UNIVERSITY of GUELPH

BIOPRODUCTS DISCOVERY & DEVELOPMENT CENTRE

Nano-enhanced polyamide biocomposites with improved dimensional stability for automotive applications

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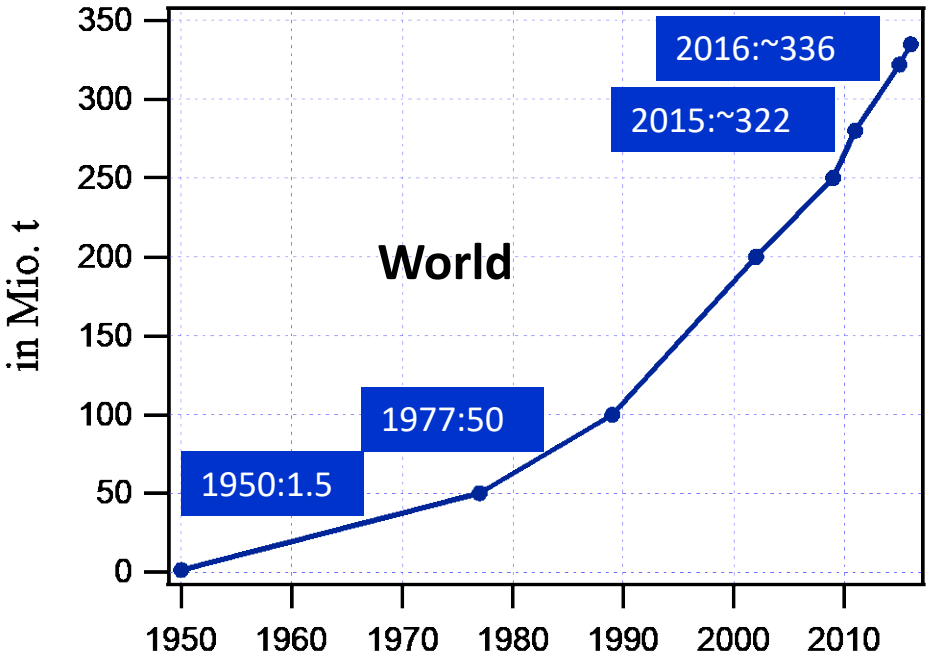
Presentation Outlines

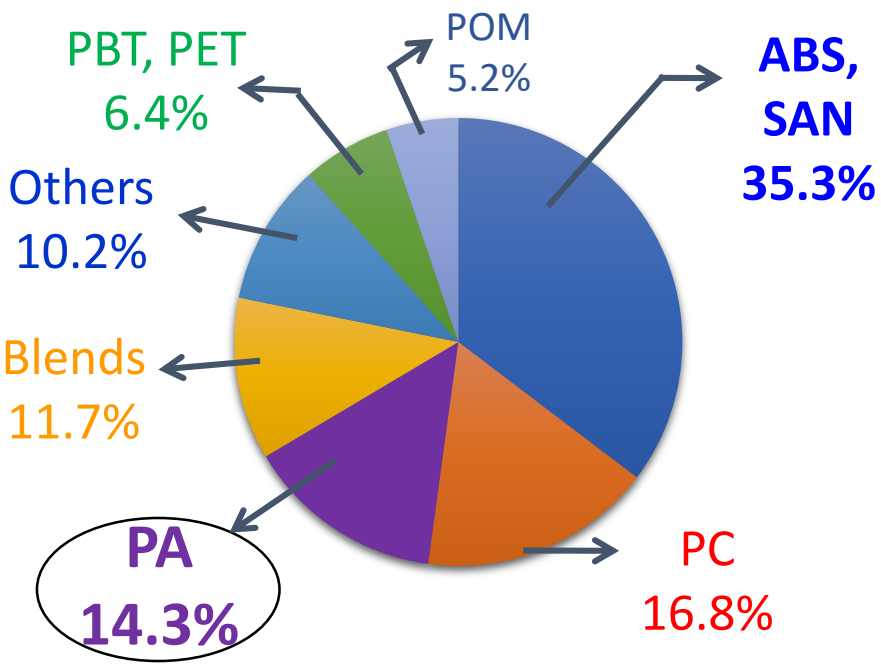
- Polyamides in Automotive industries
- CLTE and effect of nanoclay and biocarbon.
- Materials and Methods
- Characteristics of hybrid nanobiocomposites
- Conclusions

Consumption of Polymeric Materials

World Plastics Production [1)]



Engineering Plastic [2)]



- Worldwide demand of plastics about 335 MT's in 2016- a 4% increase compared to 2015.
- Around 10 % of the globally demanded plastics are Engineering plastics

1. Redraw from Plastics Europe Market Research Group (PEMRG) and Conversion Market & Strategy GmbH
2. Redraw from Plastics Europe Market Research Group (PEMRG) / Consultic Marketing & Industrieberatung GmbH

Polyamides in Automotive

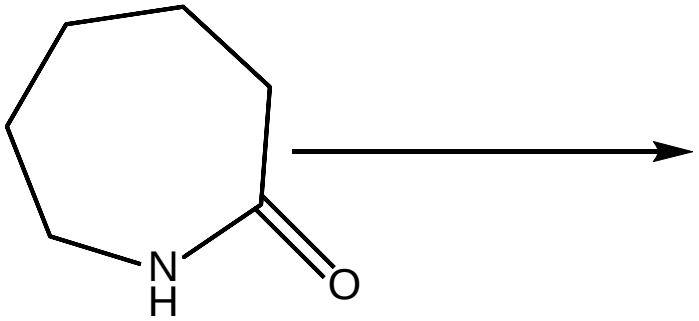
- The global **Polyamide (PAs) Market** was valued at **US$ 27.5 Mn** in **2018** and is expected to reach **US$ 33.5 Mn** by the end of the forecast period, growing at a CAGR of 4% during the period from **2018 to 2023**.[3)]
- PAs used in an **automotive** range from structural components of the vehicle to the electronic components as these materials are used as a substitute for metals. [4)]
- A **10%** reduction in the weight of an automobile can result in a 6%-8% improvement in **fuel efficiency**.[4)]
- PA 6 & PA 66, replacing metal parts in automobiles owing to:
  - High tensile strength,
  - High elasticity,
  - Excellent resistance to abrasion.

3. https://www.marketwatch.com/press-release/latest-developments-in-polyamide-market-industry-2019-growth-and-business-demand-key-vendors-types-region-and-applications-2019-02-28
4. https://www.globenewswire.com/news-release/2019/07/15/1882593/0/en/Polyamide-Market-To-Reach-USD-38-30-Billion-By-2026-Reports-And-Data.html

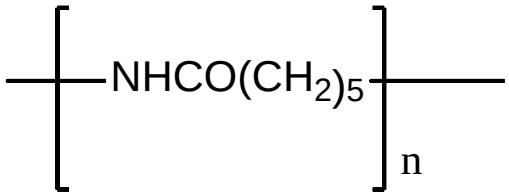
Polyamides (Nylon 6)

Polyamide 6 (PA 6)

Prepared by step-wise polymerization

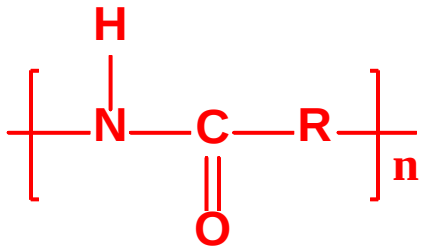


Caprolactam

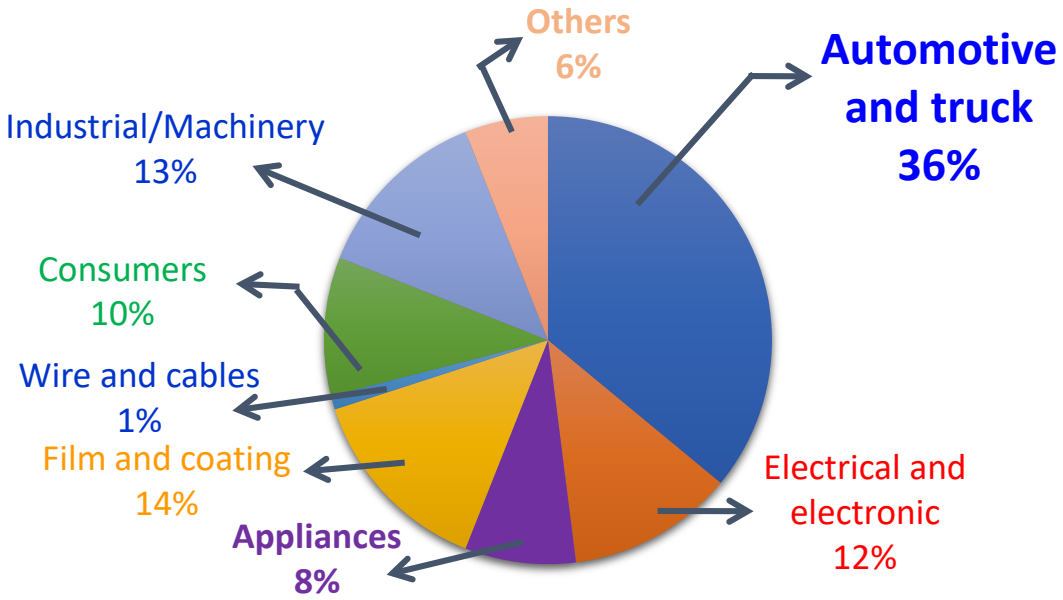


Polycaprolactam
(Nylon 6)

Polyamides



World: PA 6 Engineering resin Demand[5)]



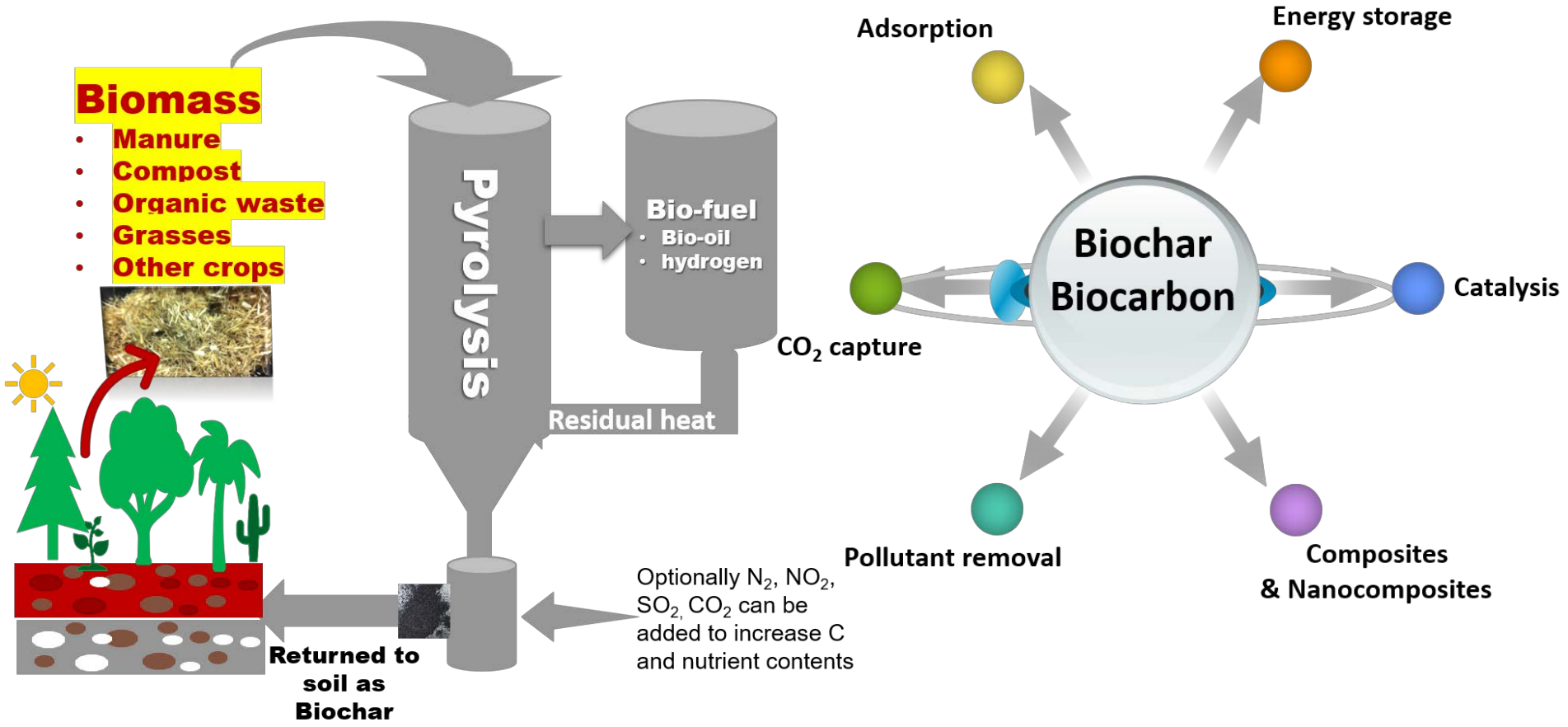
Disadvantages:

1. High water absorption,
2. Relatively high cost,
3. Dimensional instability at higher temperature **(CLTE)**

5) Redraw http://www.yarnsandfibers.com/industry-report/2015/world-nylon-report

Biocarbon and the Application

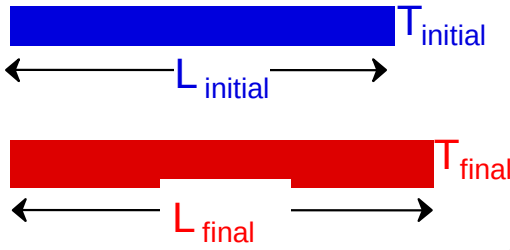
Biocarbon is produced by pyrolyzing biomass at different temperatures in the absence of oxygen (using nitrogen gas) to produce **syngas, bio-oil** and a residual carbon-rich solid which is called **biocarbon (biochar)**.



6) Adapted and redraw from http://www.biochar-international.org/technology

Coefficient of Linear Thermal Expansion (CLTE)

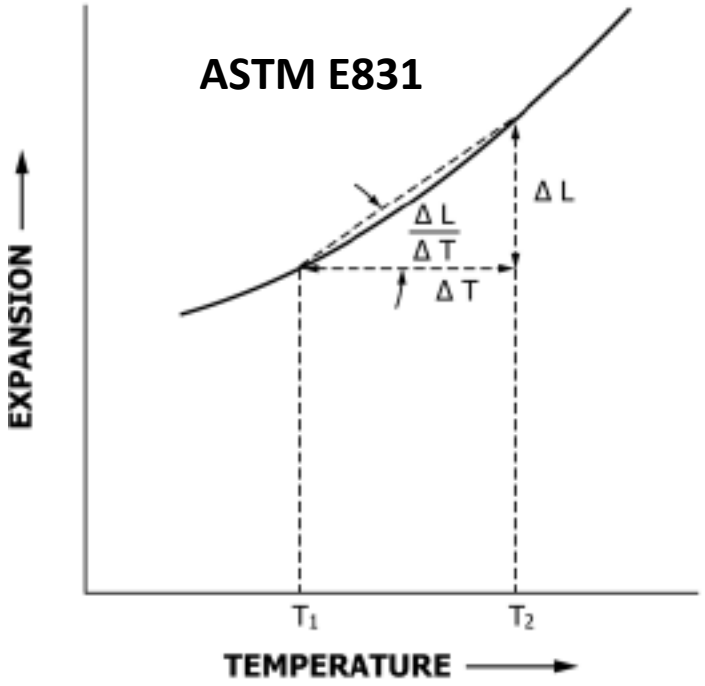
CLTE is a measure of how a material expands as it is heated.



$T_{final} > T_{initial}$

CLTE (1/K or 1/°C)

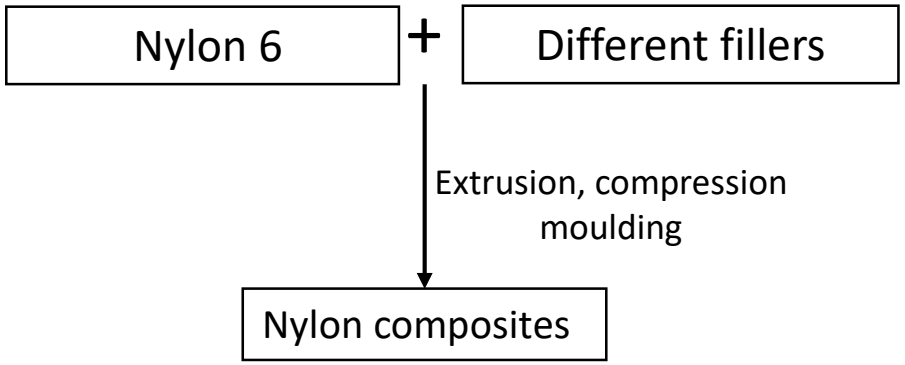
$$\frac{L_{final} - L_{inital}}{L_{inital}} = \alpha (T_{Final} - T_{inital})$$



Factors affecting the CLTE of the composites

- Proportional ratio of fillers in matrix,
- Reinforcement configuration & orientation
- Bonding between filler & matrix
- Crystalline properties (thermal treatment, e.g. annealing).
- Aspect ratio, and surface area
- Processing methods

Literature review



- As the filler loading increases, the CLTE above the T_g decreases.
- Mica filled composites exhibit lower expansion than the other filled compositions both above and below T_g.

This is due to higher reinforcing efficiency of high aspect ratio fillers, and to planar orientation of the mica flakes within the plane of the test specimen.

Filler	Wt .% loading	α_1 x 10^5 ($^oC^{-1}$) T= -30°C to T_g
Nylon 6	0	6.67
Glass sphere d= 2.48	40	3.53
Kaolin (Clay mineral) d=2.58	40	4.86
Mica d= 2.90	40	3.35
Novaculite (Fine-grained metamorphic silica rock) d= 2.65	40	4.86
Talc d= 2.70	40	4.79
Wollastonite ($CaSiO_3$) d= 2.90	40	3.88

6) Leon Segal, The Thermal Expansion of Reinforced Nylon-6 Composites Through the Matrix Glass Transition Temperature, Polym. Eng. Sci, 1979, 19, 5, 365.

Literature review

PA 6 (Tarnamid 27) 1.13 g/cm^3, melt flow index (MFI) 5.4 g/10 min

+

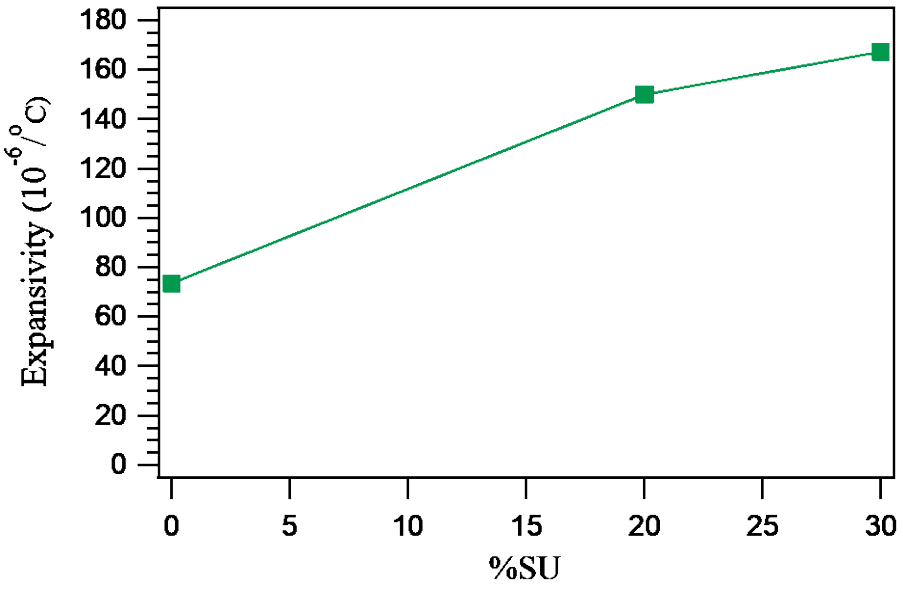
5, 15, 20, and 30 wt % of Zinc ionomer SU (Surlyn® 9020, DuPont, d= 0.96 g/cm^3, MFI 1 g/10 min).

Injected following ISO Standard 3167 →

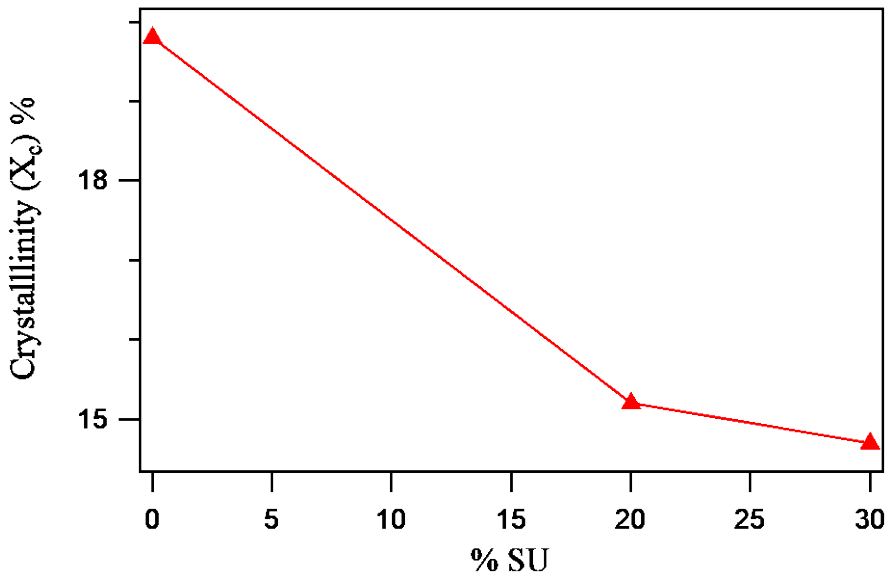
PA6 Blend

SEM showed no evidence of phase separation was detected.

CLTE measured at -140 to 100°C



Crystallinity of the blend



This effect is clearly associated with the reduction of the crystalline part. Modified PA6 loses dimensional stability at lower temperatures.

7) Magdalena Jaklewicz, Antoni Litak, Martin Ostoja-Starzewski, Friction and Scratch Resistance of Polyamide 6 Modified with Ionomeric Ethylene/Methacrylic Acid Copolymer, Journal of Applied Polymer Science, Vol. 91, 3866–3870 (2004)

Literature review

PA 6 (1020J) Mitsubishi with M.Wt. 27,700.

+

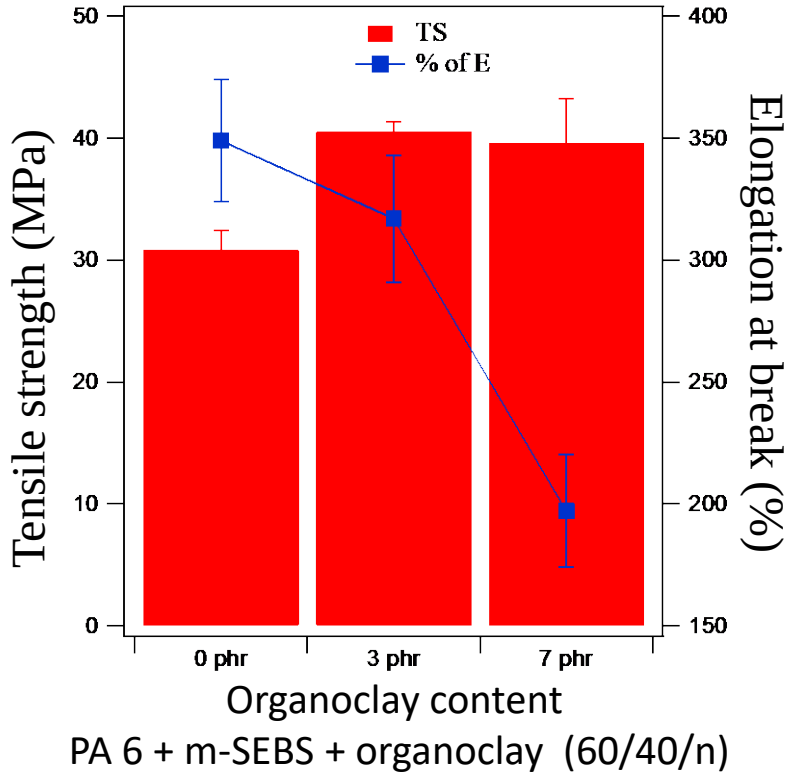
SEBS triblock elastomer used was Kraton FG PA6/clay nanocomposites containing 30 wt% of exfoliated organoclay (NPC), was obtained from Nanocor

→ twin-screw extruder at 240°C, 100 rpm, then injection moulding →

Nylon nanocomposites

The CLTE was measured at a heating rate of 5°C/min using TMA. The samples were annealed at 120°C for 2 h before test.

Table: Mechanical properties of PA6 nanocomposites.



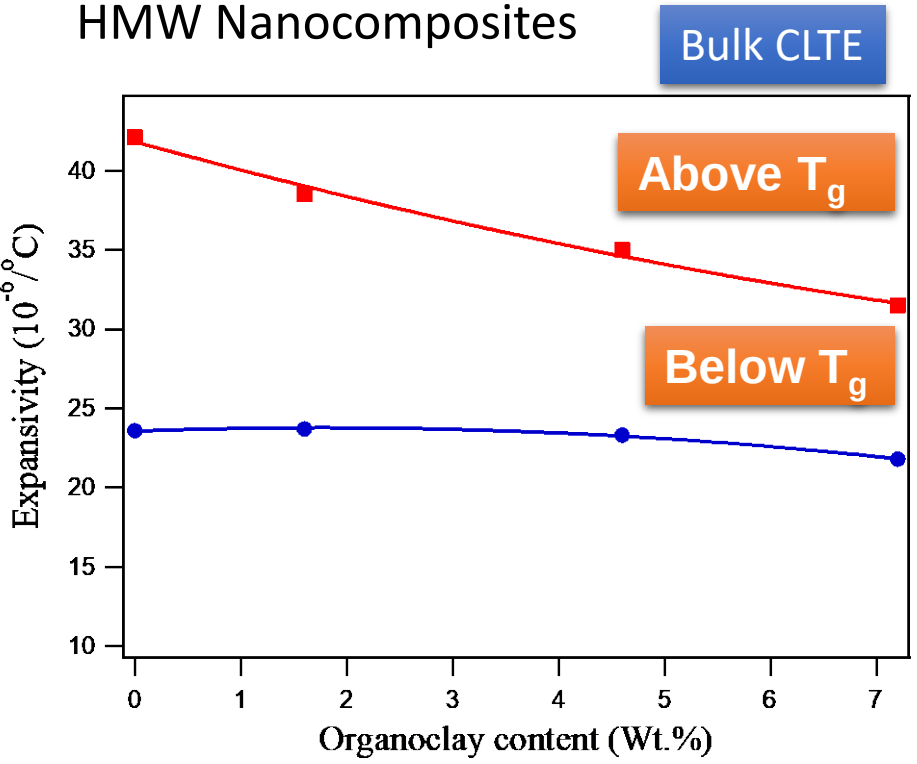
- CLTE of the PA6/SEBS blends was effectively reduced by the present of organoclay compared with the blends without organoclay.
- Addition of the organoclay to the PA6/m-SEBS alloy can promote the formation of the co-continuous nanolayer structure which would be the main drive force that reduced the CLTE.

8) Jiandi Jiang, Kun Zhang, Guozhang Wu, Effect of Organoclays on the Morphology and Thermal Expansion of PA6/SEBS Alloy Polymer Composites, 32: 2010-2016, 2011

Literature review

- High modulus, high aspect ratio, two-dimensional reinforcement Lead to low CLTE.
- Higher reduction in bulk CLTE above Tg due to more extreme differences in stiffness between the matrix & filler.
- TEM showed well-exfoliated system within the PA 6 parallel to FD.

Bulk Expansion Coefficient for annealed HMW Nanocomposites

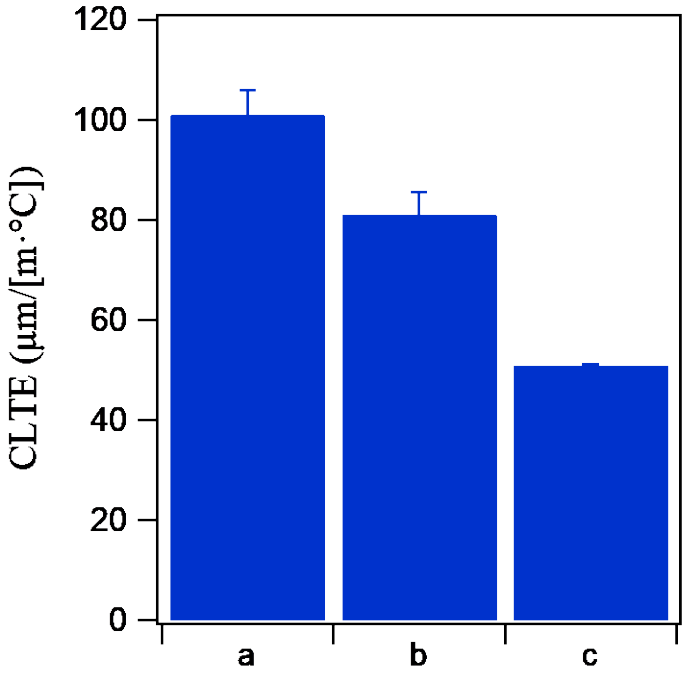


Annealing of HMW PA 6 causes a noticeable increase in CLTE above Tg for both FD and TD.

9) P.J. Yoon, T.D. Fornes, D.R. Paul, 16.4+15.9+9.8 Polymer 43 (2002) 6727–6741

Effect of biocarbon in decreasing the CLTE of polymer composites

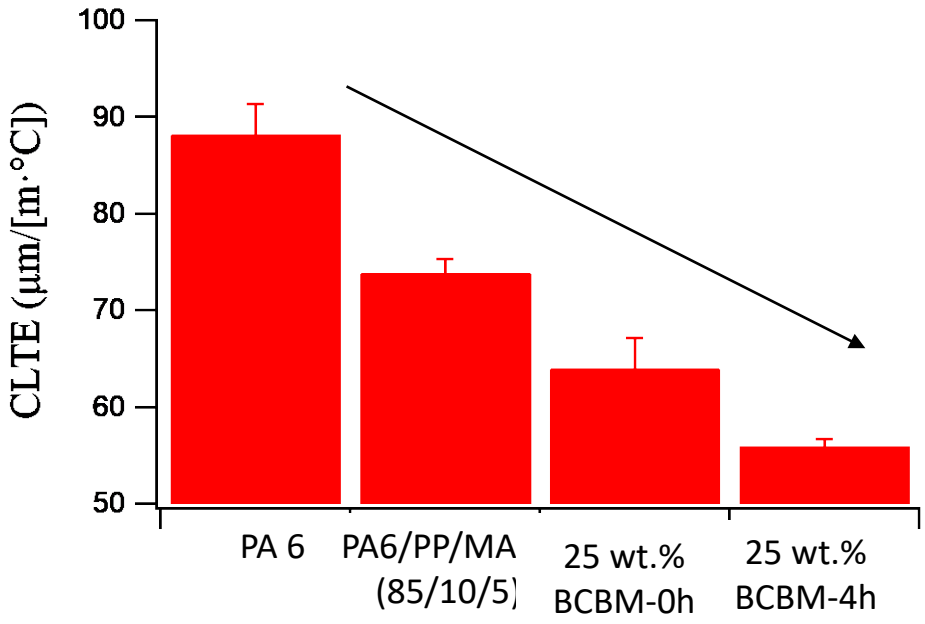
PP/PLA/PHBV composites



a) PP
b) PP/10%BC
c) 63%PP/(14.85%PLA/12.15%PHBV/10%BC)
d) 63%PP/(14.85%PLA/12.15%PHBV/10%talc)

- Reduction in CLTE by addition of 10%BC
- BC filler decreased CLTE than talc filler

PA 6/PP/Biocarbon composites

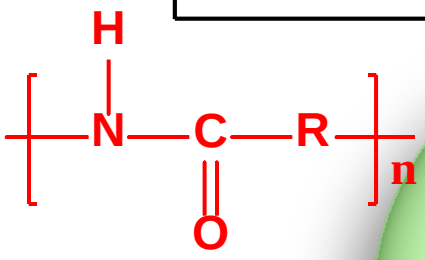


- Dimensional stability improved by addition of BC.
- Further improvement by Ball-milling.

1. Michael R. Snowdon, Amar K. Mohanty, Manjusri Misra, ACS Omega 2017, 2, 6446−6454
2. Amandine Codou, Manjusri Misraa, Amar K. Mohanty, Composites Part A 112 (2018) 1–10

Aim of the Work

- Excellent processability
- Chemical resistance
- Good mechanical properties
- Ease of coloring



Polyamide

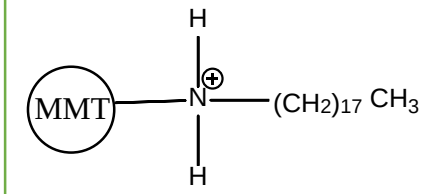
PA6

Biocarbon

BioC

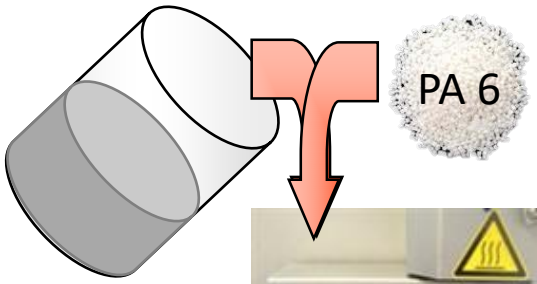
Nanoclay

- Improve polymer mechanical properties
- Enhance polymer barrier properties
- Enhance polymer resistance to fire
- Improved CLTE of the matrix



- Sustainable resources
- Low cost
- High thermal stability compared to other bio-based filler
- Functionality depend on pyrolysis condition

Composites Preparation

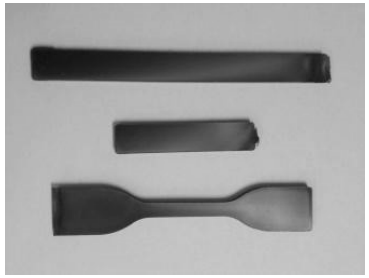


BioC+ NC

Extrusion in Twin Screw Compounder

Injection moulding

Injection moulding



PA 6 nanobiocomposites

Morphology of PA 6 nanobiocomposites

- Biocarbon particles homogeneously distributed in the material.
- Both exfoliated and intercalated tactoid structures exist in all hybrid nanobiocomposites.
- Nanoclay platelets show a high degree of alignment in the FD.

CLTE of PA 6 nanobiocomposites

- CLTE decreased in Flow direction by inclusion of biocarbon due to aspect ratio of BioC, which is close to 1.
- Inclusion of nanoclay has little effect on the CLTE in the normal and flow direction below Tg due to the immobility of the polymer matrix.
- Bulk CLTE above T_g decreased after annealing due to removal of residual stresses induced during injection moulding.

Conclusion

- Hybrid reinforcement of PA 6 with nanoclay and biocarbon resulted in nanocomposites with enhanced mechanical and dimensional stability.

- Anisotropy of the materials was highlighted by morphological and structural investigations.

- The relationship between the reduction of CLTE in the FD and the increased fraction PA 6 γ-crystals was revealed.

- PA 6 nanocomposite containing hybrid biocarbon and small amount of nanoclay demonstrated high Strength, modulus and superior dimensional stability compared to neat PA 6.

References

1. Redraw from Plastics Europe Market Research Group (PEMRG) and Conversion Market & Strategy GmbH.

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3. https://www.marketwatch.com/press-release/latest-developments-in-polyamide-market-industry-2019-growth-and-business-demand-key-vendors-types-region-and-applications-2019-02-28

4. https://www.globenewswire.com/news-release/2019/07/15/1882593/0/en/Polyamide-Market-To-Reach-USD-38-30-Billion-By-2026-Reports-And-Data.html.

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6. Leon Segal, The Thermal Expansion of Reinforced Nylon-6 Composites Through the Matrix Glass Transition Temperature, Polym. Eng. Sci, 1979, 19, 5, 365.

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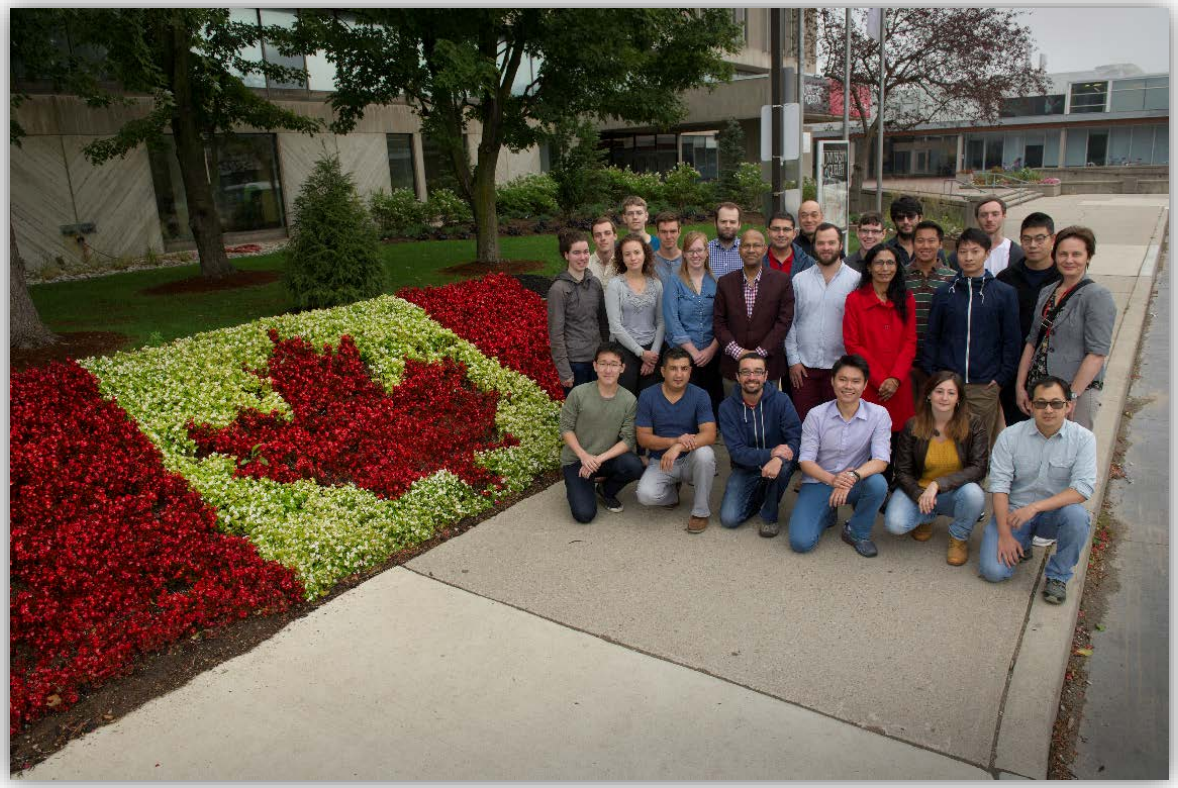
9. P.J. Yoon, T.D. Fornes, D.R. Paul, Thermal expansion behavior of nylon 6 nanocomposites, Polymer 43 (2002) 6727–6741

10. Michael R. Snowdon, Amar K. Mohanty, Manjusri Misra, Miscibility and Performance Evaluation of Biocomposites Made from Polypropylene/Poly(lactic acid)/Poly(hydroxybutyrate-cohydroxyvalerate) with a Sustainable Biocarbon FillerACS Omega 2017, 2, 6446−6454.

11. Amandine Codou, Manjusri Misraa, Amar K. Mohanty, Sustainable biocarbon reinforced nylon 6/polypropylene compatibilized blends: Effect of particle size and morphology on performance of the biocomposites, Composites Part A 112 (2018) 1–10.

Acknowledgements



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