cbecimat26
26° Congresso Brasileiro de Engenharia e Ciência dos Materiais
22 a 26 de novembro de 2026
Costão do Santinho
Florianópolis-SC

Effect of the polymerization route on styrene/limonene/castor oil copolymers

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Introduction

Different polymerization routes reveals that distinct mechanisms lead to the formation of polymeric structures with specific physicochemical characteristics. In mixed polymerization systems, the copolymerization of comonomers may result not only in intermediate properties but also in entirely different materials, depending on the propagation rate constants and the nature of the active centers. In contrast, processes involving addition and condensation steps, such as hydrogen/transfer polymerization and condensation/addition polymerization, favor the formation of copolymers with diverse architectures, including chains bearing reactive functional groups and the possibility of grafted structures. Furthermore, pseudo living addition/condensation polymerization strategies enable a high degree of structural control, allowing the synthesis of block, branched, and functionalized polymers through the sequential addition of monomers. These different mechanisms directly influence supramolecular organization and the final material properties, as evidenced by the formation of complex structures.

Objectives

To compare two polymerization routes for styrene/limonene/castor oil systems, free radical polymerization with maleinized castor oil (SLOM) and mixed polymerization with non-maleinized castor oil (SLO), and to evaluate how the route affects the appearance, the chemical structure (FTIR) and the thermal stability (TGA) of the resulting materials.

Methodology

Synthesis: SLOM was obtained by free radical polymerization of styrene, limonene and maleinized castor oil (MOMA). SLO was obtained by mixed polymerization of styrene and limonene with non-maleinized castor oil.

Characterization: TGA-FTIR (evolved gas analysis) in a PerkinElmer STA 6000 coupled to a Frontier FTIR: about 6 mg of sample in a platinum crucible, N_2 at 20 mL min^{-1}, 20 °C min^{-1} from 50 to 550 °C; gas cell at 330 °C and transfer line at 300 °C; spectra from 4000 to 600 cm^{-1} at 4 cm^{-1} resolution.

Results and Discussion

In this study, the SLOM system, synthesized through free radical polymerization of styrene, limonene, and maleinized castor oil, exhibited a crosslinked, green, and transparent resin, indicating a higher degree of network formation. FTIR spectra of this material showed more pronounced carbonyl stretching bands associated with ester and anhydride functionalities, suggesting effective incorporation of maleic groups and increased intermolecular interactions.

In contrast, the SLO sample, obtained via mixed polymerization using non maleinized castor oil, presented a plastic-like, white opaque appearance, consistent with a less crosslinked and more flexible structure. Its FTIR profile indicated comparatively lower intensity of carbonyl bands and a higher contribution from aliphatic C–H vibrations, reflecting a more linear or weakly branched architecture.

Thermogravimetric analysis (Figure 1) revealed that the SLO sample exhibited higher overall thermal stability compared to SLOM, despite presenting a slight initial mass loss at lower temperatures. This early mass loss may be associated with the volatilization of low-molecular-weight fractions or residual reagents. However, at higher temperatures, SLO showed a more gradual degradation profile and a higher resistance to mass loss, indicating greater thermal robustness. In contrast, the SLOM material displayed a more pronounced and earlier main degradation step, suggesting that, although crosslinking is present, the incorporation of maleinized groups may introduce thermally labile segments that reduce stability.

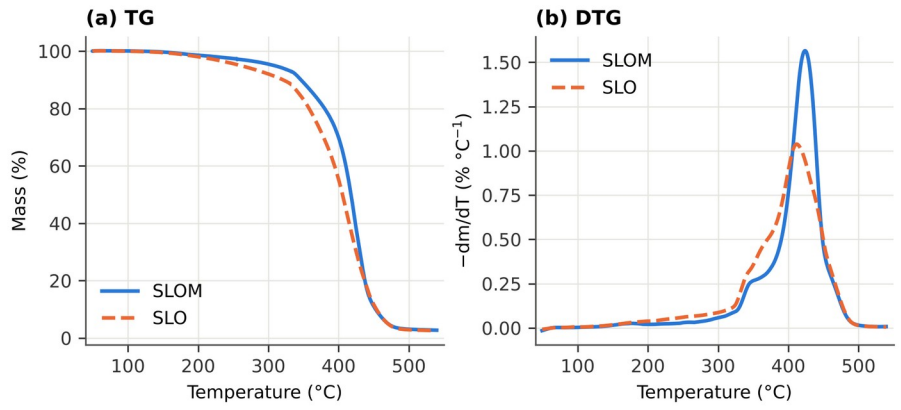


Figure 1. (a) TG and (b) DTG curves of SLOM and SLO (N_2, 20 °C min^{-1}).

Conclusions

The polymerization route defined the type of material obtained: SLOM formed a green, transparent and crosslinked resin, while SLO formed a white, opaque and more flexible plastic.

These results indicate that the network structure formed in SLOM does not necessarily translate into superior thermal resistance, and that the mixed polymerization route in SLO leads to materials with improved thermal performance under the analyzed conditions.

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Acknowledgements: the authors thank UTFPR – Campus Medianeira for the infrastructure.