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FILLING POLYMERS WITH PURPOSE: SUPRAMOLECULAR CHEMISTRY AT WORK IN CIRCULAR ECONOMY

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Introduction

The integration of biomass-derived fillers into elastomers has garnered significant attention as the polymer industry strives for renewable, cost-effective, and eco-friendly alternatives to traditional mineral fillers. Elastomeric matrices such as natural rubber, styrene-butadiene rubber (SBR), ethylene-propylene-diene monomer rubber (EPDM), and thermoplastic elastomers offer an excellent platform for utilizing bio-based fillers due to their high elasticity, low modulus, and broad processing windows. During extrusion and mixing processes, typically performed at 160–200 °C, biomass fillers undergo partial softening or thermal transitions while retaining functional groups such as hydroxyl, carboxyl, and aromatic moieties. Although short processing times limit covalent bonding between the elastomer matrix and biomass, non-covalent supramolecular interactions form rapidly in the melt and are preserved upon cooling. These interactions largely influence filler–matrix compatibility, dispersion, and the overall performance of the elastomer.

Biomass polymer fillers

Biomass fillers are structurally diverse and can be categorized based on their macromolecular or structural components relevant to elastomer reinforcement:

Cellulose and nanocellulose - derived from wood pulp, agricultural residues, or bacterial fermentation, cellulose has a high aspect ratio and hydroxyl-rich surface, enabling hydrogen bonding.

Lignin - a by-product of pulp and biorefinery processes, lignin is amorphous, aromatic-rich, and thermally stable. Its π–π interactions and phenolic hydroxyl groups facilitate supramolecular bonding with polar elastomers or compatibilizers.

Starch and starch derivatives - granular or modified starch particles have hydroxyl-rich surfaces. Thermoplastic starch can form interpenetrating phases but requires careful moisture management.

Protein, chitin, and chitosan-cased fillers - these fillers are less common but offer ionic and hydrogen bonding potential due to amine and amide groups.

Lipids and oil-derived residues - examples include used cooking oils, press cakes, and wax fractions. These fillers act as plasticizers or soft fillers, modifying elastomer flexibility. Fatty acid chains enable van der Waals interactions, while ester or hydroxyl groups allow hydrogen bonding with polar elastomers.

Mineral fillers of biological origin - examples include seashells, eggshells, and corals, primarily consisting of calcium carbonate ($CaCO_3$) with surface proteins and polysaccharides. These fillers offer rigidity and thermal stability, engaging in hydrogen bonding or ionic interactions when functionalized.

Types of supramolecular interactions in elastomer–biomass systems

Elastomers are typically hydrophobic and apolar (e.g., SBR, EPDM), while polar elastomers (e.g., nitrile rubber, polyurethane-based elastomers) expand the range of interactions. Key non-covalent supramolecular bonding mechanisms include:

Hydrogen bonding - hydroxyl groups in cellulose, starch, or lignin form hydrogen bonds with polar elastomer segments. Compatibilizers with polar groups (e.g., maleated rubbers, silanes) enhance such interactions.

π–π interactions - aromatic domains in lignin interact with aromatic elastomers (e.g., styrene units in SBR) or other additives, improving filler–matrix adhesion.

Ionic interactions - modified biomass fillers with carboxylate or sulfate groups interact ionically with cationic compatibilizers or ionomeric elastomers, forming reversible crosslinks that enhance toughness and self-healing.

Van der Waals forces - predominant in non-polar elastomers, these interactions are weak but can be amplified by increasing filler surface area.

Host–guest inclusion complexes - modified fillers or additives enable selective supramolecular recognition, though this is less common in elastomer applications.

The balance and strength of these interactions govern filler dispersion, interfacial adhesion, and reinforcement efficiency. Supramolecular bonds can reorganize under stress, providing improved energy dissipation, damping, and self-healing properties.

Conclusions and future perspectives

Biomass fillers represent a promising class of sustainable reinforcements for elastomers. Unlike traditional covalent coupling agents, supramolecular approaches rely on reversible, non-covalent interactions that form rapidly during processing and are locked in upon cooling. These interactions significantly influence composite morphology and performance. Future advancements will likely focus on surface modifications that incorporate specific supramolecular motifs into biomass fillers, enabling tunable and responsive interfacial bonding. Such strategies could lead to elastomer composites that combine sustainability with advanced functionalities like adaptive damping, recyclability, and self-healing.

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