

Effect of Suberin Depolymerization Conditions on the Flammability and Thermal Stability of Rigid Polyurethane Foams

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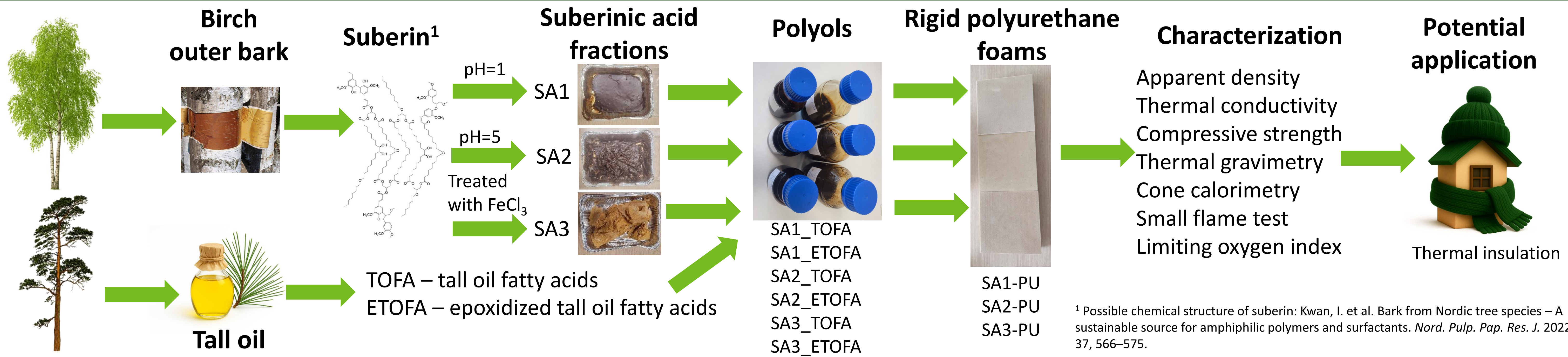
Introduction

- Suberin, a natural polyester abundant in birch bark, represents a promising renewable feedstock for the development of bio-based polymeric materials.
- The suberin depolymerization conditions (e.g., pH) can influence the composition and properties of the resulting suberinic acids, including their total phenolic content.
- Since phenolic compounds are known to affect thermal stability and flame resistance, variations in suberinic acid composition could impact the performance of polyurethane foams derived from suberinic-acid based polyols.

Hypothesis

- **Polyphenolic content of suberinic acids may affect flame resistance and thermal stability of rigid polyurethane foams derived from suberinic acids-based polyols.**

Experimental design



Results

Suberinic acid fractions

Three suberinic acid fractions were obtained under different conditions:

- SA1 (precipitated at pH=1),
- SA2 (precipitated at pH=5),
- SA3 (treated with FeCl₃).

SA fractions were characterized by dry mass content, yield, acid value, and total phenolic content (TPC) estimated from the Py-GC/MS/FID analysis.

Sample	Dry mass content, %	Yield, %	Acid value, mg KOH/g	TPC, %
SA1	32.5±0.7	50.5±1.7	90±3	3.84
SA2	46.4±0.9	46.2±1.2	90±3	2.71
SA3	74.2±1.6	22.8±0.7	106±3	1.12

SA1 exhibited the highest TPC (3.84%), whereas SA3 showed the lowest (1.12%). In the case of SA3, treatment with FeCl₃ resulted in the isolation of both polyphenolic compounds and oligomeric fractions of SA. Consequently, the overall yield of SA3 was nearly two-fold lower than that of SA1.

Polyols

Two SA-based polyols were synthesized from each suberinic acid fraction—one using TOFA and the other using ETOFA— in combination with trimethylolpropane, resulting in a total of six polyols.

Polyol	H _a , mg KOH/g	OH _v , mg KOH/g	Water content, %	Viscosity, mPa·s
SA1_TOFA	7.3	248	0.020	6280
SA1_ETOFA	3.6	341	0.047	461000
SA2_TOFA	8.7	291	0.020	9250
SA2_ETOFA	5.9	406	0.010	286000
SA3_TOFA	6.9	291	0.012	3090
SA3_ETOFA	5.8	392	0.022	144000

Polyol stability was assessed visually; all were stable except SA2_ETOFA, which showed phase separation. Polyols from SA3 showed the lowest viscosity.

Rigid polyurethane foams

Formulations

Component	SAx-PU	Rigid polyurethane foam formulations followed the optimization reported by Ivdre et al. ² except that no flame retardant was added , allowing clearer evaluation of the polyols' effect on flammability. Polymeric methylene diphenyl diisocyanate content was adjusted to maintain NCO/OH ratio 1.2 .
SAx_TOFA	67	
SAx_ETOFA	33	
Total water	0.5	
PC CAT TKA 30	0.5	
Polycat NP10	1.55	
L-6915	2.5	
Opteon 1100	24.3	

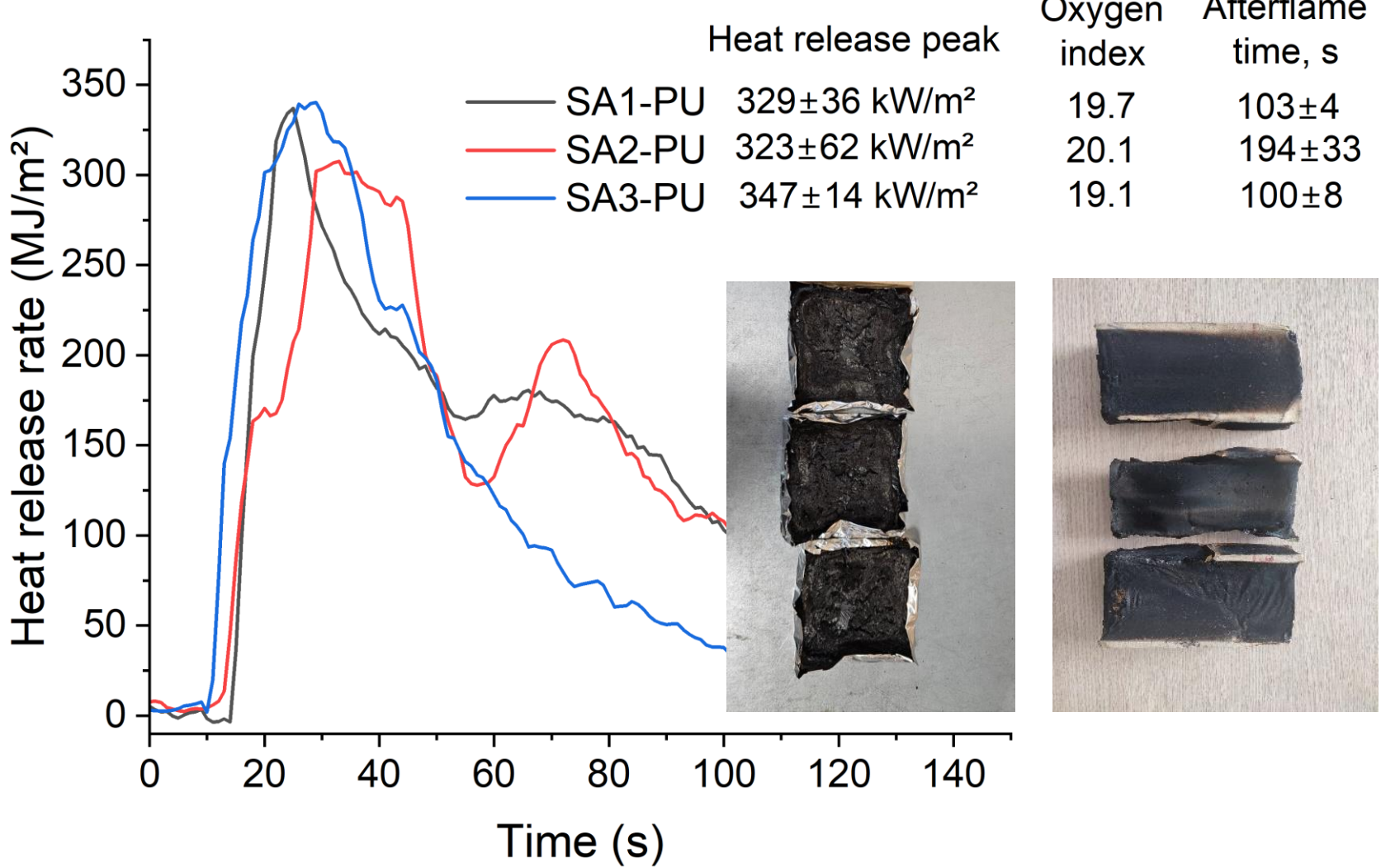
² Ivdre, A. et al. Rigid polyurethane foams from polyols based on depolymerized suberin and tall oil fatty acids. *Polymers* 2024, 16, 942.

Overall characterization

	SA1-PU	SA2-PU	SA3-PU
Suberinic acid content, %	16.7	15.7	15.5
Total renewable material content, %	33.6	31.5	31.3
Foaming start time, s	45	36	26
Foam gel time, s	135	64	110
Foam rise time, s	188	89	119
Shrinkage, %	5.6	0.3	1.2
Apparent density, kg/m ³	45	42	40
Compressive strength parallel to foaming direction, MPa	0.19	0.23	0.24
Thermal conductivity, mW/(m·K)	20.6	19.9	20.5

Flammability

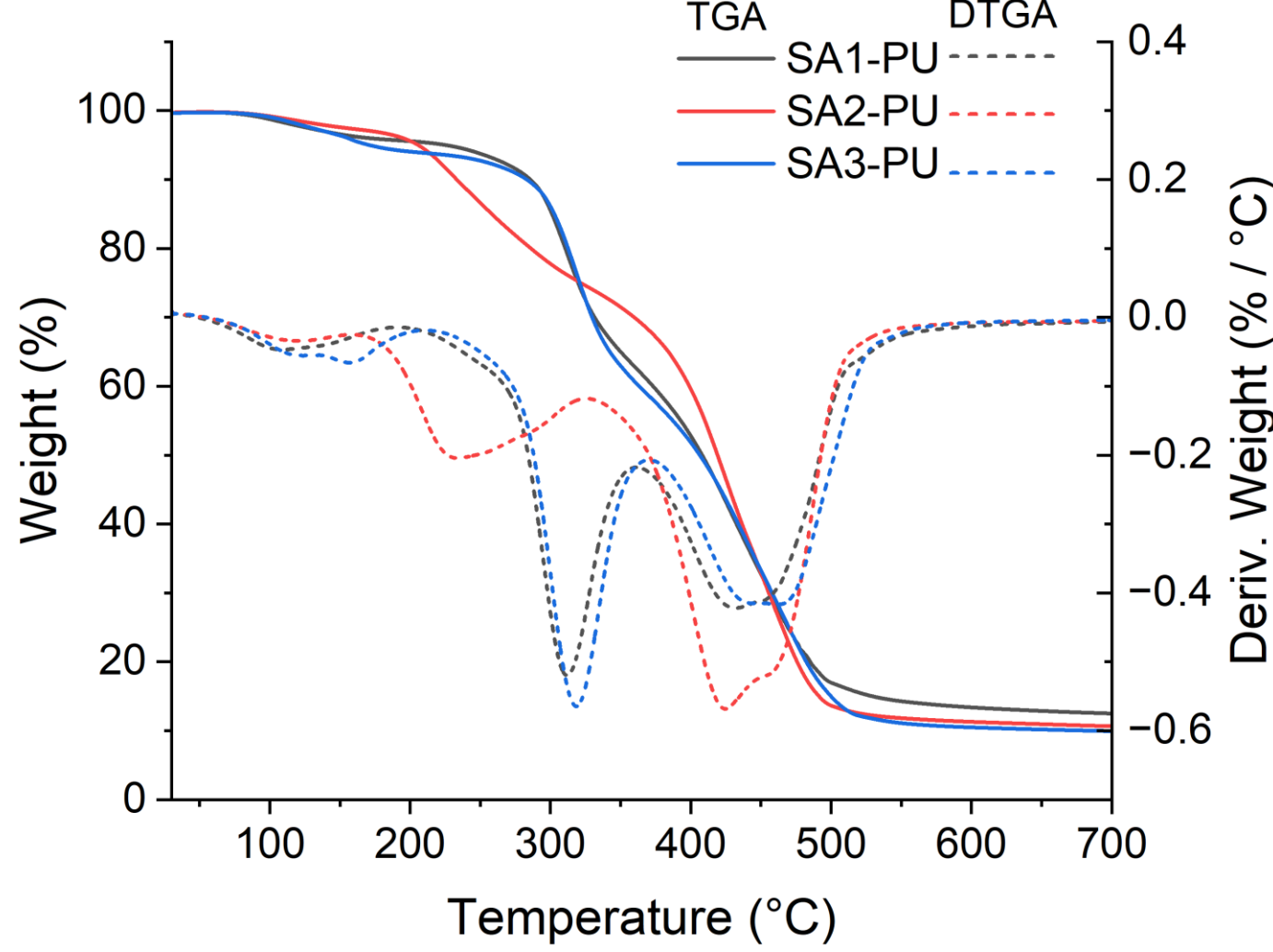
The flammability of rigid polyurethane foam samples was analyzed using the small flame test, the cone calorimeter, and the limiting oxygen index.



The results indicated no significant differences in flammability among the samples. The small flame test was inconclusive, as all samples ignited along their full length. Heat release peaks were consistent within the experimental error, and the measured oxygen indices were comparable, ranging from 19 to 20.

Thermal stability

Thermogravimetric analysis (TGA) and its derivative (DTGA) were used to assess the thermal stability of the polyurethane foam samples.



The SA2-PU sample exhibits an earlier onset of the second degradation stage, beginning at approximately 120 °C, with the corresponding DTGA peak maximum observed at around 280 °C. This behaviour suggests a comparatively lower thermal stability in this region compared to both the SA1-PU and SA3-PU samples.

Conclusions

- ✗ **Hypothesis not confirmed:** Although TPC differed among suberinic acid fractions, no significant differences in flammability were observed for rigid PUR foams derived from SA1, SA2, and SA3.
- ✓ **Selection criteria beyond flammability:**
 - ✗ **SA2_ETOFA polyols:** showed phase separation → unsuitable.
 - ✗ **SA2-PU:** lower thermal stability.
 - ✓ **SA3_TOFA and SA3_ETOFA polyols:** lower viscosity → easier processing.
- ✓ **Total renewable content:** Rigid polyurethane foams reached ~32% renewable content.
- ✓ **Decision for further experiments:** The SA3 fraction was chosen for further studies on rigid polyurethane foam flammability.

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