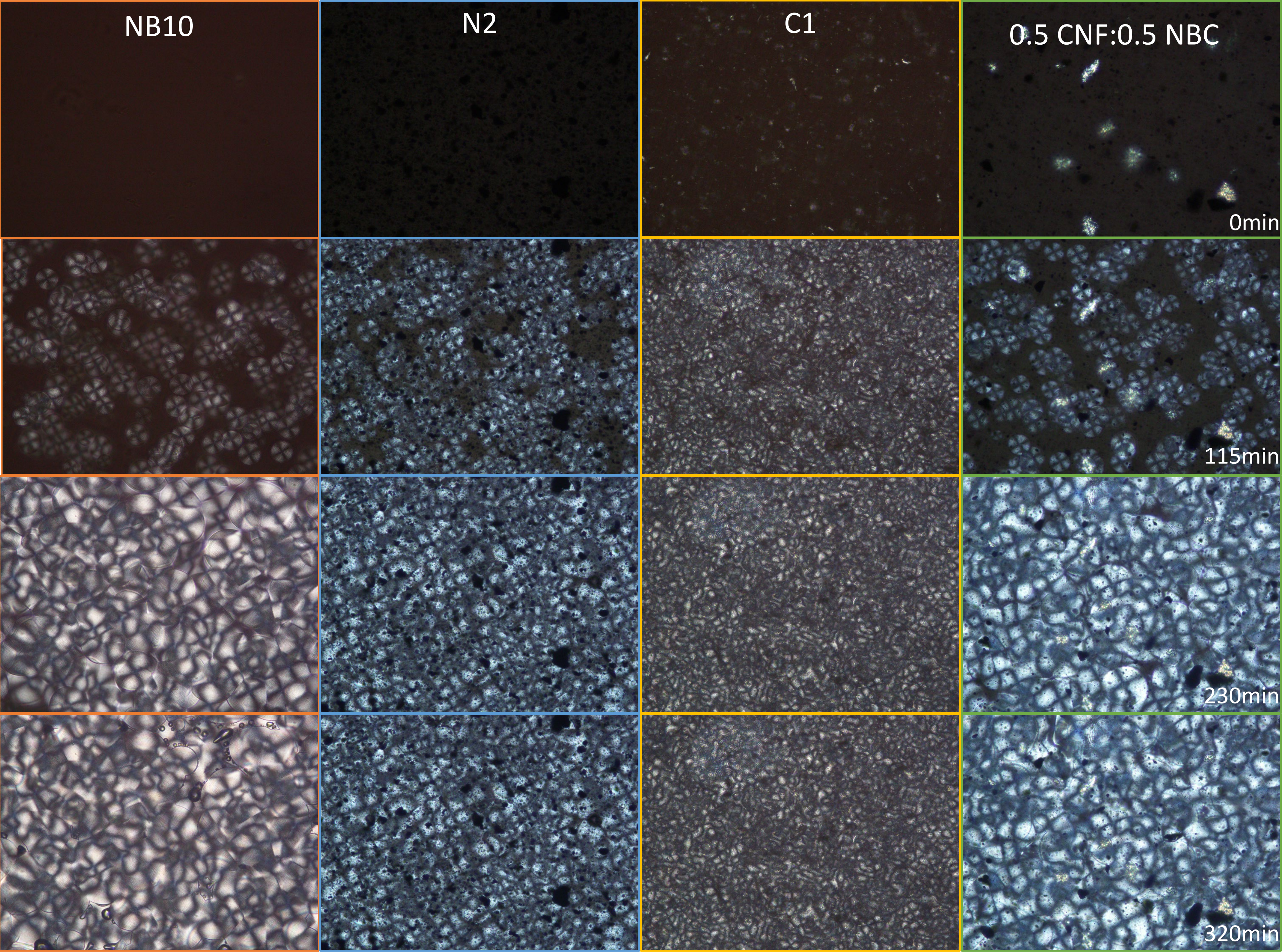


Figure.
Changes in crystallization morphology of (L-R):

- **Neat PHBHHx**
- **PHBHHx/NBC2,**
- **PHBHHx CNF 1**
- **Hybrid PHBHHX/NBC/CNF**

SPHERULLITE MORPHOLOGY, NUCLEATION DENSITY AND CRYSTALLIZATION RATE

Neat PHBHHx

PHBHHx / CNF 1%

170°C Melting, 60 °C Isothermal crystallization

*Video speed increased by 4x

SPHERULLITE MORPHOLOGY, NUCLEATION DENSITY AND CRYSTALLIZATION RATE

Neat PHA

CNF 1%

180°C Melting, 60 °C Isothermal crystallization

*Video speed increased by 6x

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