Thermal degradation study and gas analysis of biobased thermosets

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FFG Forschung wirkt.

Introduction

Thermosets synthesized from lignin-based resources currently show cost-reducing and sustainable properties, while also maintaining similar mechanical characteristics as their fossil-based counter parts [1]. In this study we have investigated the thermal degradation of epoxy resins and compared them to their bio-based alternatives, since many newly developed thermosets lack information on thermal degradation properties. To identify any hazardous components that might be released during thermal degradation or in case of a fire, we have coupled a TGA to an FTIR spectrometer and recorded the evolution of gaseous degradation products. To further assess the developed products, we adsorbed the analytes onto a sorbent tube that is afterwards qualitatively analyzed by thermodesorption-GC-MS or liquid extraction and subsequent GC-MS analysis.

Experimental

The bisphenol based resin is a commercially available product. The lignin-based epoxy resin was synthesized by epoxidation of purified kraft lignin with epichlorohydrin and aniline in an aqueous sodium hydroxide solution. After purification the resin was crosslinked with maleic anhydride [2]. Both resins were analyzed by TGA-FTIR. To further qualitatively investigate degradation products, sorbent tubes (TENAX TA – sorbent) were connected to the TGA. After the measurement, the adsorbed analytes were qualitatively assessed *via* thermodesorption-GC-MS or by liquid extraction with acetonitrile and GC-MS analysis. This procedure gives insights on new degradation products that cannot be assessed with TGA-FTIR and is therefore complementary.

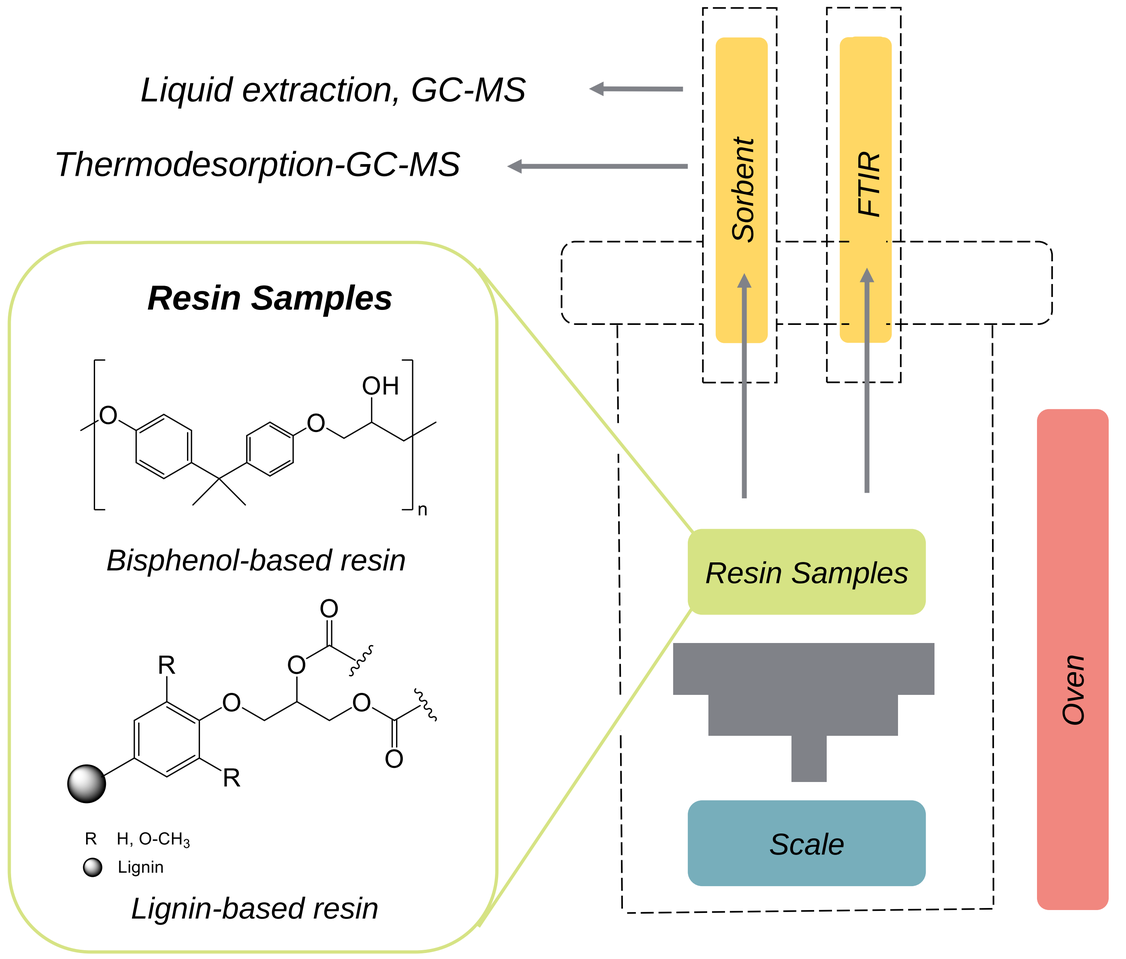

Figure 1. Thermal degradation study of thermosets (bisphenol- and lignin-based resin) by TGA-FTIR. Further investigations were performed by trapping gaseous substances with a sorbent and subsequent analysis by liquid extraction and GC-MS or thermodesorption-GC-MS.

Results

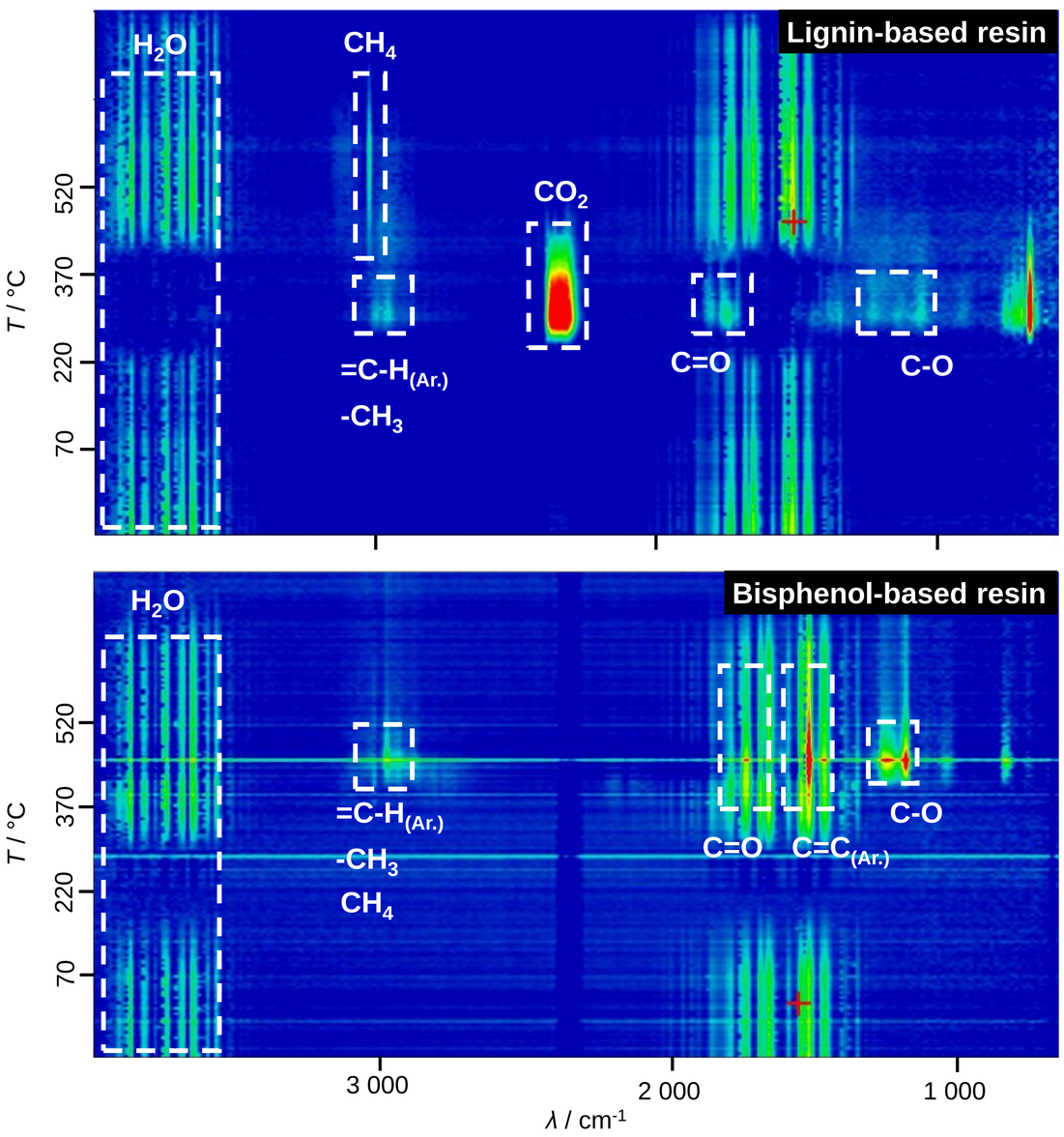

Figure 2. Thermal degradation study of thermosets (lignin-based resin and bisphenol-based resin) by TGA-FTIR between 30°C – 800°C under inert atmosphere.

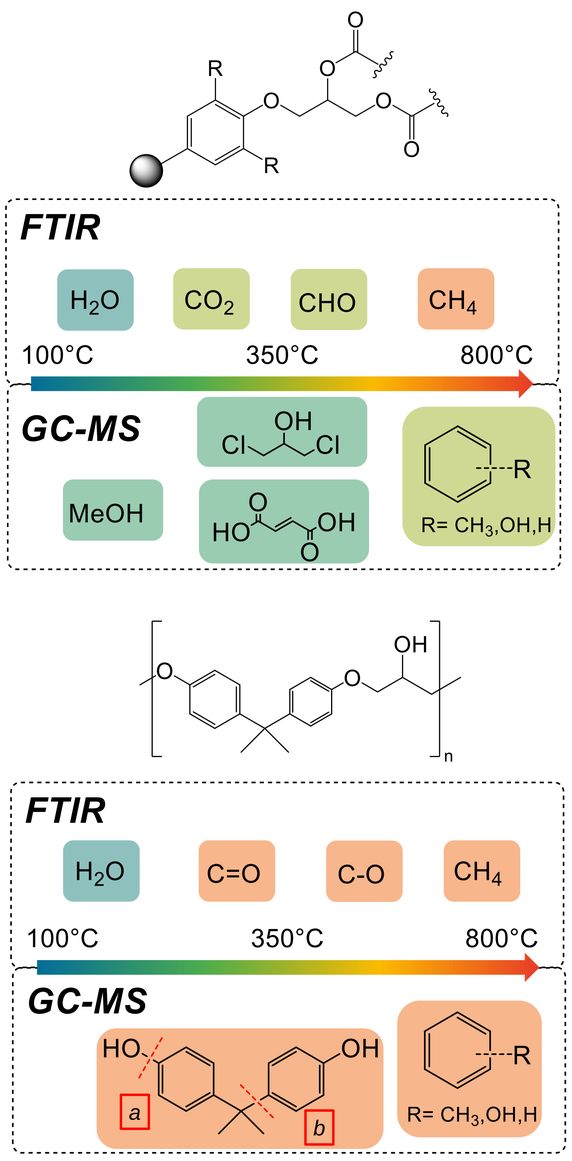

Figure 3. Assignment of degradation products from thermosets according to their temperature occurence with FTIR and GC-MS.

The degradation of the lignin-based resin can be defined by three major weight loss steps. In the first step (<200°C) C-O bonds are preferably broken and products like maleic acid and methanol are released. The second and highest mass loss (250°C – 350°C) involves the release of CO_2, aromatic hydrocarbons, phenolic compounds and aldehydes, coming from the degradation of polymeric monolignols. Methane is released above 400°C and can be mainly assigned to the degradation of methyl groups. Although small, volatile compounds can be determined *via* FTIR (Figure 2 - 3), the qualitative assignment of aromatic structures was mainly done with GC-MS (Figure 3).

While the amorphous and highly branched structure of lignin leads to continuous thermal cleavages, the structure of the bisphenol-based resin degrades in one major step. Here carbonyl rich functionalities, like aldehydes, but also degradation products (Figure 3a and 3b) of monomeric bisphenol A can be assigned by GC-MS (Figure 3). Compared to the branched monolignols, monomeric bisphenol A shows a higher thermal stability and therefore prevents the formation of smaller gaseous compounds.

Conclusion

With this method, the identification and temperature dependent occurrence of products stemming from thermal degradation processes of lignin- and bisphenol-based resins can be shown. Overall, lignin-based resins show a three-step degradation with a high content on small gaseous molecules like CO_2 or CH_4, while the bisphenol-based resins degrade in one step, releasing mostly compounds from partially cleaved monomeric bisphenol A.

References

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[2] Verdross P., Guinchard S., Woodward R.T., Bismarck A., Black liquor-based epoxy resin: Thermosets from untreated kraft lignin, *Chemical Engineering Journal*, (**2023**), *475*, 145787