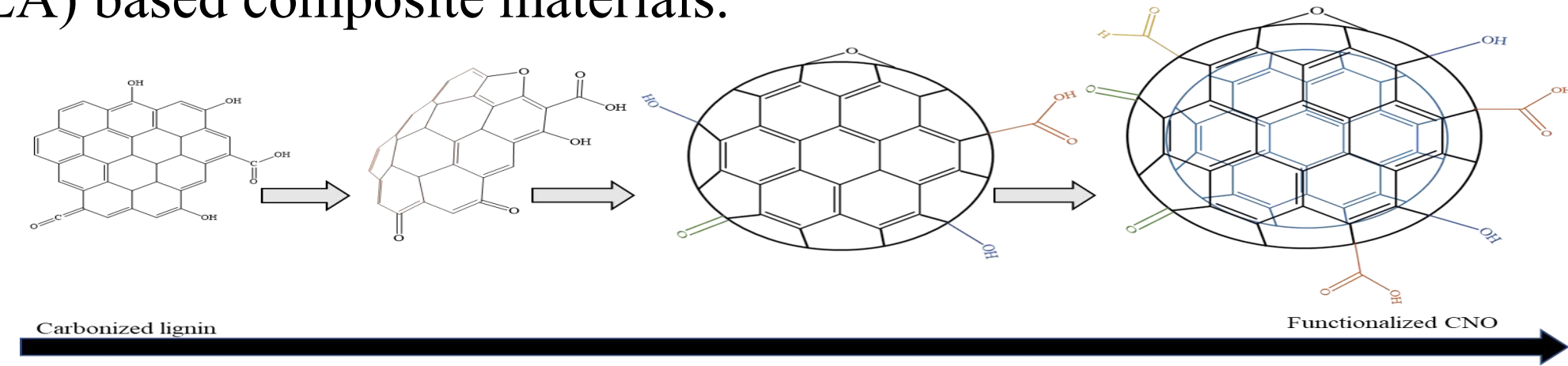


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Oxygenated Carbon Nano Onion (CNO) Fabrication from Biomass for Ultra-high Strength Polylactic Acid (PLA) Composite.

Introduction

- Carbon nano onion (CNO) is a zero dimensional allotropes of carbon characterized by closely packed quasi-spherical and polyhedral graphitic layers, possess unique structural features.
- CNO is a new class of carbon nanomaterials with various applications such as electronics, photovoltaics, polymer additives energy storage, biosensing, biomedicine, and catalysts.
- However, its widespread applications are hindered due to the high costs associated with hydrocarbon precursors and synthesis conditions involving hazardous chemicals, catalysts, non-atmospheric pressures, and prolonged processing time at high temperatures.
- In this work, we report a joule heating-based synthesis of oxygen-functionalized low-cost CNO using biomass residues without catalysts, chemicals, and solvents..
- Also, The CNOs were utilized as fillers in the development of high performance polylactic acid (PLA) based composite materials.



Materials and Methods

CNO Synthesis:

- Organosolv lignin (OL), Kraft lignin (KL), and Biochar (BC) were used as precursor.
- Lignin was water washed and carbonized at 700 ° C for 1hr.
- Joule heating was performed with a maximum voltage and current set at 32 V and 4A.
- TEM, XPS, XRD and Raman was performed to investigate the shape and structure of CNO.

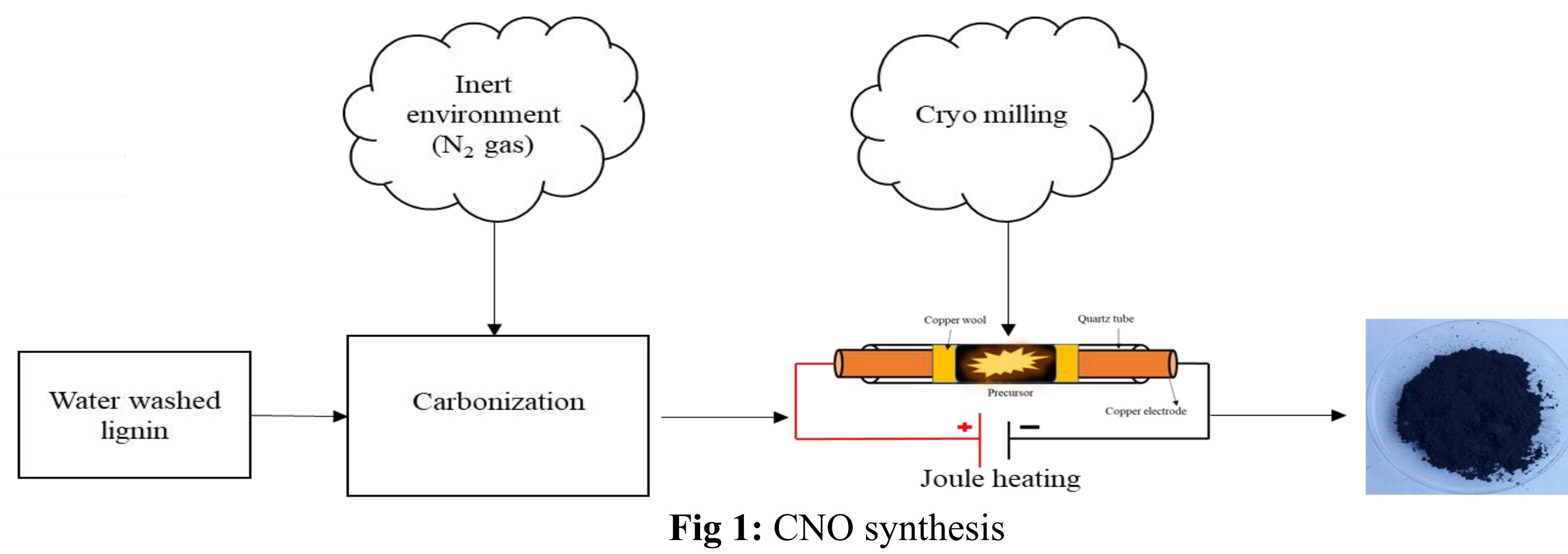


Fig 1: CNO synthesis

PLA/CNO Composite Fabrication:

- Ingeo 2500 HP PLA from NatureWorks was used.
- A solution mixing followed by injection molding process was used to fabricate the composite.
- Tensile, flexural and thermal degradation properties of the composite was determined.
- Interaction of CNO in PLA composites was determined using SEM and FTIR.

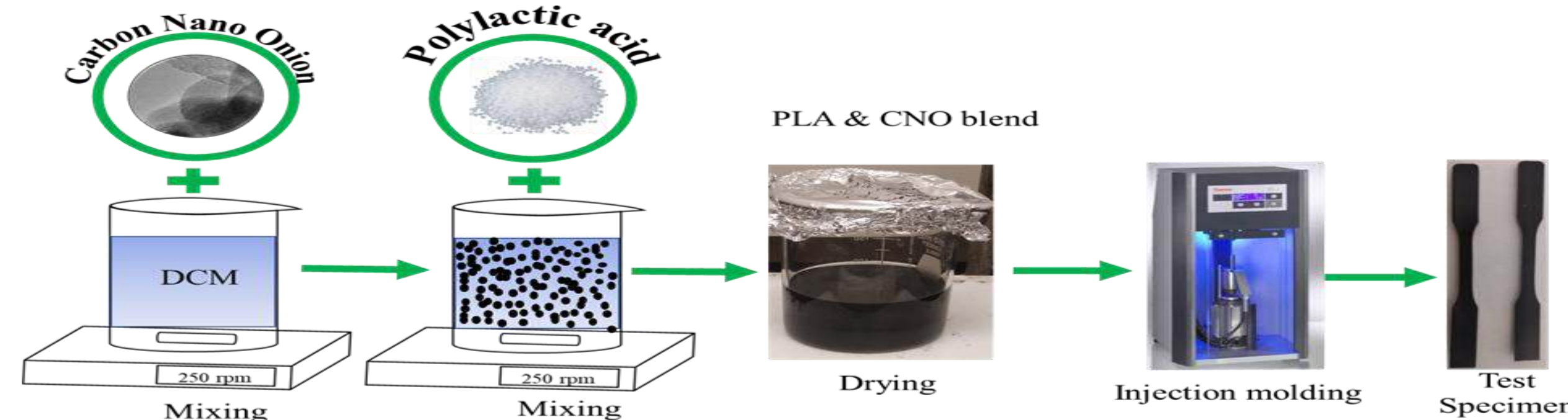


Fig 2: PLA/CNO composite fabrication

Results and Discussion

CNO Characteristics:

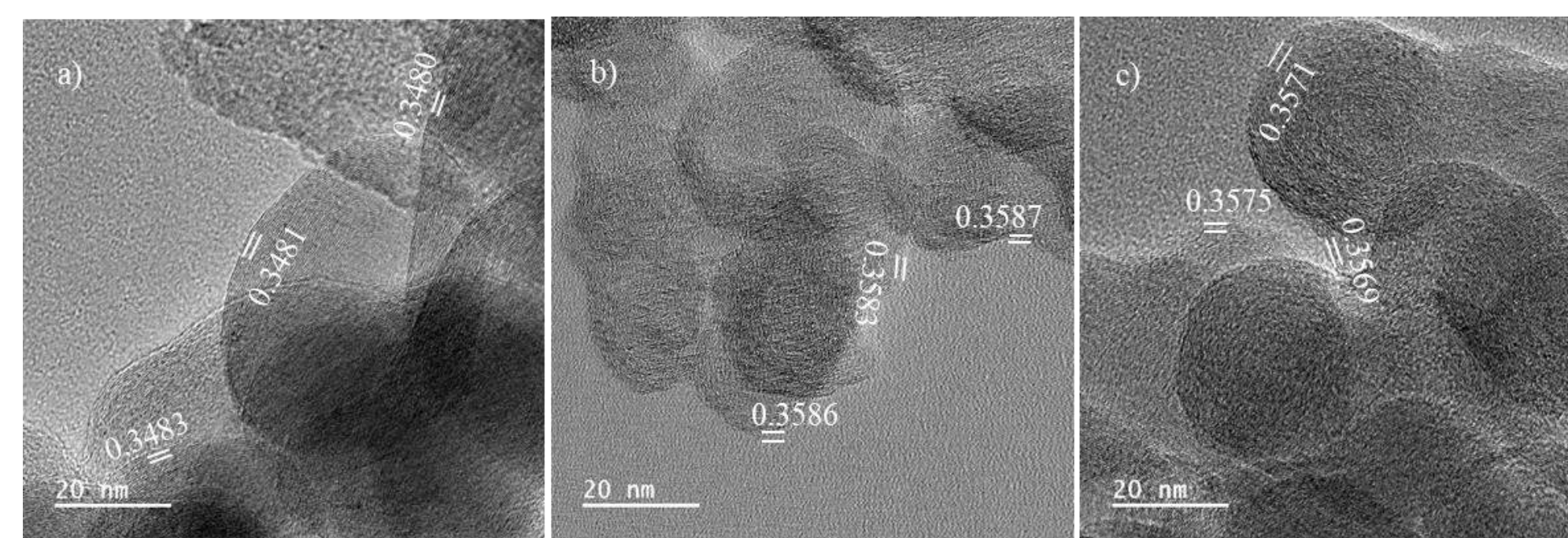


Fig 3: TEM images; a) OL-CNO; b) KL-CNO; c) BC-CNO

Table 1. XRD and Raman results

Sample	XRD			Raman		
	d ₀₀₂ (nm)	L _c (nm)	L _a (nm)	A _D /A _G	I _D /I _G	I _{2D} /I _G
OL-CNO	0.3472	3.57	14.45	0.6	0.52	0.42
KL-CNO	0.3540	2.49	7.95	0.67	0.51	0.45
BC-CNO	0.3545	3.62	12.39	0.77	0.72	0.46

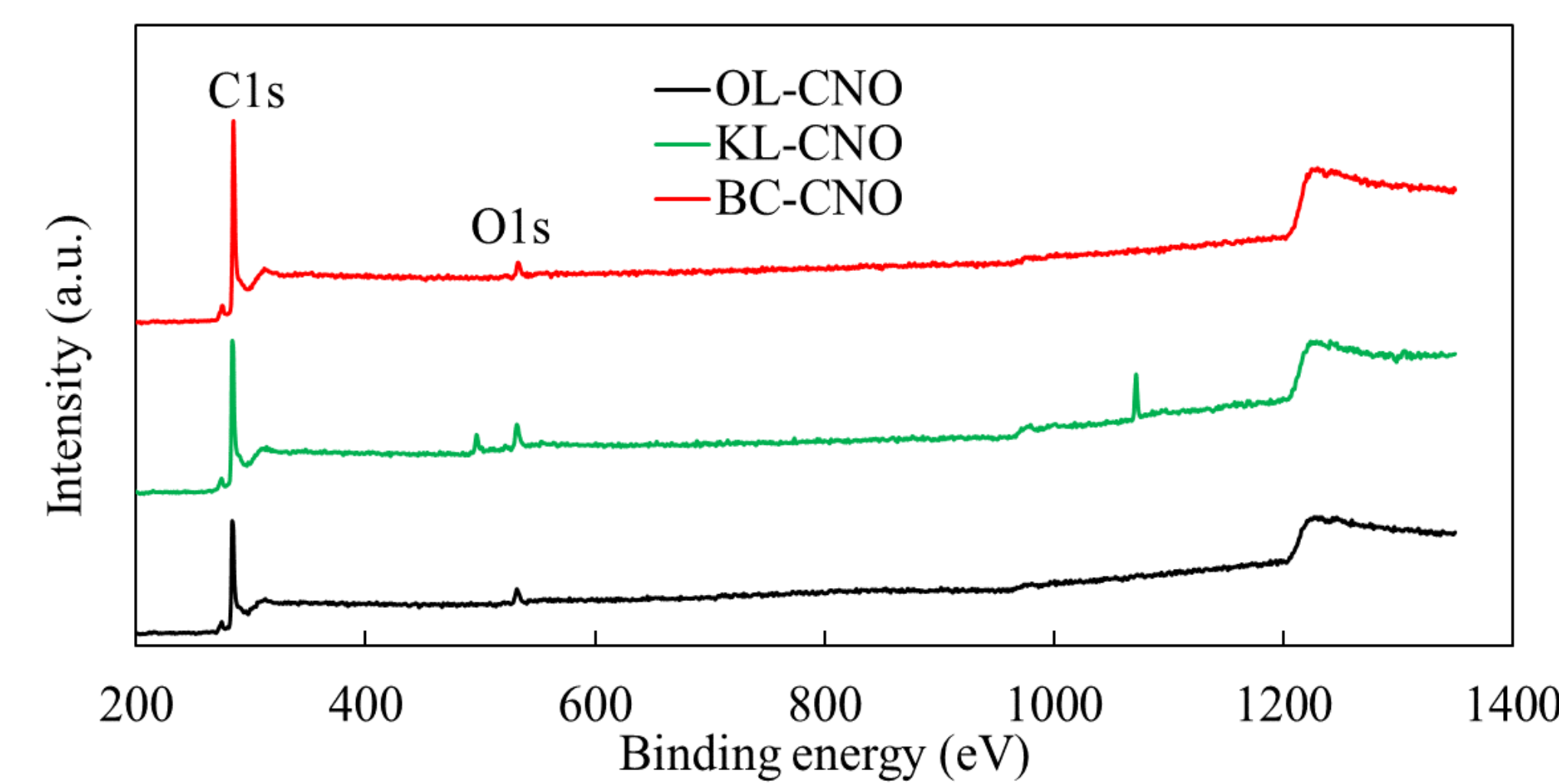


Fig 4: XPS survey scan

Table 2. Deconvoluted C1s peak

Sample	sp ² carbon				
	(%)	-C-O	-C=O	O-C=O	π-π*
OL-CNO	86.52	8.00	2.98	1.53	0.98
KL-CNO	86.86	7.82	2.32	1.64	1.36
BC-CNO	90.24	7.19	1.20	0.83	0.54

- Carbon nano-onion structure was confirmed by TEM images.
- The d₀₀₂ values of CNO were greater than the d₀₀₂ of the conventional Bernal (AB-stacked) graphite (0.337 nm) confirming the formation of turbostratic graphitic CNO.
- Multilayered stacking of the ordered sp² carbon network was confirmed by the presence of 2D band in Raman spectra.
- CNOs contain reactive oxygen-functional groups.
- The nanocrystal size and functional groups of CNO are tunable.

PLA/CNO Composite Properties

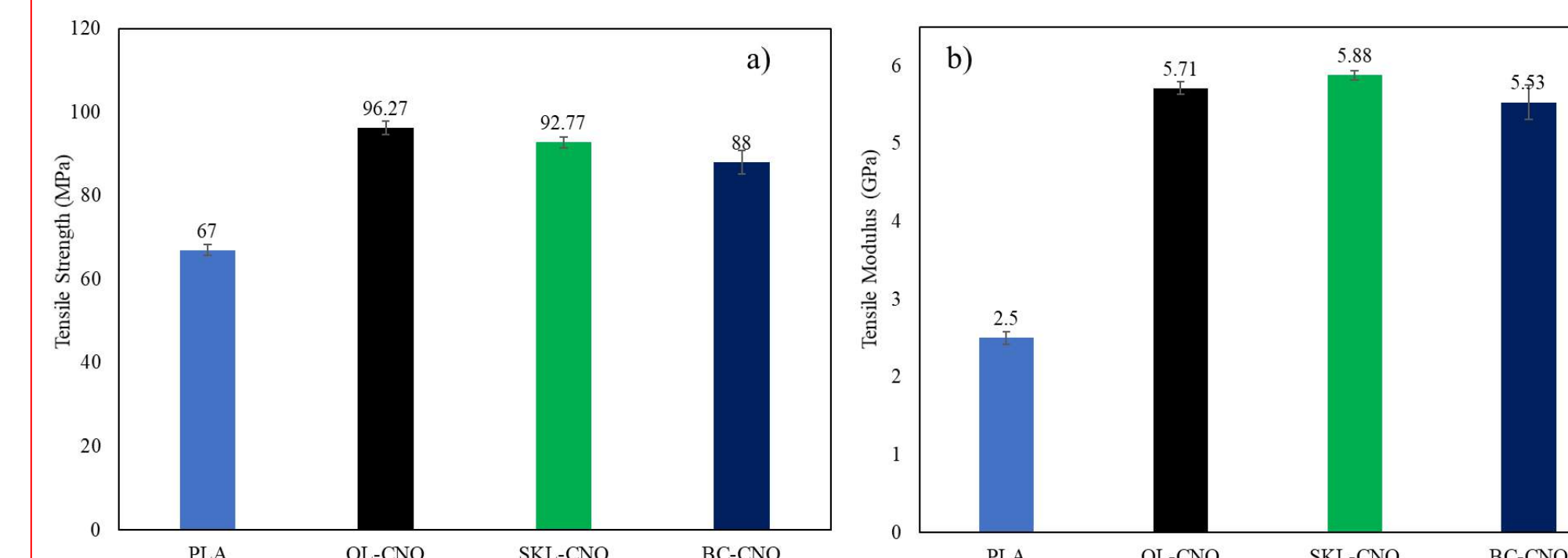


Fig 4: Tensile properties of the composite

Table 3. XRD and Raman results

	Tensile properties		Flexural properties		Impact Strength (J/m)
	Strength (MPa)	Modulus (GPa)	Strength (MPa)	Modulus (GPa)	
PLA	67	2.5	140.3	4.0	24.0
OL-CNO	96.3	5.7	154.2	5.6	38.5
Commercial GNP	90	5.7	135.9	3.7	25.7

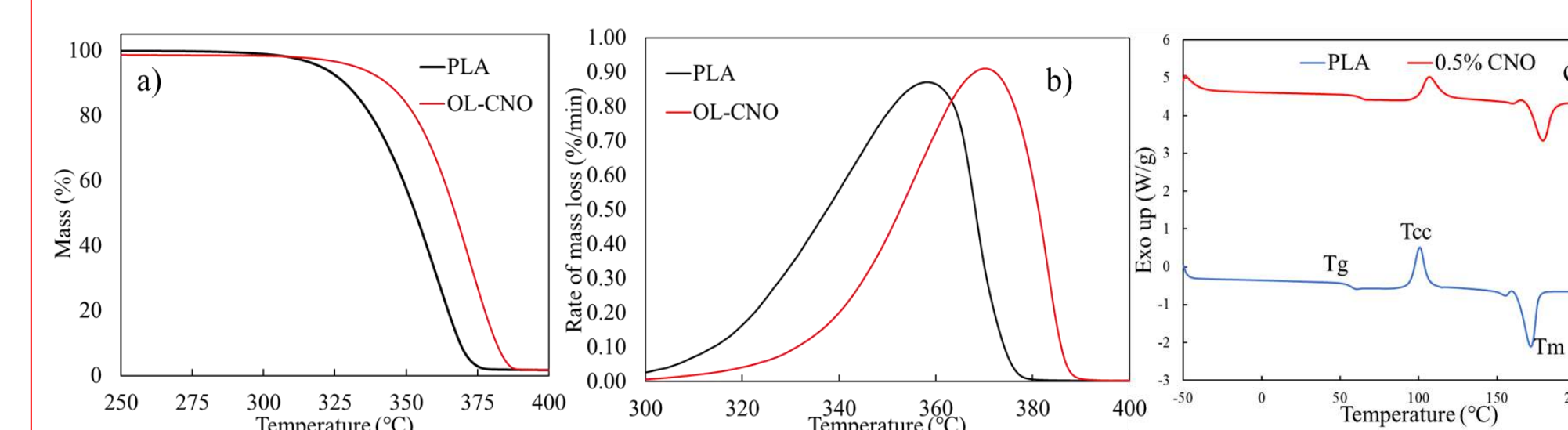


Fig 5: Thermal properties : a) TGA ; b) DTG and c) DSC curve

Table 4. Thermal stability comparison of PLA/CNO composite

Material	T _g (°C)	T _{cc} (°C)	T _m (°C)	T _d (°C)	T _{max} (°C)
PLA	57.1	100.8	171.5	319.0	358.0
OL-CNO	63.4	106.9	179.2	332.7	370.2

Effects of BCNO filler on PLA properties:

- Adding 0.5% CNO resulted in significant increases in tensile and 3-point flexural properties of PLA.
- Tensile strength and modulus of PLA increased by 43.9% and 128.4%, respectively, with 0.5% OL-CNO.
- Flexural strength and modulus increased by 17.2% and 69.6%, respectively, compared to neat PLA.
- Flexural strength and flexural modulus of PLA/OL-CNO were 20.9% and 69.9% higher than that of PLA-graphene nanoplatelets (GNP).
- Impact strength of the PLA/CNO was increased by 60.41% compared to the pure PLA.
- Thermal decomposition temperature and maximum decomposition temperature of the PLA/CNO composite was improved by 13 ° C and 12 ° C respectively compared to pure PLA.
- Glass transition temperature and melting temperature was increased by 6.3 ° C and 6.1 ° C respectively.

PLA/CNO Interaction

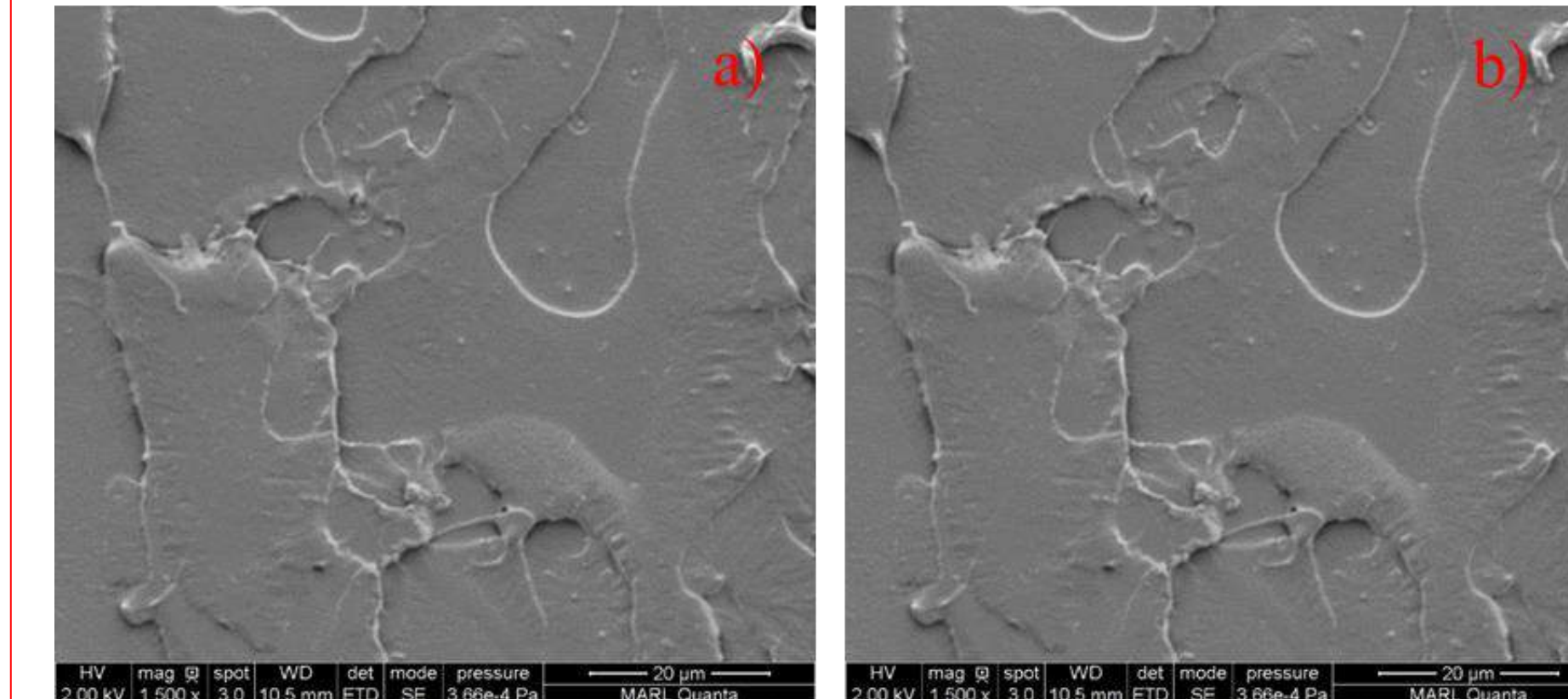


Fig 6: SEM images: a) PLA; b) PLA/OL-CNO

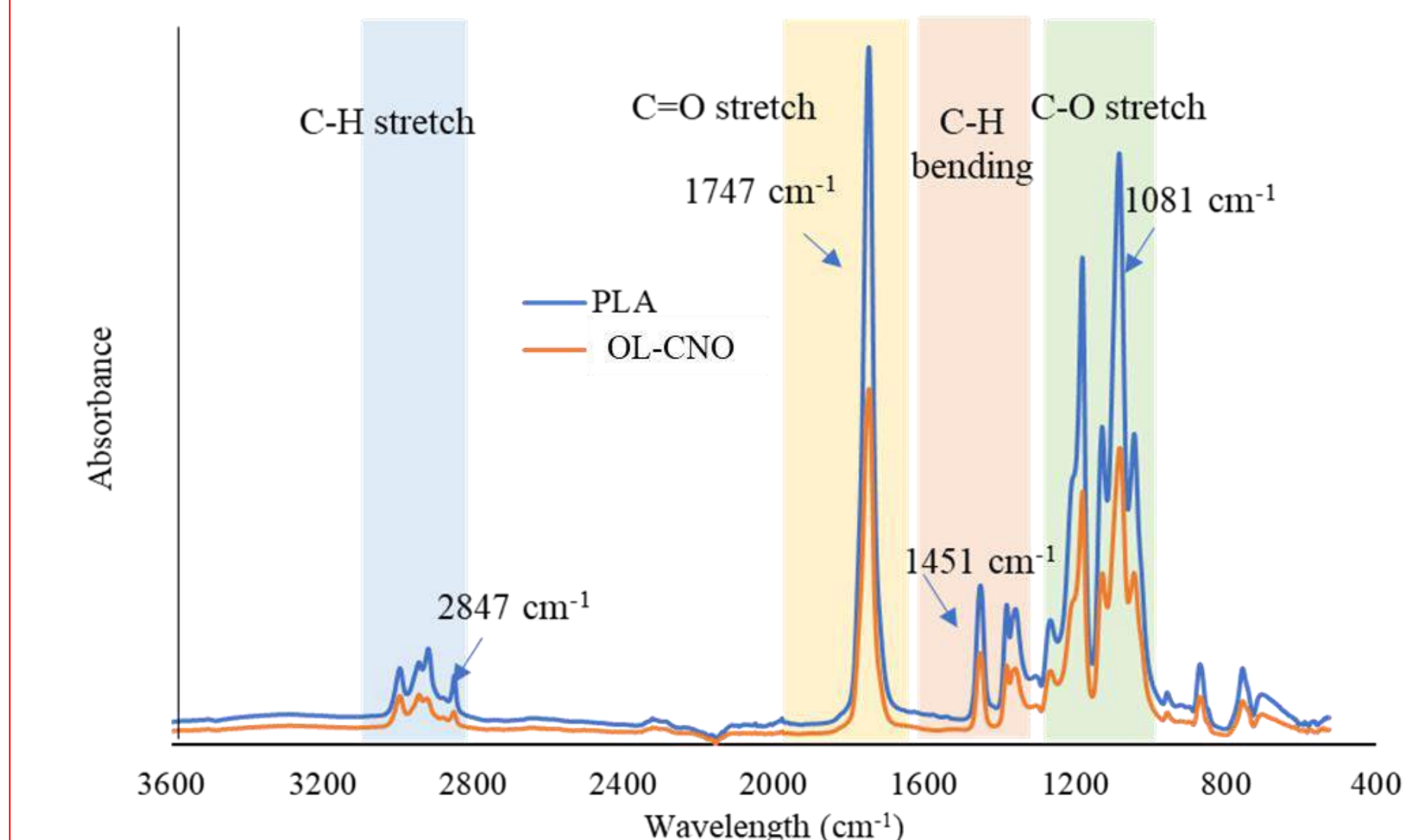


Fig 7: FTIR spectra of the composite

- Agglomerated nanoparticles were nearly not noticeable in the SEM image of the fracture surface of the PLA/OL-CNO tensile bar.
- From FTIR spectra, C-O stretch, C-H bending, and C-H stretch, and C=O stretch decreased noticeably in the PLA/OL-CNO composite compared to PLA.
- The decreased FTIR peak intensities are usually due to increased chemical bonding in the microstructure, requiring more energy to stretch or bend the bonds.
- The SEM and FTIR result confirms strong chemical interactions between PLA and CNO in the composite.

Conclusions

- A robust and low-cost synthesis method was developed to produce property-tunable CNOs using biorefinery residues and biochar.
- Applying CNOs as a low-cost filler in PLA showed dramatic improvement in the mechanical and thermal properties of the composites.
- The evaluation demonstrated that when it comes to enhancing PLA performance, the oxygen-functionalized CNO additive outperforms other commercial GNP.
- The initial results suggest that recyclable, biobased polymer composites with superior performance could be produced at low costs.

Future work

- Developing new biobased composite with biomass, PLA and CNO.