

# INFLUENCE OF SOY HULL BASED BIOCARBON AND GRAPHENE NANOPLAQUELETS ON THE PERFORMANCE OF POLYPROPYLENE BIOCOMPOSITES FOR AUTOMOTIVE APPLICATIONS

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## Abstract

Polypropylene (PP) shows wide usage in the automotive industry, owing to its strength, chemical resistance, and processing ease. The movement away from petroleum-dependence has led to research into sustainable fillers to partly replace the PP matrix, with biocarbon (BioC) being of particular interest. However, this filler commonly diminishes mechanical strength, and to address this the compatibilizer maleic anhydride grafted polypropylene (MA-PP), as well as the nanomaterial graphene nanoplatelets (GnP), were incorporated as a second filler. It was observed that the optimal formulation was PP/17%BioC/3%MA-PP/3%GnP, which led to mechanical and thermal properties beyond that of neat PP. Flexural strength and modulus were raised by around 28 and 59%, respectively, owing to the stiffness of the filler particles and restriction of chain mobility. This restriction in chain mobility had the added benefit of enhancing the heat deflection temperature by 28%, as well as the dimensional stability, as observed through a decrease in the coefficient of linear thermal expansion by around 17% as compared to neat PP. Overall, these biocomposites provide a direction to the improvement of PP properties while simultaneously decreasing its petroleum content, making them ideal for automotive applications.

## Introduction

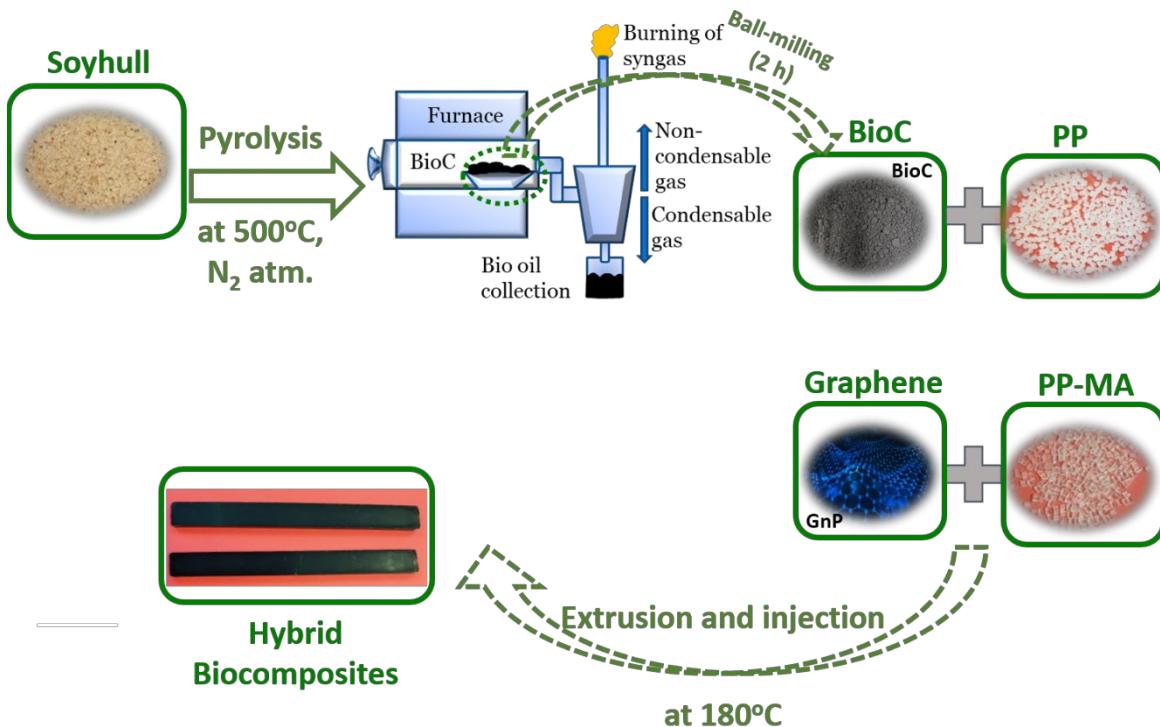
Polypropylene (PP) is widely used in automotive applications due to its chemical and heat resistance, low density, and comparatively strong mechanical properties, with usage in dashboards, bumpers, and hoods [1]. However, PP is a petroleum-based polymer that is typically either discarded at landfills or incinerated and as such contributing to the global issue of climate change [2]. A variety of publications have analyzed the effect of biocarbon (BioC) addition as a biofiller to a PP matrix due to its cost-effectiveness, low density compared to conventional fillers (glass fiber and talc), and ability to increase the biocontent of composites in a petroleum-dominated field [3]. It has been found that high-temperature pyrolysis of waste feedstock to produce BioC is more compatible with a PP matrix, but lower temperatures have improved yield and thus are more realistic for industrial applications [4,5]. This biofiller commonly leads to drops in mechanical strength, but its high thermal stability can be seen to enhance the thermal properties of PP composites [4,6].

To account for worsened adhesion between the PP matrix and BioC, the compatibilizer maleic anhydride-grafted-polypropylene (MA-PP) has been found to be efficient [7,8]. To further restore any lost mechanical strength of the composites, incorporation of nanofillers like graphene nanoplatelets (GnPs) have received increasing attention [9-11]. GnPs lack the presence of functional groups, making them compatible with nonpolar PP matrices, as demonstrated through a study by Jun et al. [9]. This study found that smaller particle diameters ( $< 15 \mu\text{m}$ ) had improved dispersion within the matrix, leading to stronger stress transfer interactions. However, this nanomaterial often suffers from agglomeration due to strong  $\pi$ - $\pi$  and *van der Waals* interactions that serves to limit its effectiveness [10].

This study is based on our recent work, which was the first study to characterize PP composites containing both BioC and GnPs [11]. The goal of this research was to develop cost-effective composites at an elevated bio content that enhanced the mechanical and thermomechanical properties beyond that of neat PP. It is expected that the hybridization of BioC's thermal stability and the mechanical strength of GnPs have the potential to accomplish this. A brief characterization of the soy hull BioC has been performed, along with the morphological (SEM and TEM), mechanical (flexural properties), and thermomechanical characterization of the fabricated composites.

## Experimental

The process of biocomposite fabrication has been outlined in Scheme 1. The PP (grade PP1350N) was purchased directly from Pinnacle Polymers (USA), while MA-PP (Fusabond P353) was purchased from Dupont (USA), and the GnPs (grade M5) were purchased from XG Sciences Inc. (Lansing, MI, USA). The biocarbon powder was prepared through pyrolysis of soy hull (supplied by Nieuwland Feed, Drayton, ON, Canada) at  $500^\circ\text{C}$  with a heating rate of  $7.5^\circ\text{C}/\text{min}$  and residence time of 1 h in a GLO Carbolite 10/11-1G pyrolyzer with an inert nitrogen atmosphere. Following pyrolysis, the biocarbon was collected and ball-milled for a total of 2 hr. Materials apart from the hydrophobic PP pellets were dried prior to pyrolysis, and then mixed according to the specified composite formulation. This material then underwent extrusion and injection using a Micro-compounder DSM (Netherlands) at  $180^\circ\text{C}$  to fabricate flexural bars conforming to ASTM D790 standards. These fabricated composites then underwent mechanical and thermomechanical testing to examine their material properties. Thermogravimetric analysis coupled to Fourier transform infrared spectroscopy (TGA-FTIR) was applied under inert gas ( $\text{N}_2$  gas) with a heating rate of 20  $\text{ml}/\text{min}$  for soy hull powder, using a TA 5500 connected to a FTIR Nicolet iS20 from Thermoscientific, USA. Scanning electron microscopy (SEM) of the cryofracture samples was accomplished using a SEM Desktop Phenom ProX Microscope (Netherlands) at 15 kV. Transmission electron microscopy (TEM) of the hybrid composite was analyzed using a TEM 2010F Joel Microscope at 200kV. Heat deflection temperature (HDT) measurements of the composite samples were performed with a load 0.455 MPa using TA Instruments (TA Q800) according to ASTM 648 standard. The coefficient of linear thermal expansion (CLTE) of the PP composite samples were analyzed in the flow direction (FD) with a force 0.05 N and heating rate of  $5^\circ\text{C}.\text{min}^{-1}$  using TA Instruments (TA Q400).



*Scheme 1: Preparation of PP hybrid biocomposites.*

## Results and Discussion

### TGA-FTIR analysis of Soy hull gases

To determine the environmental impact of the pyrolyzed BioC for industrial-scale applications, TGA-FTIR analysis was conducted to examine the release of volatile compounds. The gas products start to evolve at around  $253^{\circ}\text{C}$  and finished at around  $600^{\circ}\text{C}$ , as observed in Figure 1. The major volatile shifts identified included water/alcohols, hydrocarbons, carbon monoxide, carbonyl compounds, ether compounds, and carbon dioxide. The strongest absorption peak correlated to carbon dioxide, which constituted over 64% of the released volatiles during the pyrolysis process. There were other minor contributions by carbonyl compounds (~15%), ether compounds (~8%) and water/alcohols (~6%). A promising aspect for the usage of soy hull feedstock is that carbon monoxide emissions from the pyrolysis process are very low (~1%).

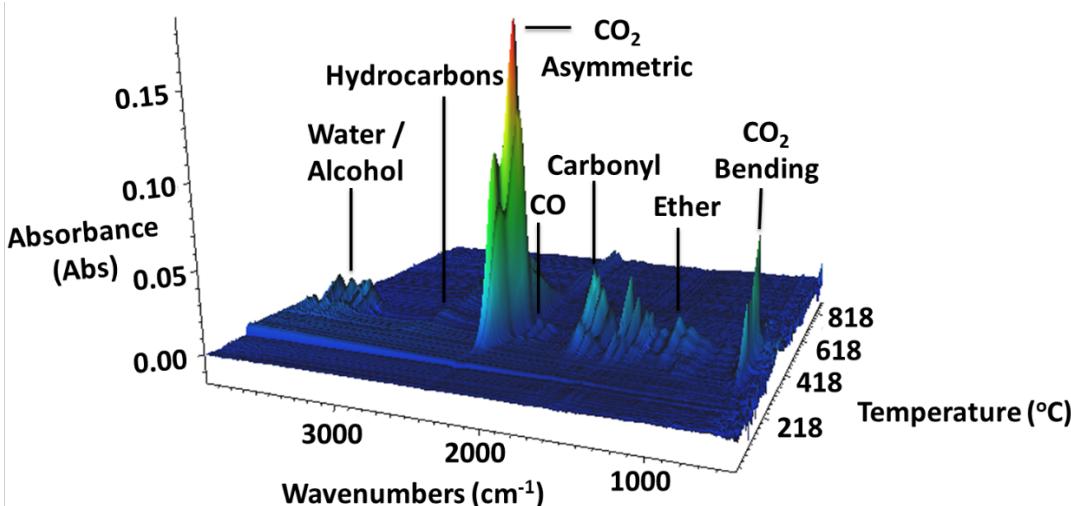


Figure 1: TGA-FTIR generated soy hull 3D surface plot, with relevant released volatile compounds indicated [11].

## Composite Morphology

To examine the effect of filler addition on a PP matrix, scanning electron microscopy (SEM) analysis was employed to image the cryo-fracture interface. As expected, based on previous studies, the addition of 20 wt.% BioC in Figure 2a showed clear signs of phase separation and post-fracture particle pull-outs. This arose due to an absence of interactions between the polar BioC filler and non-polar polymeric matrix, and was partly recovered via compatibilizer incorporation, as identified in Figure 2b. It was determined based on mechanical and thermomechanical characterization that the optimal GnP incorporation was at 3 wt.%, with a composite formulation of PP/BioC/MA-PP/GnP at loadings of 77/17/3/3 wt.%. This composite is visible in Figure 2c, and due to the 6-8 nm thickness of individual GnP layers, the identified graphene layers constitute a multitude of stacks that appeared poorly dispersed within the PP matrix. This agglomeration was attributed to intermolecular forces and residual moisture content within the nanomaterial. However, due to the nanoscale of this filler, it is more appropriately characterized through transmission electron microscopy (TEM), as in Figure 2d. This further reinforced the outcomes seen through SEM imaging, where agglomeration of nanoplatelets were recognized.

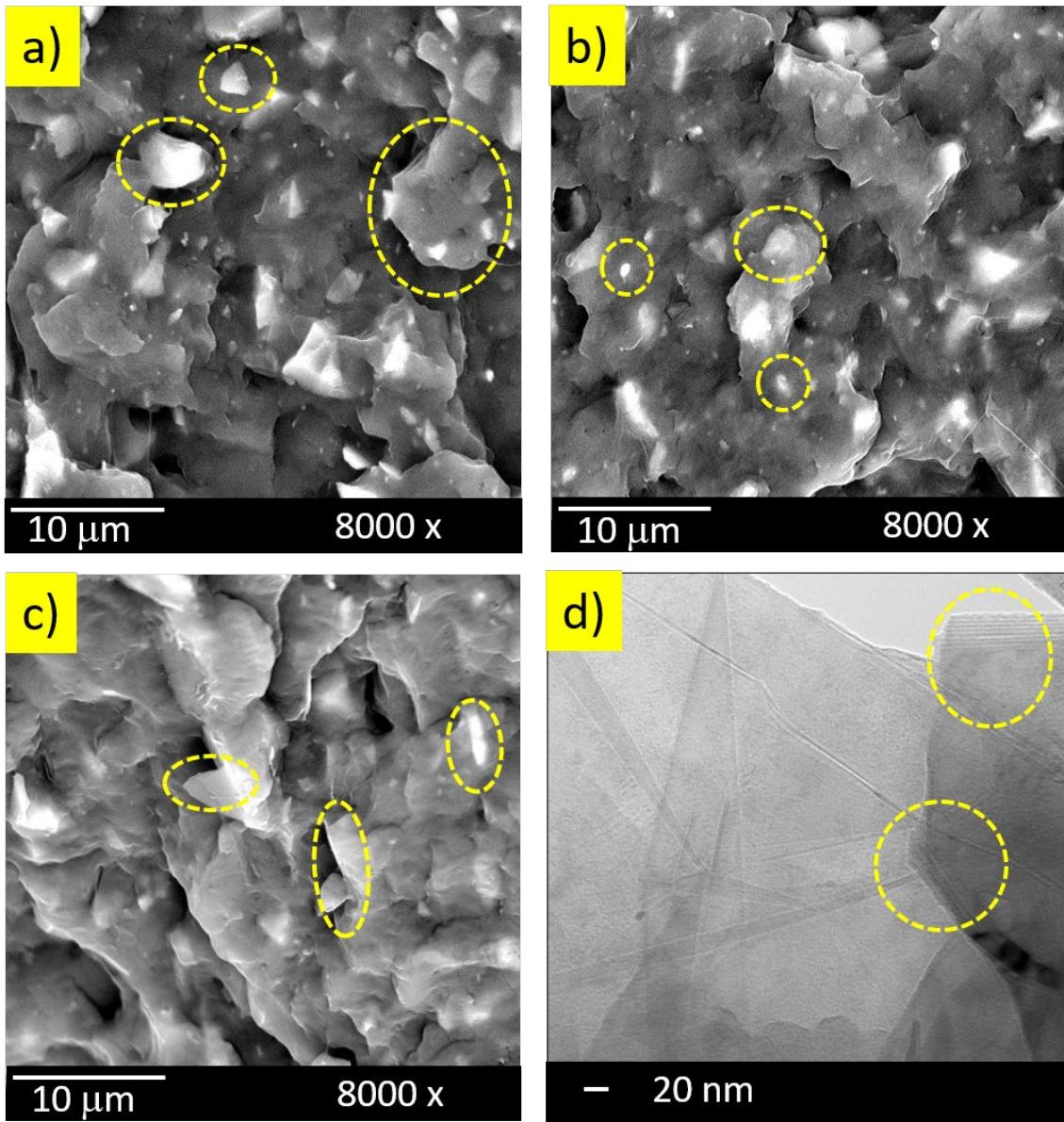
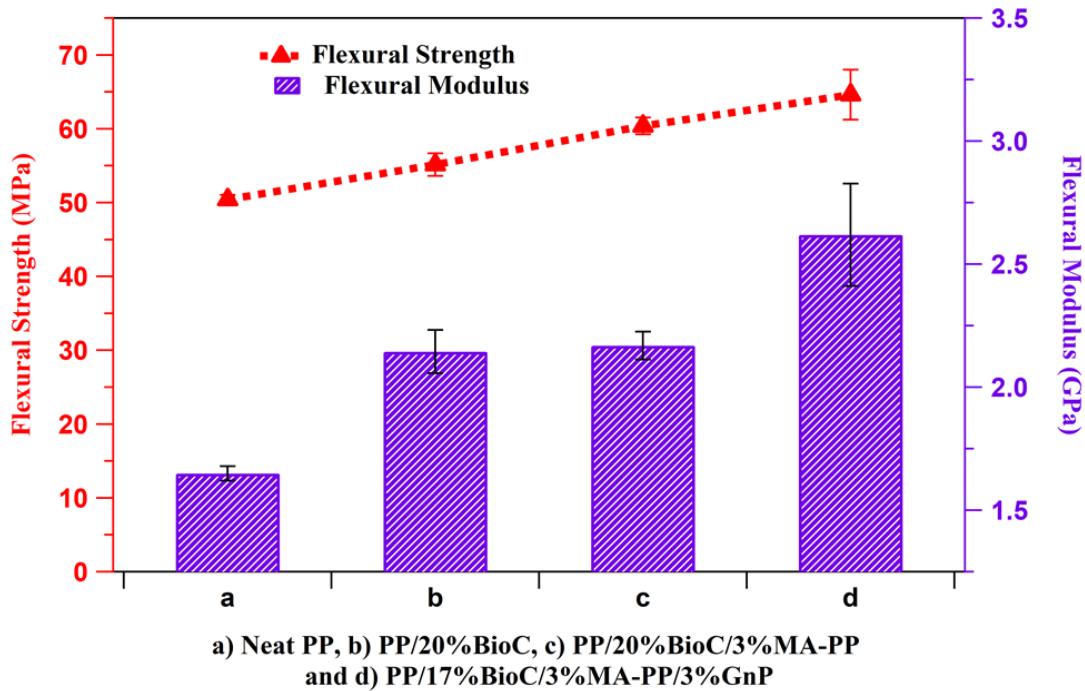


Figure 2: SEM micrographs of cryo-fractured composites: a) PP/20%BioC, b) PP/20%BioC/3%MA-PP and c) PP/17%BioC/3%MA-PP3%GnP. d) TEM micrographs of PP/17%BioC/3%MA-PP3%GnP [11].

## Flexural Properties

Flexural properties of neat PP and the fabricated biocomposites can be seen in Figure 3. Surprisingly, it was observed that the addition of BioC led to an improved flexural strength, unlike tensile strength as observed in a previous study [11]. Compatibilizer addition led to an increase in flexural strength due to improved bonding within the matrix, which can resist elastic deformation. Even a minor addition of GnP led to a comparatively large increase in strength. These improvements in flexural strength may be due to the stiffness of both the GnP sheets and BioC particles. BioC had the benefit of being well dispersed within the matrix, and its particles aided deformation resistance while under load. In comparison, natural GnPs are far stiffer than

BioC due to their two-dimensional hexagonal lattice structure, meaning even small incorporations serve to enhance mechanical properties [12]. The modulus also saw improvement through filler addition, as the stiff particles restricted mobility of the PP matrix. BioC and GnP have both been seen to have this effect on PP, while MA-PP had little effect on modulus [13,14]. As seen, the fabricated biocomposites have a flexural strength and modulus that has been improved by up to 28 and 59% as compared to neat PP, respectively.

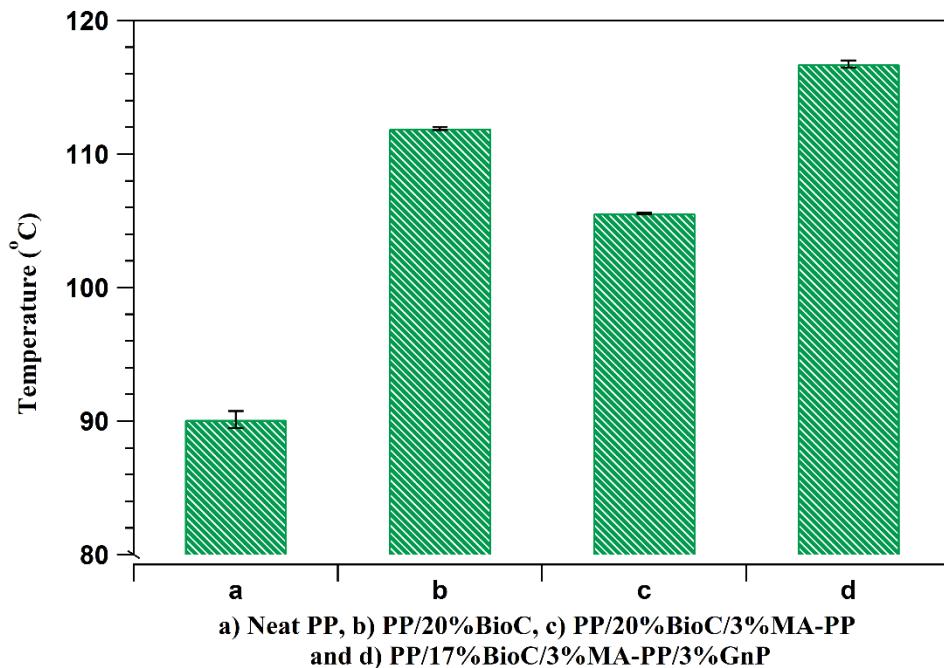


*Figure 3: Flexural properties of PP hybrid biocomposites.*

## Thermomechanical Characterization

### Heat Deflection Temperature (HDT)

HDT, being a description of heat resistance, is an important property for automotive composites as thermal stability must be maintained over extended use in warm environments. The HDT values of all fabricated biocomposites can be observed in Figure 4, and neat PP saw a large increase by 21°C through BioC addition. This derives through PP chain mobility restrictions as deformation is thus hindered, and this effect has been observed elsewhere [6,14,15]. The rubbery nature of MA-PP led to a subsequent decrease in HDT, but was improved through further chain restrictions from GnP addition. This is a very promising property of the biocomposites, with the optimal formulation leading to a 28% increase in HDT.



*Figure 4: HDT of PP hybrid biocomposites.*

## CLTE Analysis

CLTE is another property that indicates dimensional stability of the composites, as it describes how material size changes at varying temperatures. A high CLTE is not desirable in automotive applications. There are two major regions of the CLTE, being glassy (measured from -30 to 30°C) and rubbery (-30 to 100°C) states. As seen in Figure 5, BioC addition (20 wt.%) resulted in a reduction in the CLTE value in the rubbery state by 18.5% as compared to neat PP, which underwent another 7.6% decrease upon GnP inclusion. It can be concluded from this that the well-dispersed BioC particles served to hinder polymeric movement, which supports HDT data and corresponds to findings by other studies [1,13,15]. While not having a major impact in the rubbery state, MA-PP resulted in a minor reduction in CLTE in the glassy state, which was attributed to improvements in bonding between the biofiller BioC and the matrix. GnPs have a naturally low coefficient of thermal expansion and a high surface area, which serves to explain the improvements it had on CLTE [14]. The optimal biocomposite had a CLTE that was reduced by 25% as compared to neat PP, indicating that it has a higher dimensional stability.

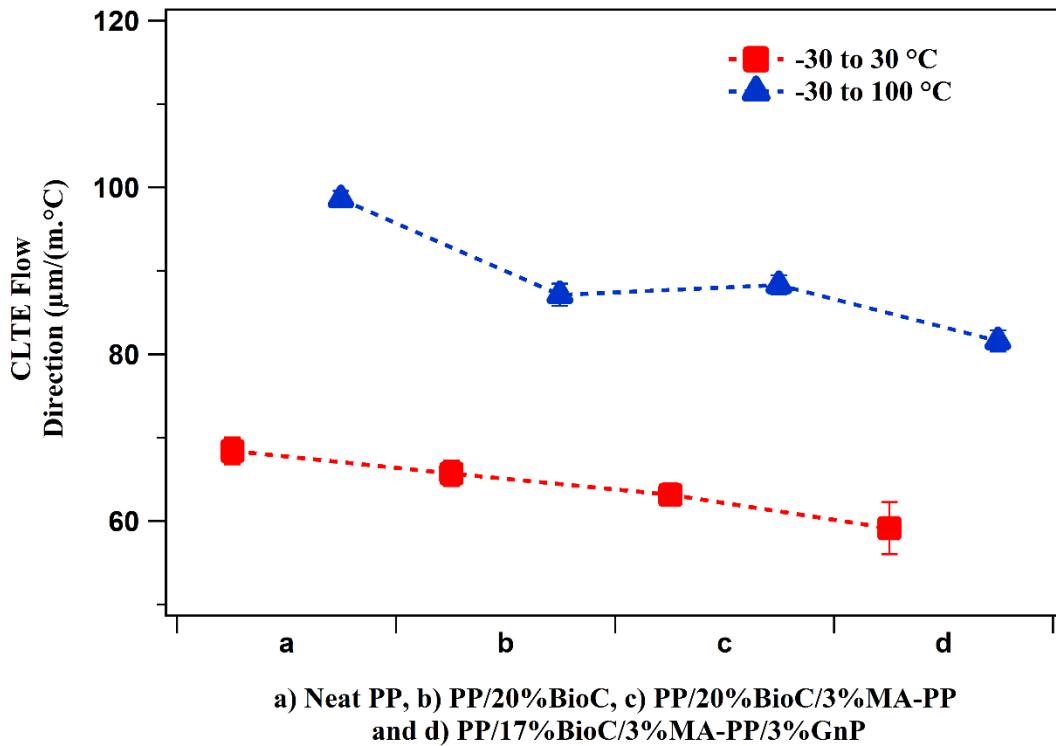


Figure 5: CLTE of the PP hybrid biocomposites in the flow direction.

## Summary and Next Steps

BioC and GnP was successfully incorporated into a PP matrix to form biocomposites, with an optimal formulation of PP/17%BioC/3%MA-PP/3%GnP. Poor interaction between the biofiller and PP matrix was improved through compatibilizer incorporation, while GnPs showed signs of agglomeration due to intermolecular forces. Despite this, the biocomposites still saw significant increases in both mechanical and thermomechanical properties. Flexural strength and modulus improved beyond neat PP by 28 and 59%, owing to the stiffness of both BioC and GnP. The chain restrictions imparted through filler addition led to a subsequent improvement in HDT by up to 28%, as well as a stronger dimensional stability as measured through CLTE analysis. These biocomposites show great promise for automotive applications, as they have improved mechanical strength, as well as thermal stability for heat-intensive applications at an elevated biocontent. Based on the results obtained, these composites would benefit through future study on GnP dispersion methods. Agglomeration partially limited the benefits GnPs can provide on both mechanical and thermal properties, and proper dispersion could lead to superior biocomposites.

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