2nd Conference on Green Chemistry and Sustainable Coatings

greenchemco

Pisa, Italy, 28th-30th June 2023

Tall oil fatty acids valorization for acrylate synthesis and bio-based polymer development via Michael addition reaction

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Keywords: fatty acids-based Michael acceptor; bio-based acrylate; Michael addition; bio-based polymer

Introduction

It is crucial to adapt the processing of forest bio-resources into biochemicals and bio-based advanced materials in order to transform the current economic climate into a greener economy. Tall oil, as a by-product of the Kraft process of wood pulp manufacture, is a promising resource for the extraction of various value-added products. Tall oil fatty acids-based multifunctional Michael acceptor acrylates were developed. The suitability of developed acrylates for polymerization with tall oil fatty acids-based Michael donor acetoacetates to form a highly cross-linked polymer material via the Michael addition was investigated. With this novel strategy, valuable chemicals and innovative polymer materials can be produced from tall oil in an entirely new way, making a significant contribution to the development of a forest-based bioeconomy.

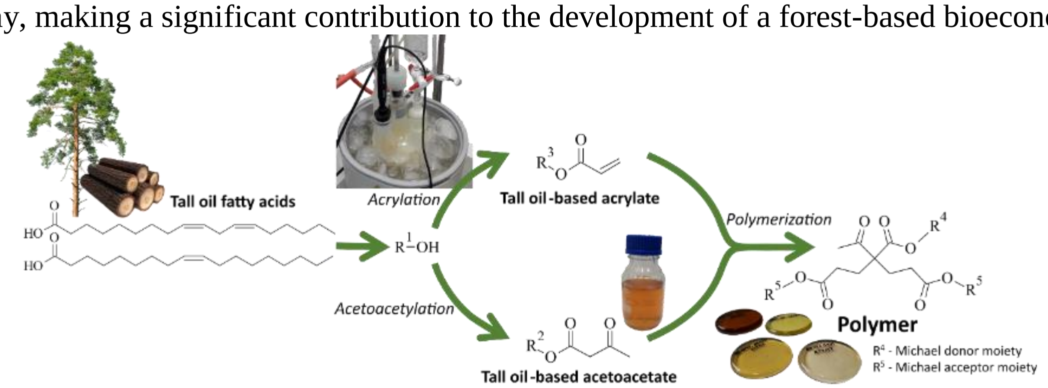

Figure 1. Conceptual scheme of the proposed design of polymer development

Experimental

Two different tall oil-based acrylates (epoxidized tall oil fatty acids 1,4-butanediol polyol acrylate (E^{IR}TOFA_BD_Acryl); epoxidized tall oil fatty acids trimethylolpropane polyol acrylate

(E^{IR}TOFA_TMP_Acryl)) were successfully synthesized and characterized. Synthesized acrylates were successfully used to synthesize bio-based thermoset polymers with tall oil-based acetoacetates.
Gel permeation chromatography (GPC), Fourier-transform infrared (FT-IR) spectroscopy, matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectrometry (MS), and nuclear magnetic resonance (NMR) were used to analyze the chemical structure of synthesized acrylates. The Michael addition was used to synthesize novel bio-based thermoset polymers from the developed tall oil fatty acids-based acrylates and acetoacetates. Dynamic mechanical analysis (DMA), thermal gravimetric analysis (TGA), and universal strength testing equipment were used to investigate the physical and thermal properties of developed bio-based thermoset polymers.

Results and Discussion

E^{IR}TOFA_BD_Acryl contained 0.0039 mol/g acrylic groups, but E^{IR}TOFA_TMP_Acryl contained0.0035 mol/g acrylic groups. Considering the data of rheology, FT-IR, NMR, GPC, and MALDI-TOF MS, the obtained tall oil polyol-based acrylates are suitable for polymer synthesis by the Michael reaction. Obtained polymers had a wide variety of mechanical and thermal properties (glass transition temperature from –12.1 to 29.6 °C by DMA, Young's modulus from 15 to 1 760 MPa, and stress at break from 0.9 to 16.1 MPa). The results showed that the developed bio-based thermoset polymer samples were thermally stable up to 300 °C.
Moreover, the synthesized tall oil polyol-based acrylates are promising in producing other polymers, such as coating production by UV-initiated free radical polymerization.

Conclusions

The functionality of the utilized monomers had a significant impact on the polymer's characteristics. Polymers with higher cross-link density had higher glass transition temperatures. The tensile properties of polymers were also different because of different cross-linking densities. It was demonstrated that the mechanical properties of polymers can be customized when different functionalities of tall oil-based Michael monomers are used for polymer synthesis. It is possible to obtain rubber-like polymers from 1,4-butanediol-based components, while hard polymers can be obtained from trimethylolpropane-based components.

Acknowledgements

This research was funded by the Latvian Council of Science, project "High bio-based content thermoset polymer foam development from plant origin oils (Bio-Mer)" (No. lzp-2020/1-0385). This publication was supported by LZA and CAS mobility project "Innovative bio-based polyols and advanced methods of their characterization" (No. LZA-22-02).

Biography

Ralfs Pomilovskis is a PhD student at the Riga Technical University. His thesis topic is "Michael donor monomer synthesis from tall oil fatty acids as raw materials for bio-based thermoset polymers". Ralfs also holds a position of engineer at the Polymer laboratory of the Latvian State Institute of Wood Chemistry.