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
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.

Polyamides (Nylon 6)

Polyamide 6 (PA 6)
Prepared by step-wise polymerization

Polycaprolactam (Nylon 6)

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

World: PA 6 Engineering resin Demand

Automotive and truck 36%
Industrial/Machinery 13%
Electrical and electronic 12%
Appliances 8%
Film and coating 14%
Wire and cables 1%
Consumers 10%
Others 6%

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).
Coefficient of Linear Thermal Expansion (CLTE)

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

\[
\text{CLTE} = \frac{L_{\text{final}} - L_{\text{initial}}}{L_{\text{initial}}} = \alpha \left( T_{\text{final}} - T_{\text{initial}} \right)
\]

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
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.

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

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.

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.

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

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

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

Aim of the Work

Polyamide

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

Biocarbon

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

Nanoclay

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

Polyamide PA6

Biocarbon BioC

Nanoclay

MMT

$\text{(CH}_2\text{)}_{17}\text{CH}_3$
Composites Preparation

Extrusion in Twin Screw Compounder

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 $T_g$ 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.
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.
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