Development of Carrier System for Cellulose Nanofibrils in Polymer Composites

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Outline

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  - *Challenge of using NC in hydrophobic polymer matrices*
  - *Thermoplastic Starch*
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Why Cellulose Nanofibers (NC)?

- ***Low density, low cost, high specific strength and modulus, renewability, biodegradability and availability***
- ***Non-toxicity, easiness to handle, economic development opportunity for non-food farm products in rural areas, high ability for surface modification.***

Table 1. Properties of cellulose compared to engineering materials.

Materials	Density (g/cm^3)	Modulus (GPa)	Modulus/Density
Cellulose	1.5	138	92
E-Glass	2.5	69	28
Aramid	1.4	67	48
Steel	7.8	200	26
Aluminum	2.7	69	26
MWNT	1.75	10000	5714

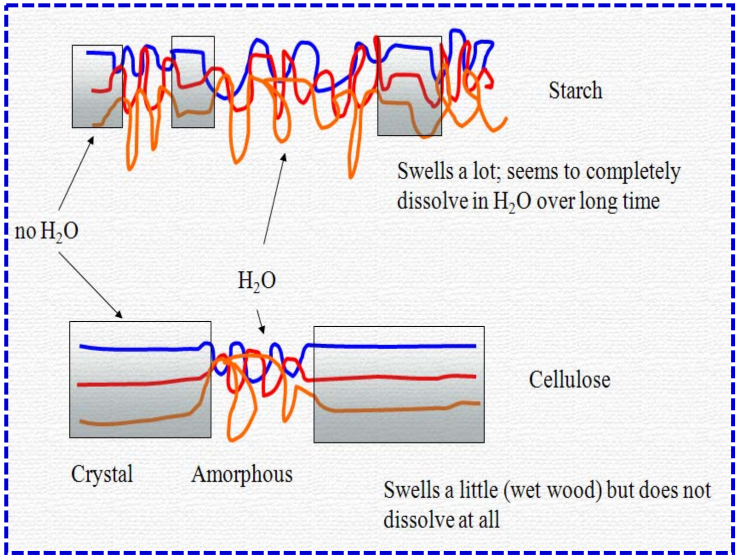
- ***Poor adhesion and dispersion in nonpolar matrix, high moisture absorption***
- ***Limited thermal stability, low permissible temperatures of processing and use.***

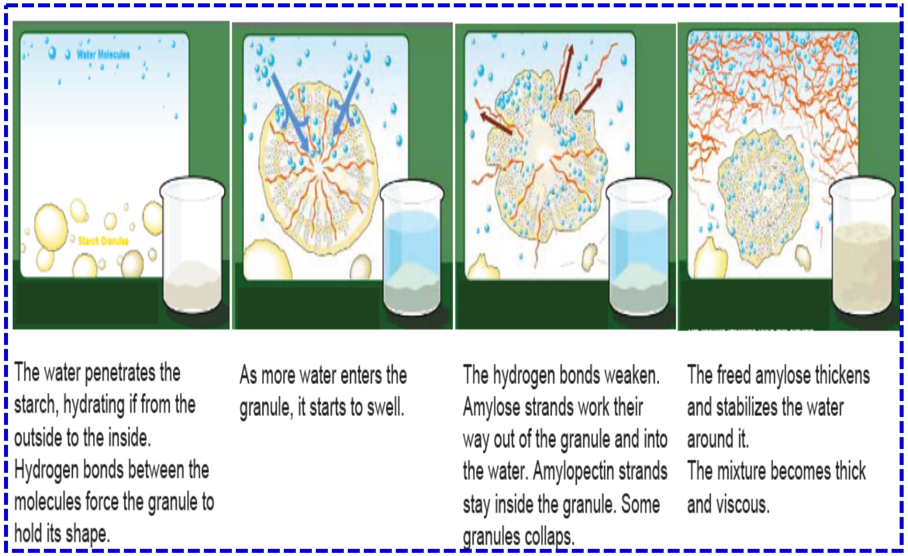
Challenge of Using NC in Nonpolar Matrices

- ***Because of the hydrophilic nature of NC many studies in the literature have focused on nanocomposites based on polar matrices.***
- ***NC cannot be simply added to the polymer melt in thermal compounding processes due to the potential for agglomeration and heterogeneous dispersion.***
- ***The traditional approach to solve this problem is surface functionalization (SF). Reports on SF of cellulose nanofibrils are limited in number and SF of cellulose nanofibrils is also difficult and time consuming.***
- ***To solve this dilemma, NC suspension will be processed with a novel carrier system, using thermoplastic starch, to create compatibility between the NC suspension and a conventional polypropylene matrix.***

Thermoplastic Starch

- ***The literature is confusing and describes thermoplastic, destructurized, gelatinized and plasticized starch.***
- ***Plasticization is the easiest and cheapest way to put technological materials a processable state.***
- ***Structure is overcome with a combination of plasticizer, heat and pressure to get starch into a processable state.***





Our Approach

Base Polymer
(Hydrophobic Matrix)

+

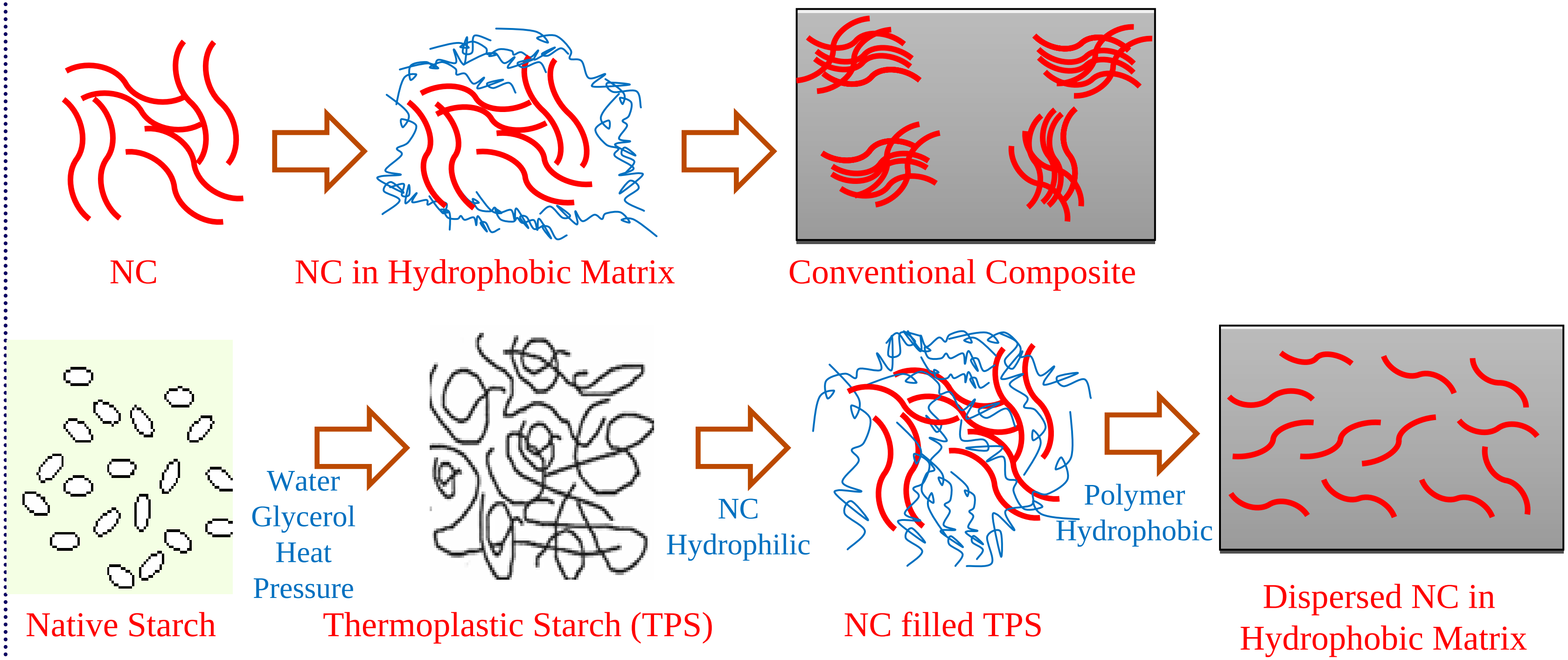
Nanoscale Additive
(Filler, Dispersed Phase NC)

+

Carrier System
(Thermoplastic Starch)

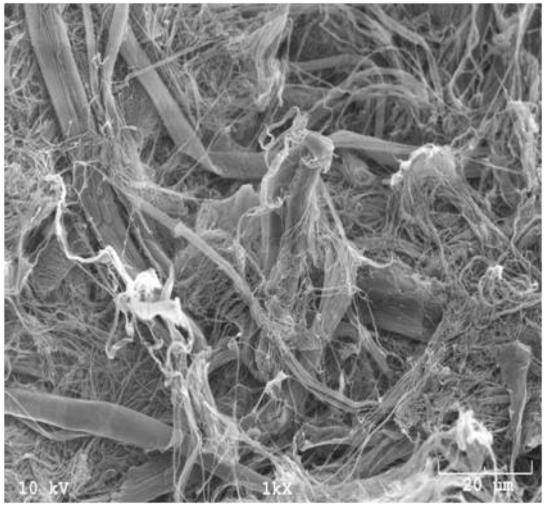
=

Hydrophobic Thermoplastic Composites
with better dispersion and improved properties

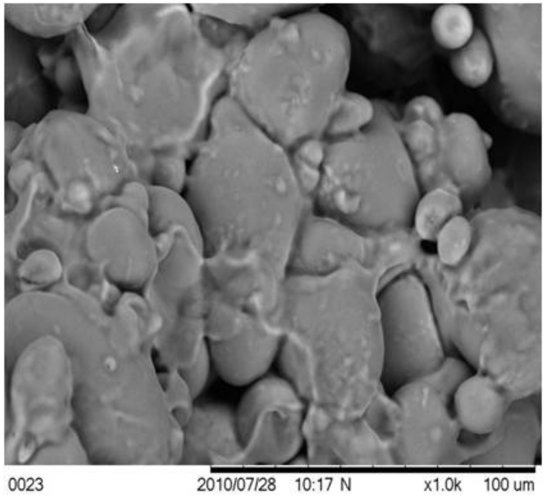


Materials

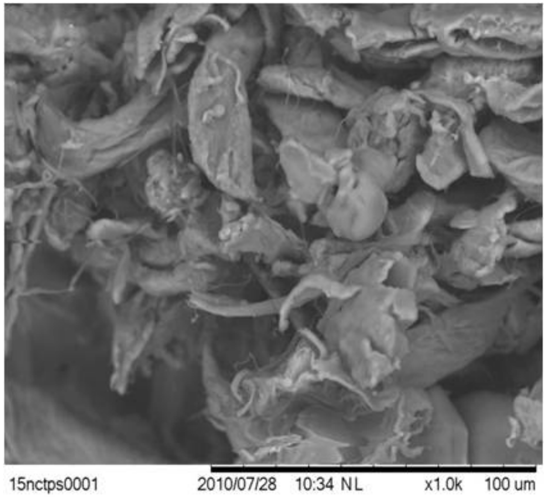
- ***The impact modified polypropylene (IMPP) was supplied as polymer pellets by Polystrand, Inc., USA. The density was 0.9 g/cm3 and the melt flow rate (MFR) was 35 g/10 min (230°C, 2.16 kg).***
- ***NC was supplied by Daicel Chemical Industries, Ltd., Japan. This product consisted of a 35 wt% fiber content slurry.***
- ***The potato starch and the glycerol (99% purity) were purchased from Sigma Aldrich Co., USA and used as received.***



Cellulose Nanofibrils (NC)



Thermoplastic Starch (TPS)



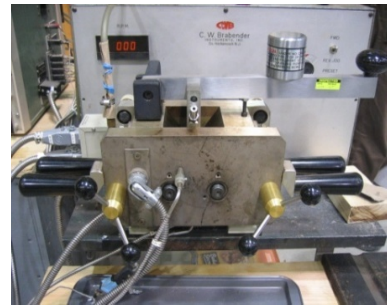
15% NC filled TPS

Formulations

TPS Composition							
Sample Code	Starch	Glycerol	Water	CN	Glycerol/Water	Plasticizer/Starch	Total
TPS	50	15	35	-	0.43	1	100
5NCTPS	47.5	14.25	24.25	14	0.43	1	100
10NCTPS	45	13.5	12.5	29	0.43	1	100
15NCTPS	42.5	12.75	1.75	43	0.43	1	100

Composition of Composites						
Sample Code	PP	TPS	5NCTPS	10NCTPS	15NCTPS	Total
Neat PP	100	-	-	-	-	100
PP+TPS	90	10	-	-	-	100
PP+5NCTPS	90	-	10	-	-	100
PP+10NCTPS	90	-	-	10		100
PP+15NCTPS	90	-	-		10	100

Methods-Production



NCTPS
PP

High Speed Mixer

Melt Blend
Brabender

Dry Ground Mixture

Injection Molding

ASTM Test Samples

Experimental Approaches

CELLULOSE NANO COMPOSITES

Mechanical Properties

- *Tensile and Flexural Strength*
- *Tensile and Flexural MOE*
- *Elongation at Break*
- *Notched Izod Impact Strength*
- *Storage and Loss Modulus*
- *Tan Delta*

Thermal Properties

- *Glass Transition Temperature*
- *Melting Temperature*
- *Crystallization Temperature*
- *Crystallinity*
- *Thermal Stability*
- *DTGA Temperature*
- *Residual Mass*

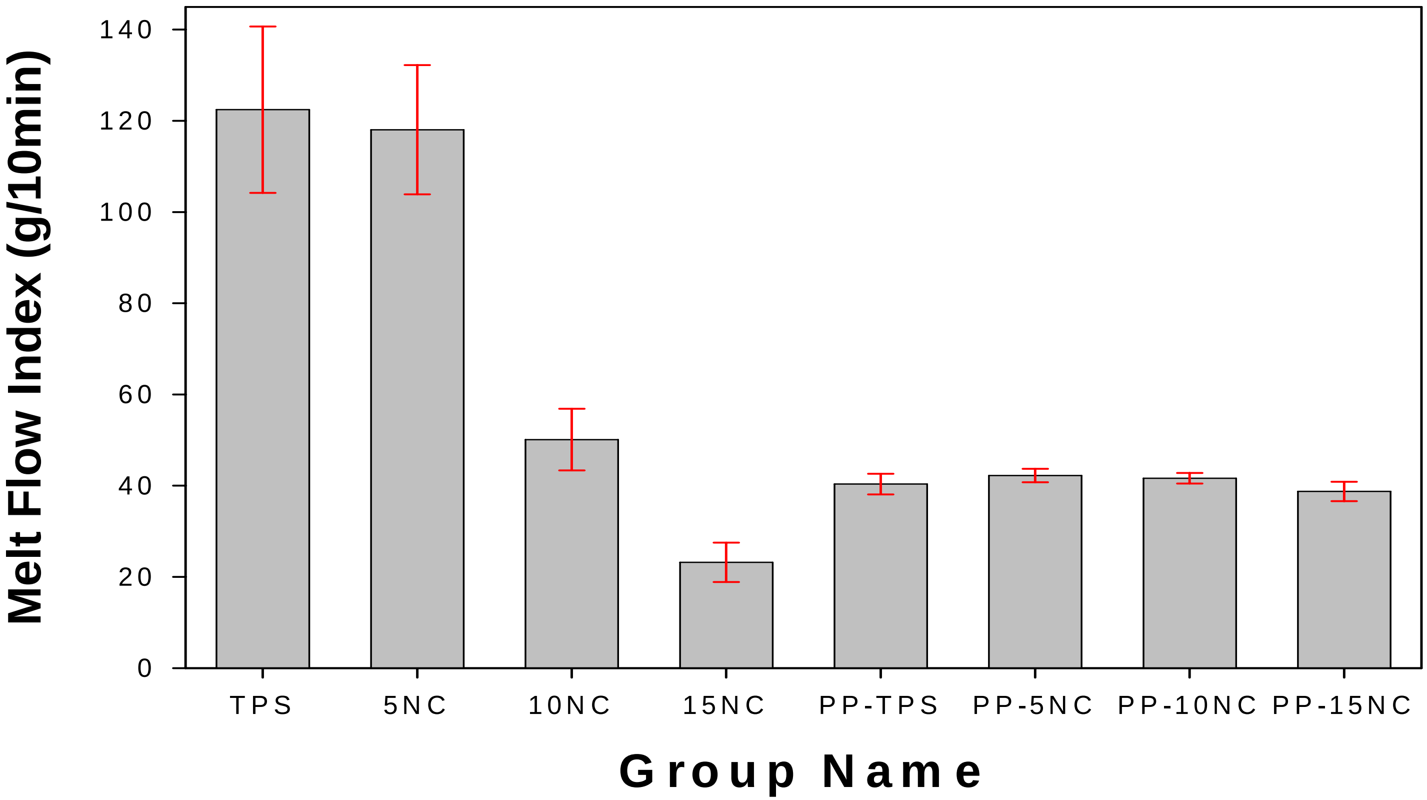
Chemistry& Morphology

- *Surface Topography*
- *Dispersion*
- *Surface Energy*
- *Interaction*
- *Adhesion/Cohesion Ratio*

Rheology and Density

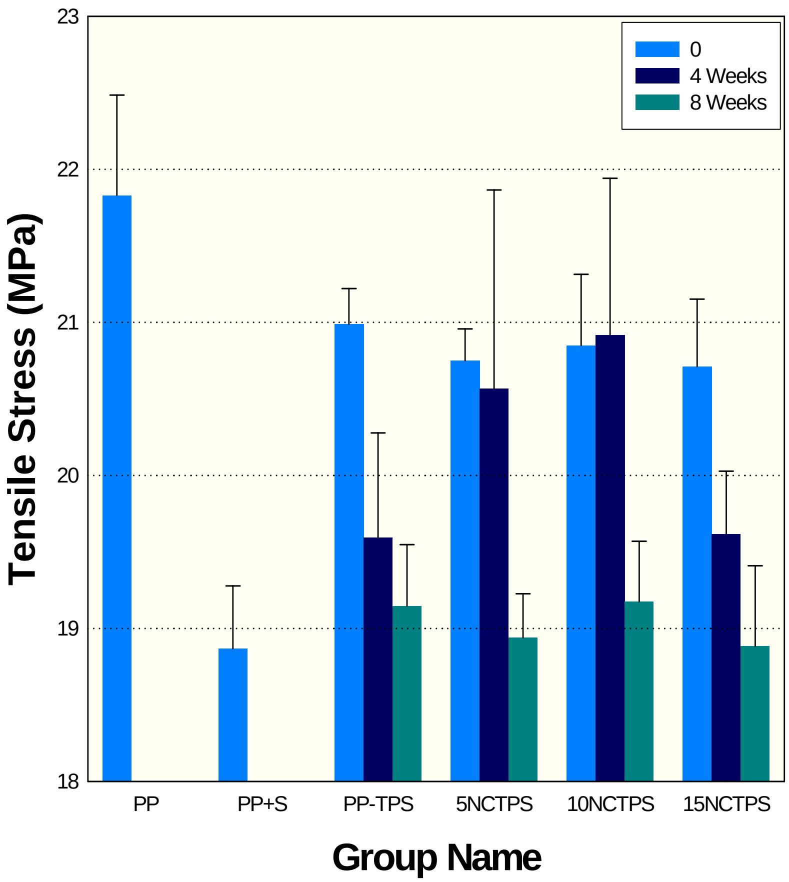
- *Viscosity*
- *Shear Stress*
- *Melt Flow Index*
- *Density*
- *Density versus MOE*

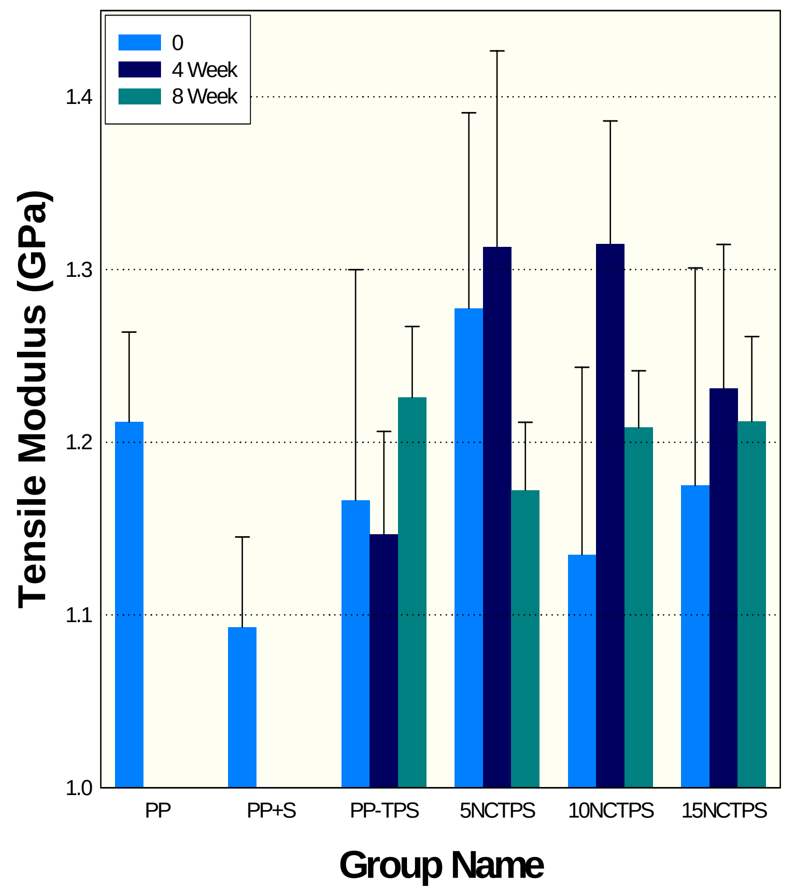
MFI for Plasticization



TPS was much more fluid. The incorporation of high amount NC reduced the fluidity of TPS.

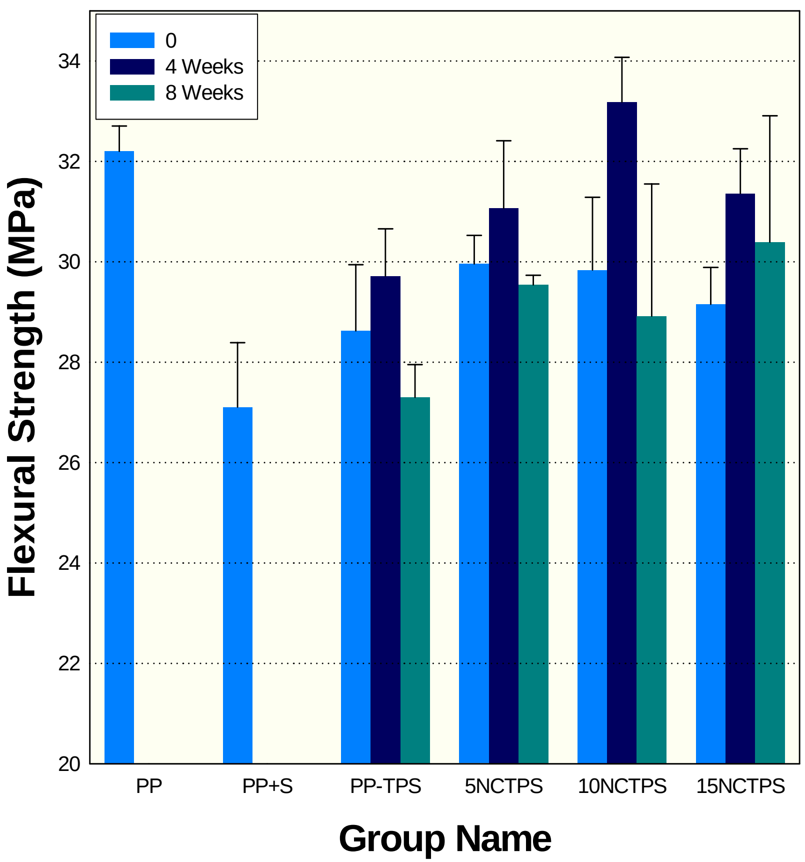
Tensile Properties of the Composites

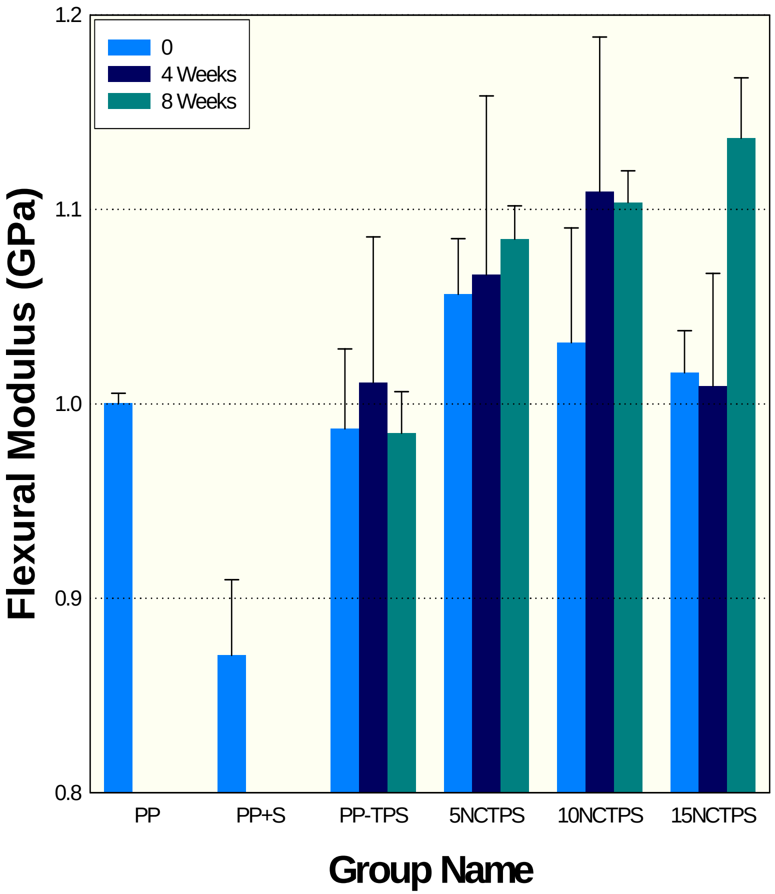




TPS and NCTPS filled PP composites showed comparable or lower tensile strength and modulus compared to control samples.

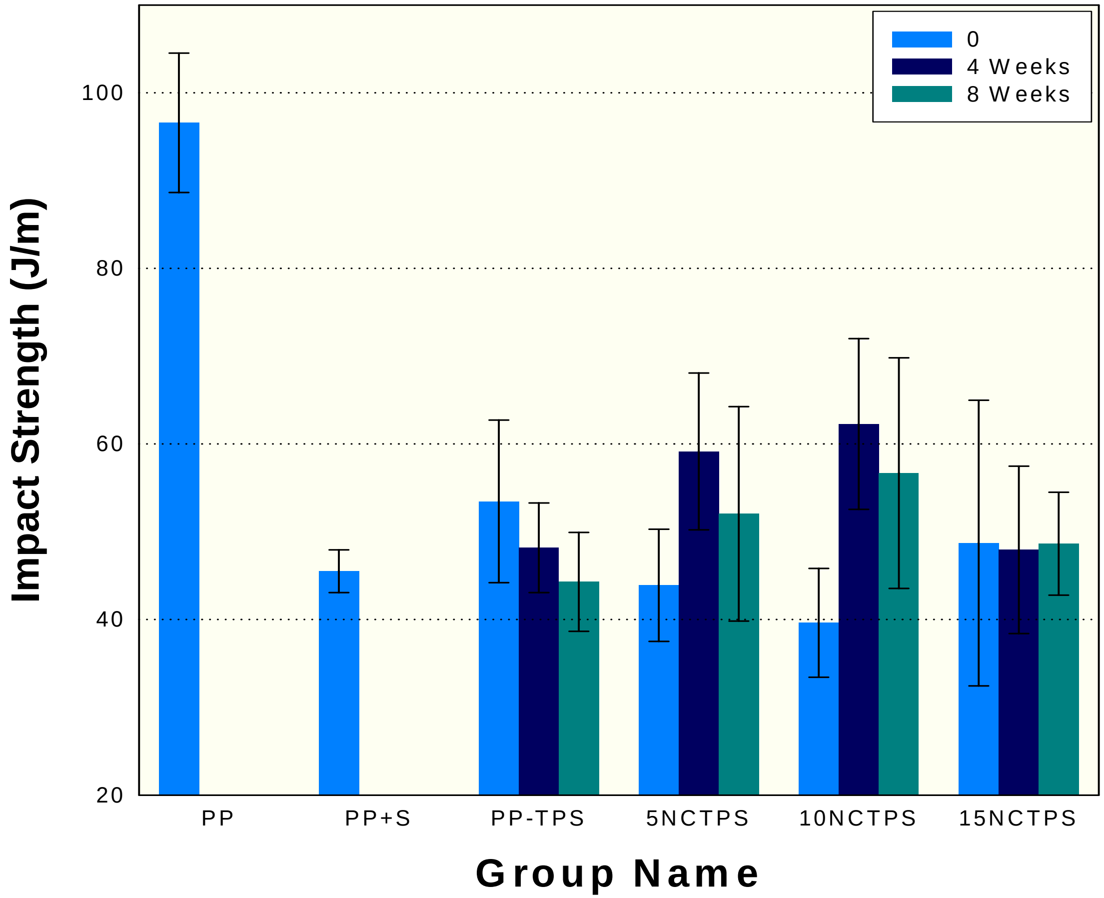
Flexural Properties of the Composites





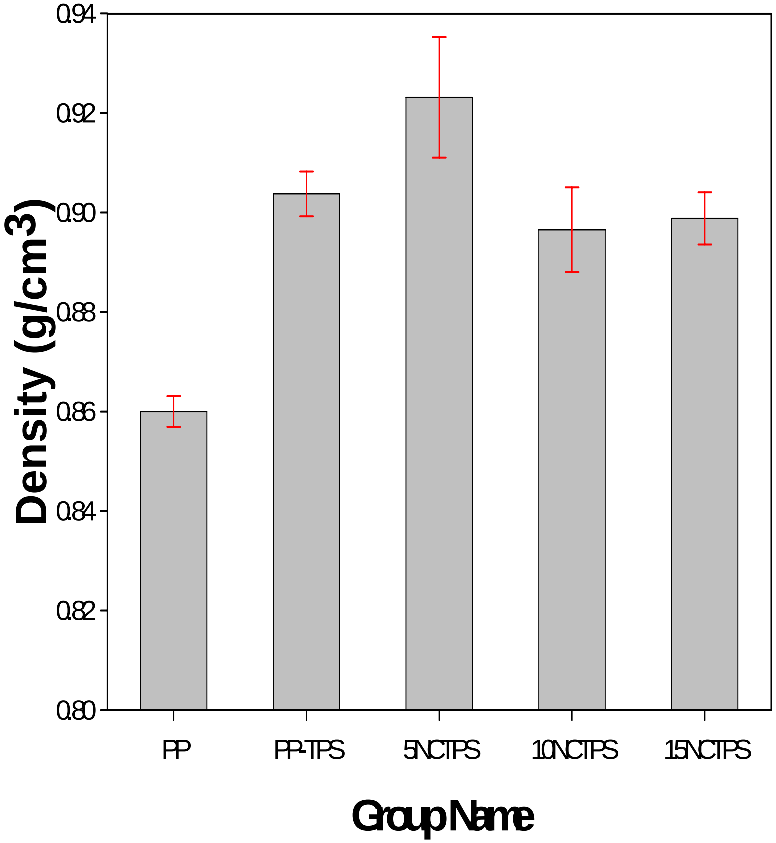
TPS and NCTPS filled PP composites showed comparable or lower flexural strength and modulus compared to control samples like tensile properties.

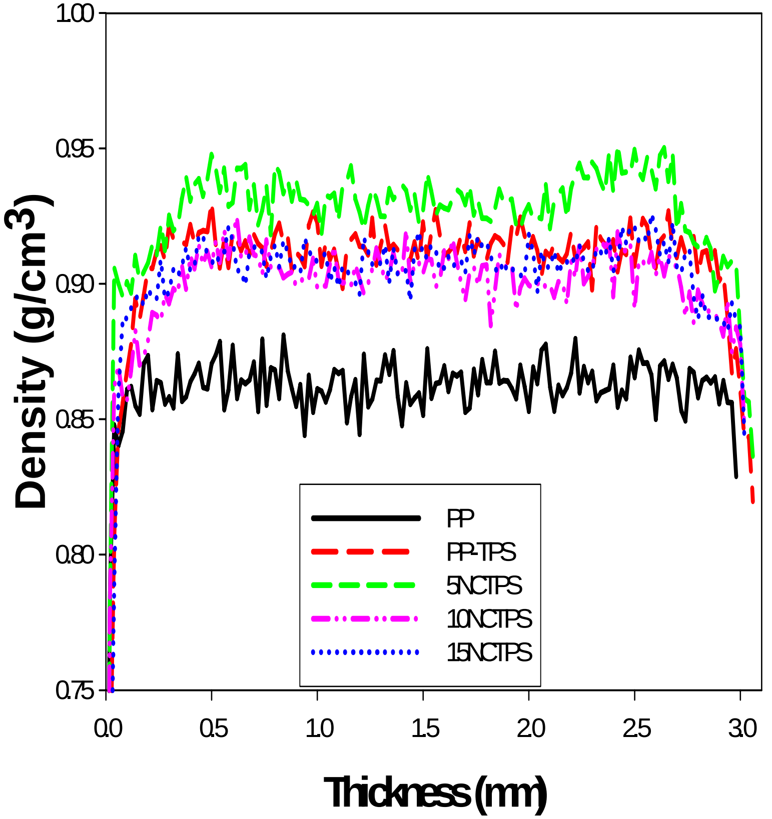
Impact Properties of Composites



Impact strength of composites decreased with addition of TPS and NCTPS.

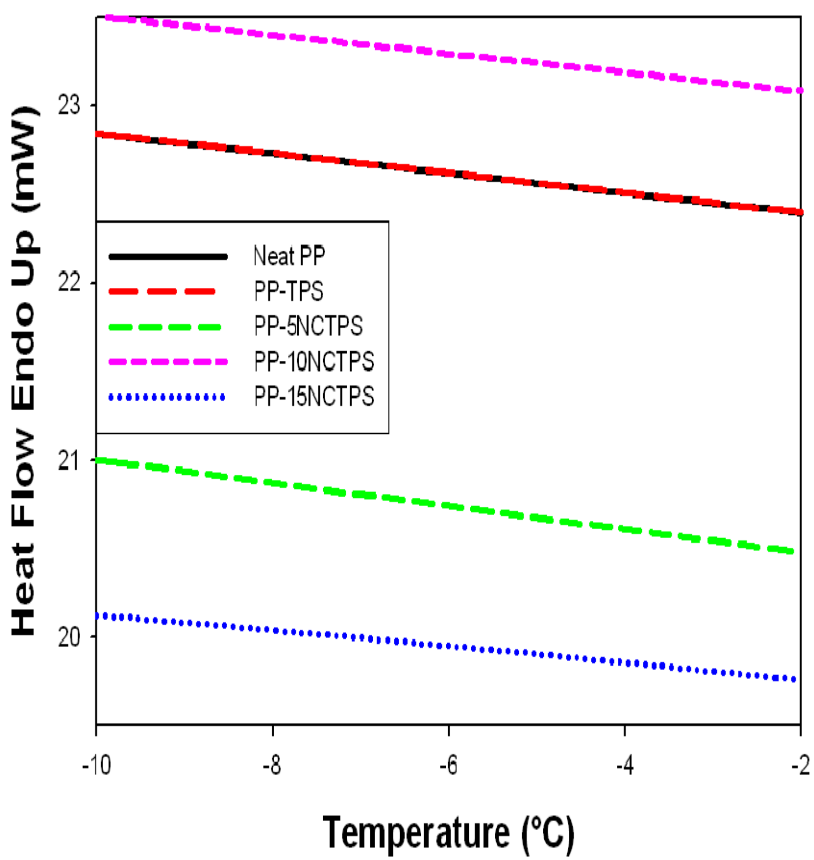
X Ray Vertical Density

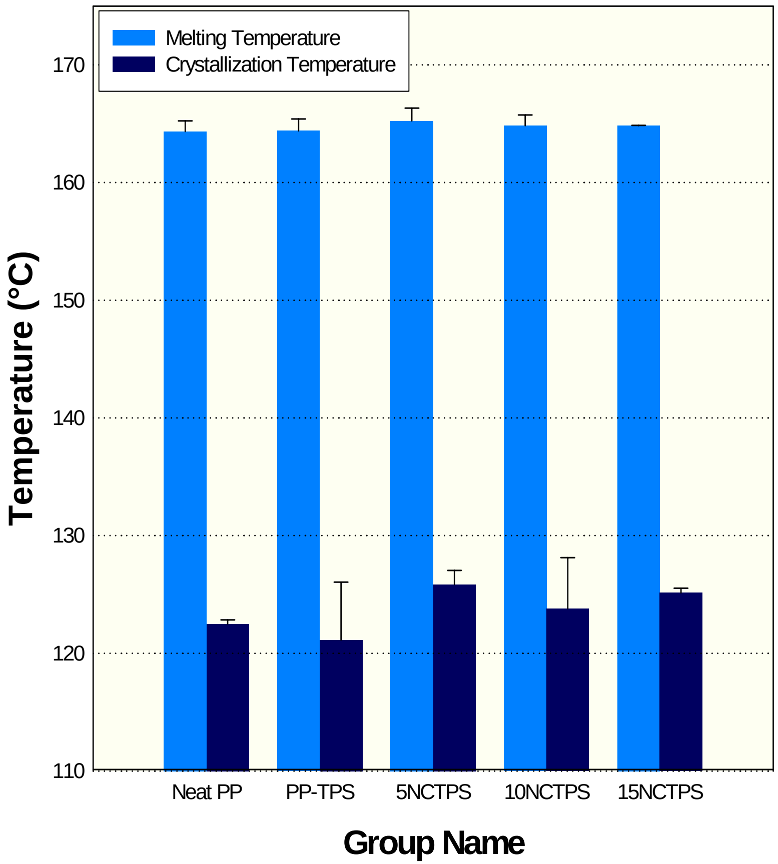




As expected TPS and NCTPS filled composites manufactured by injection method had highly uniform density distribution throughout the sample.

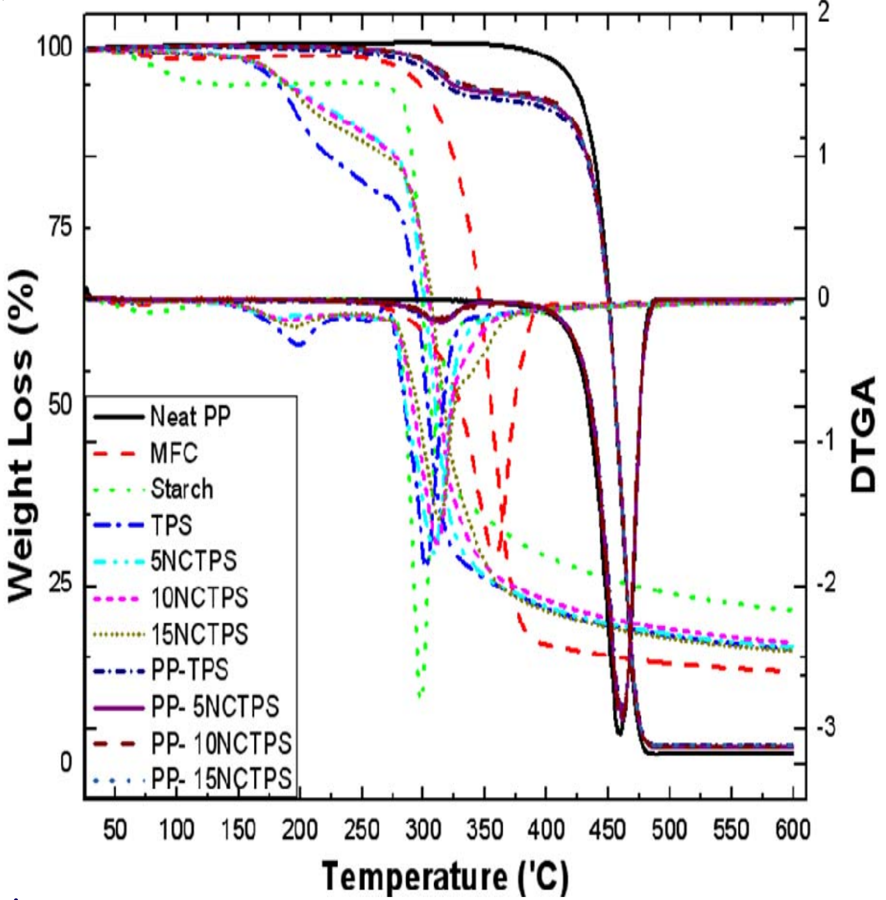
DSC of Composites

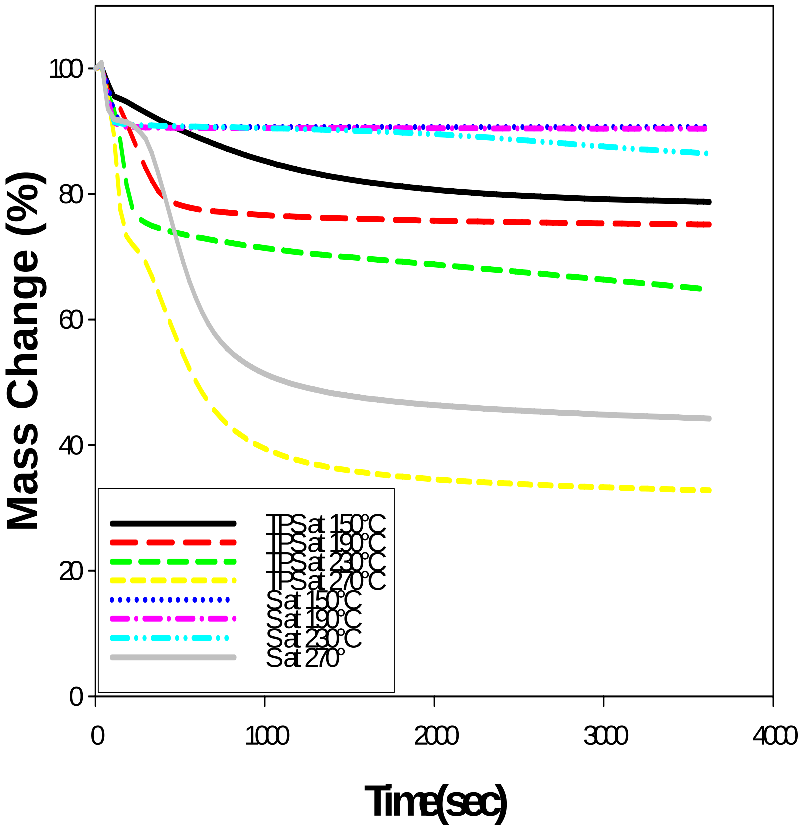




TPS and NCTPS does not change the T_g, T_m and T_c of the composites.

TGA and DTGA of Composites





TGA and DTGA results showed that thermal stability of composites decreased marginally with the addition of TPS and NCTPS.

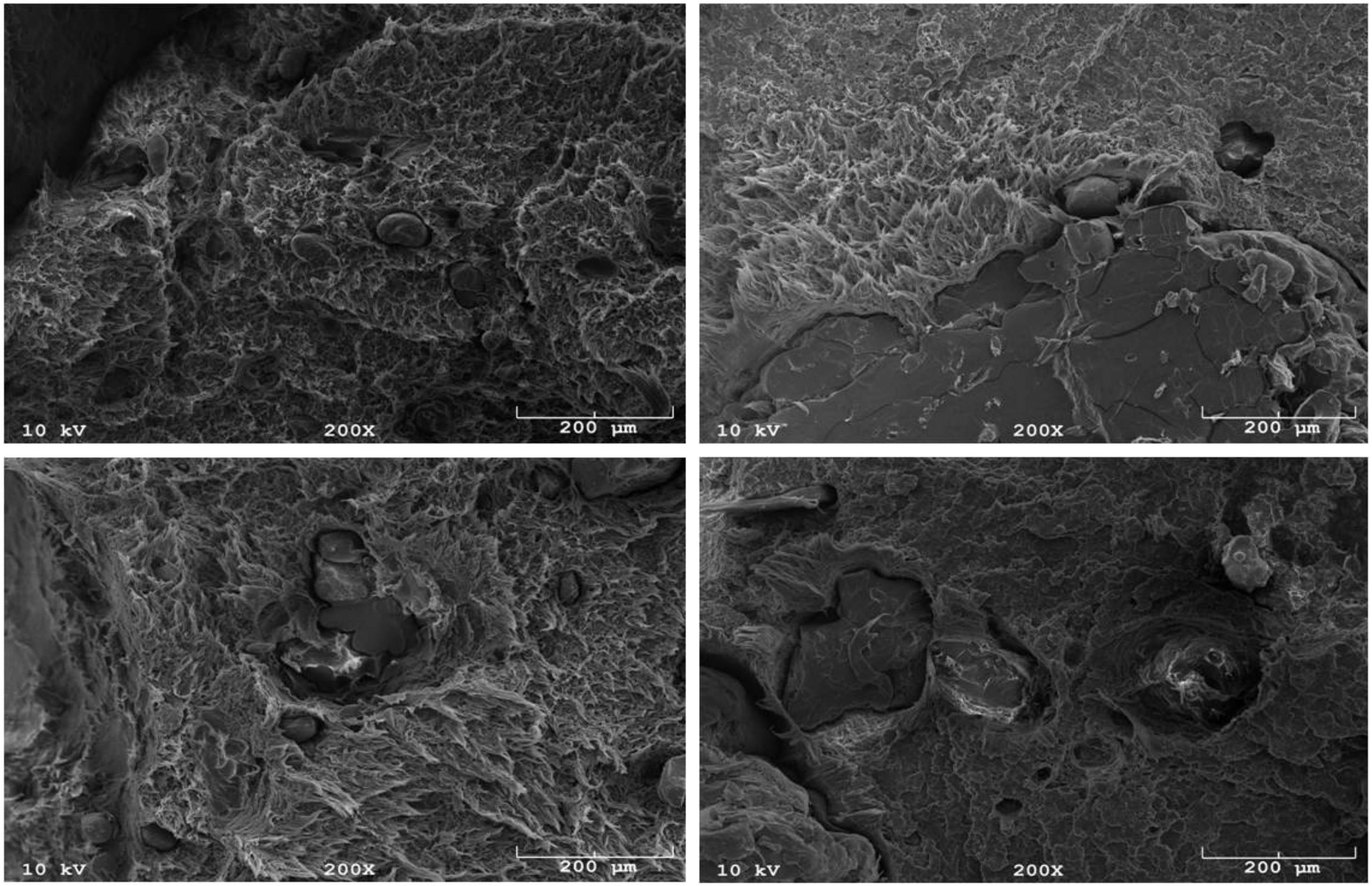
SEM Micrographs of TPS-Based Comp.

PP-TPS

PP-5NCTPS

PP-10NCTPS

PP-15NCTPS



The fibrils were embedded in TPS. This is due to strong interactions between the cellulose fibrils and the plasticized starch matrix.

Conclusions

- ***This study provided an initial insight into the use and characteristics of a novel carrier system to create compatibility between the NC and nonpolar polymer matrices.***

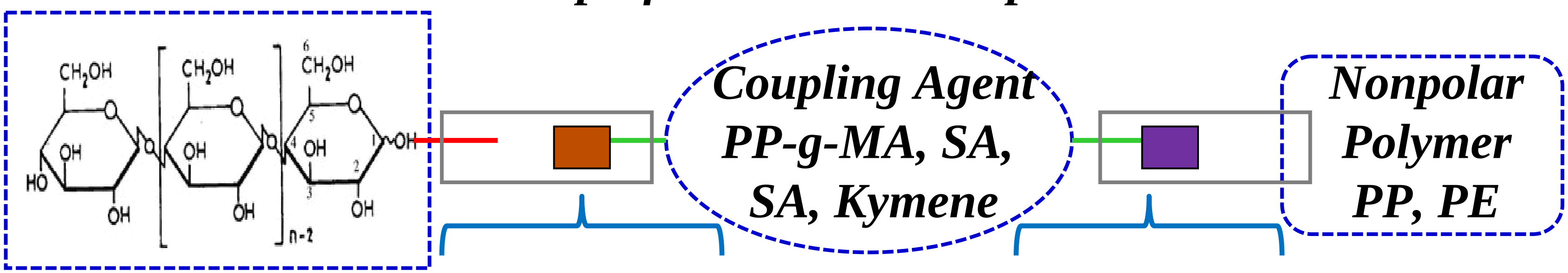
- ***The incorporation of TPS and NCTPS to PP showed comparable or lower mechanical properties without adding any compatibilizers or other additives. There were no TPS–matrix interactions.***

- ***There was no consistent or significant influence of the TPS-based composites on the Tg, Tc and Tm of the composites.***

- ***Although the thermal stability of PP composites decreased with the addition NCTPS, the thermal stability of TPS was improved with addition of NC.***

Future Studies Surface Functionalization of NC

- The mechanical properties of NC/plastic composites are strongly influenced by the quality of the fiber/matrix interface.
- NC (hydrophilic) vs Plastic matrix (hydrophobic)
- Lack of compatibility, bad dispersion
- Decrease in mechanical performances in composite materials.



Chemical reaction

Reduction of interfacial energy
Chemical reaction

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THANK YOU
QUESTIONS?