

# POLYURETHANE ADHESIVES BASED ON LIGNIN OXYPROPYLATED VIA REACTION WITH PROPYLENE CARBONATE

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## Introduction

In the last decades, due to social concerns regarding sustainability and the imminent depletion of fossil resources, renewable precursors for polyurethane (PU) synthesis have been extensively investigated. Conventionally, PUs are synthesized via reaction between polyols and diisocyanates, mostly petroleum-based raw materials. In this context, lignin, an aromatic biopolymer found in plants, has been showing a huge potential as polyol. Several works successfully synthesized lignin-based PU<sup>1-3</sup>. However, the use of lignin as the only polyol in PU formulations is discouraged, since it results in material with high brittleness. Therefore, lignin is usually blended with petroleum-based polyols<sup>2</sup> or vegetable oils, as castor oil<sup>1</sup>. Furthermore, the lignin reactivity towards isocyanate is commonly improved by chemical modifications. The most used modification route is the oxypropylation with alkylene oxides (ethylene and propylene oxides), which was first studied by Wu and Glasser in the 1980's<sup>4</sup>. Nevertheless, alkylene oxides are flammable, toxic, and carcinogenic. In order to replace these reagents for more sustainable ones, Kühnel et al.<sup>5</sup> investigated the lignin oxypropylation via reaction with propylene carbonate (Figure 1), a compound with low toxicity and high boiling point. According to the researchers, lignin oxypropylated by this alternative route has potential as a polyol in PU synthesis. However, there are no reported studies that have used it for this purpose yet.

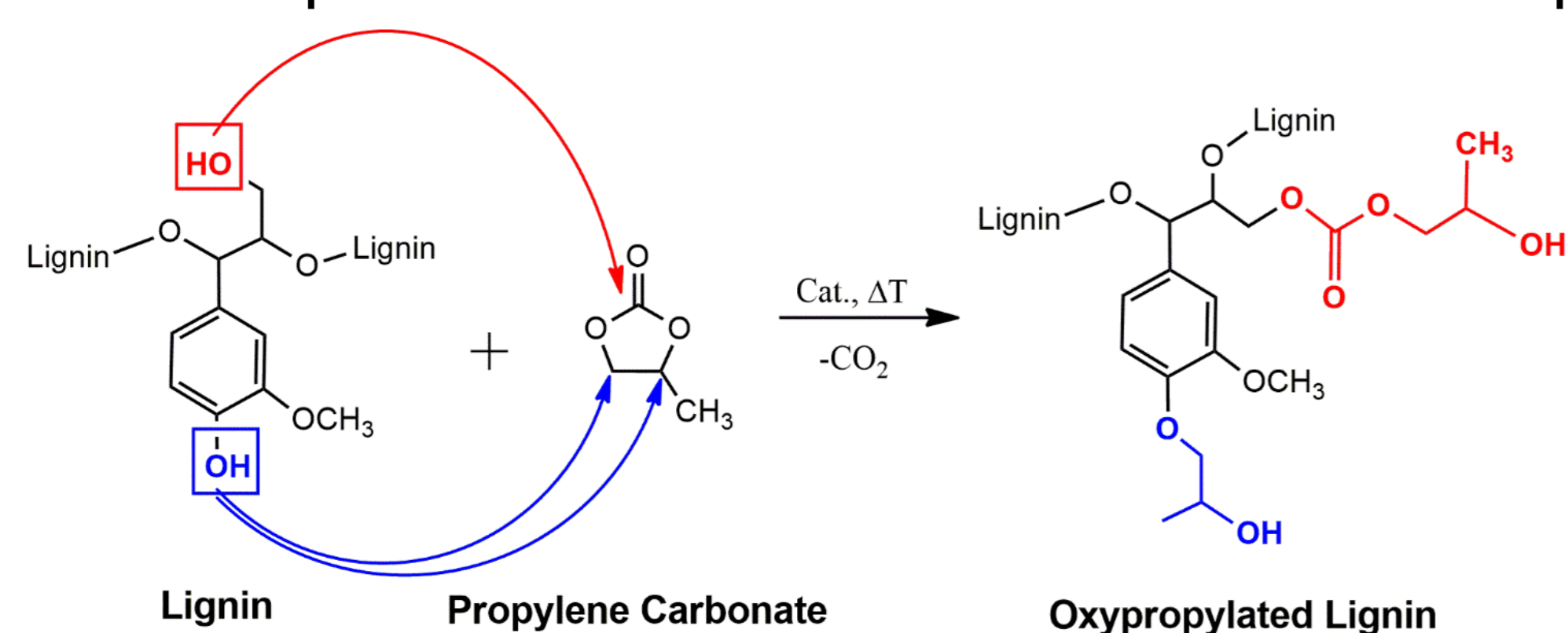


Figure 1. Lignin oxypropylation with propylene carbonate

In the present work, for the first time, Kraft lignin oxypropylated with propylene carbonate was employed as a polyol in PU adhesives formulations. Castor oil was also used as polyol. The curing kinetics, mechanical properties and adhesion performance of the lignin-based adhesives, as well as the influence of lignin concentration on these properties, were evaluated.

## Experimental

**Lignin modification:** Kraft Lignin was dissolved in propylene carbonate. To this solution, catalyst (1,8-Diazabicyclo[5.4.0]undec-7-ene or simply DBU) was added. The mixture was kept at 170 °C under stirring in N<sub>2</sub> atmosphere for 3 h. The reaction mixture was cooled to room temperature, and then, added to an aqueous solution of HCl. The result solution was vacuum-filtered, and washed five times with distilled water. The solid residue was dried in an oven at 40 °C for 24 h.

**Chemical characterization of modified lignin:** Fourier-transform Infrared Spectroscopy (FTIR), <sup>31</sup>P Nuclear Magnetic Resonance Spectroscopy (NMR)

**Adhesives preparation:** Modified lignin (HKL\_PC) and castor oil (CO) were mixed in three different mass concentration (CO/HKL\_PC = 70/30, 80/20 and 90/10). The polyols mixture were mixed with MDI (NCO:OH = 1.2) for 3 minutes. The adhesives were cured in an oven at 60 °C for 6 h.

**Study of curing kinetics:** Temperature Modulated Optical Refractometry (TMOR).

**Thermomechanical analysis:** Uniaxial tensile test (five specimens for each condition), Dynamic Mechanical Analysis (DMA).

**Practical adhesion:** Single-lap shear test (three specimens for each condition). Evaluated substrates: wood, PU and steel. An adhesion promoter, 3-Glycidyloxypropyltrimethoxysilane, was used for steel substrate.

## Results

### Lignin chemical characterization:

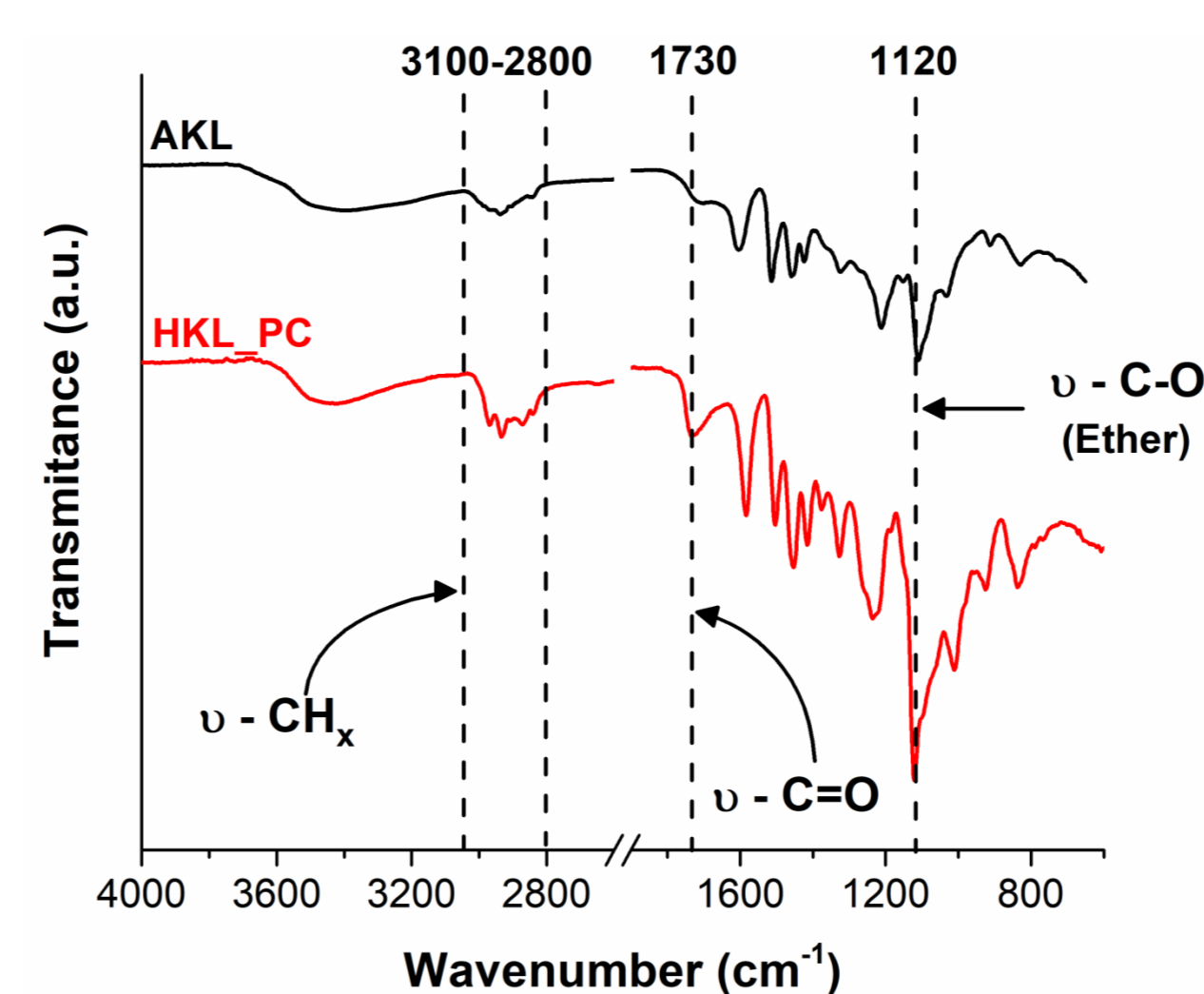
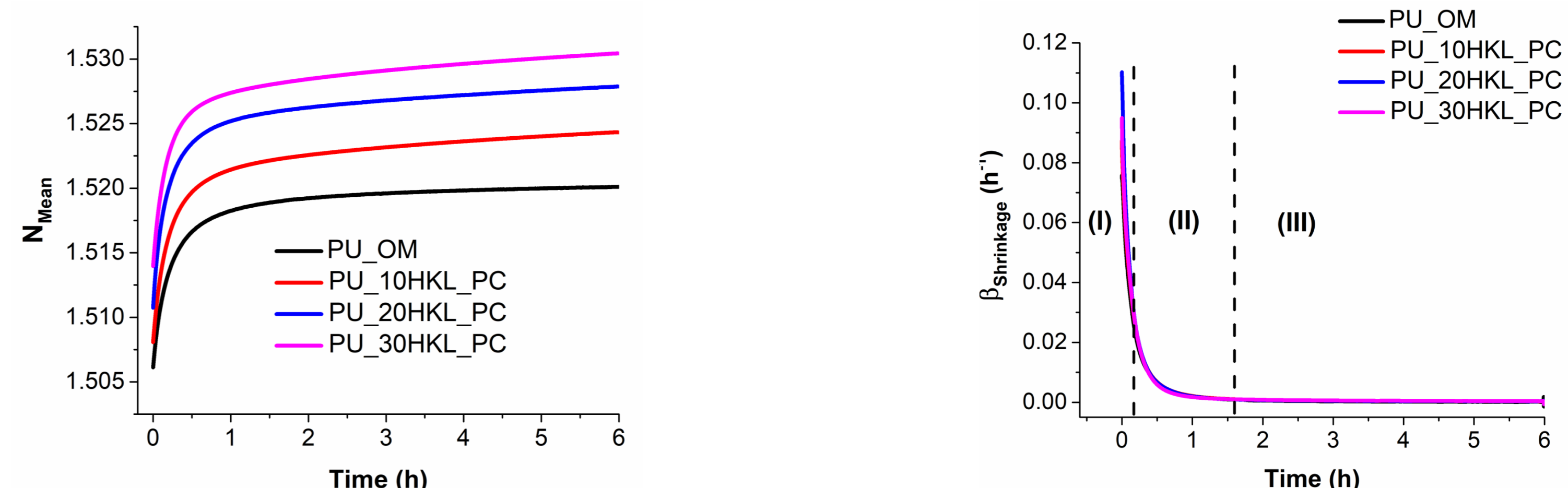


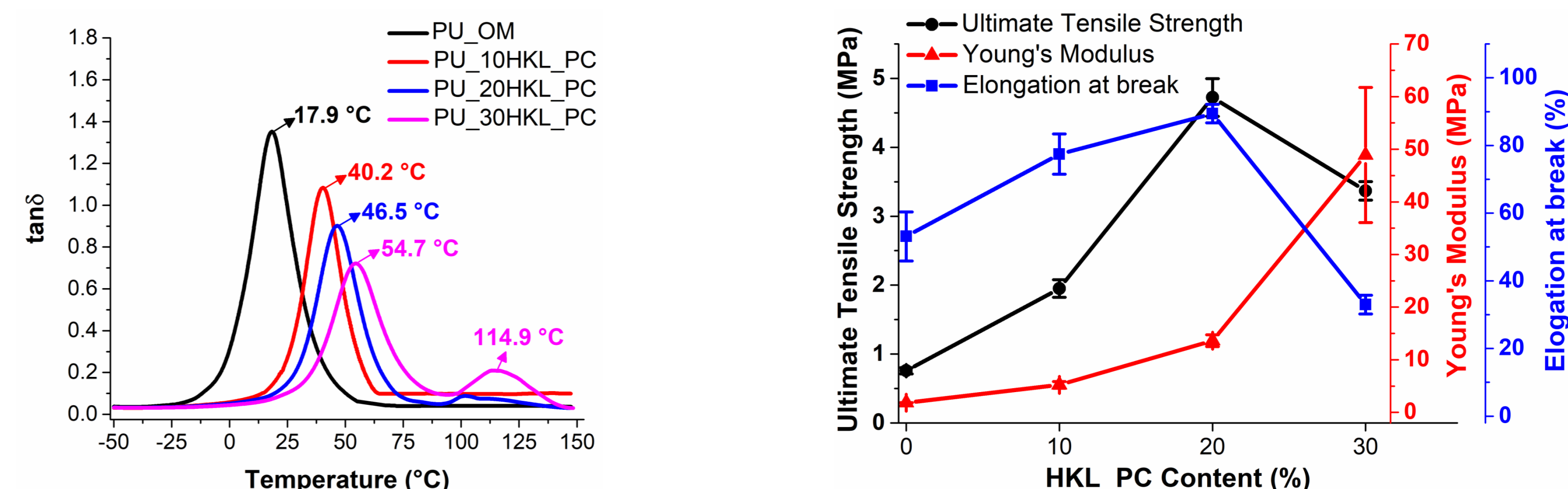
Table 1. <sup>31</sup>P NMR results.

Lignin Sample	Aliphatic OH (mmol.g <sup>-1</sup> )	Phenolic OH (mmol.g <sup>-1</sup> )				Total
		Syringyl	Condensed Guaiacyl	Non-condensed Guaiacyl	p-Hydrofenil	
AKL	1.00	2.05	1.07	0.90	0.13	4.15
HKL_PC	3.08	0.00	0.00	0.00	0.00	0.00

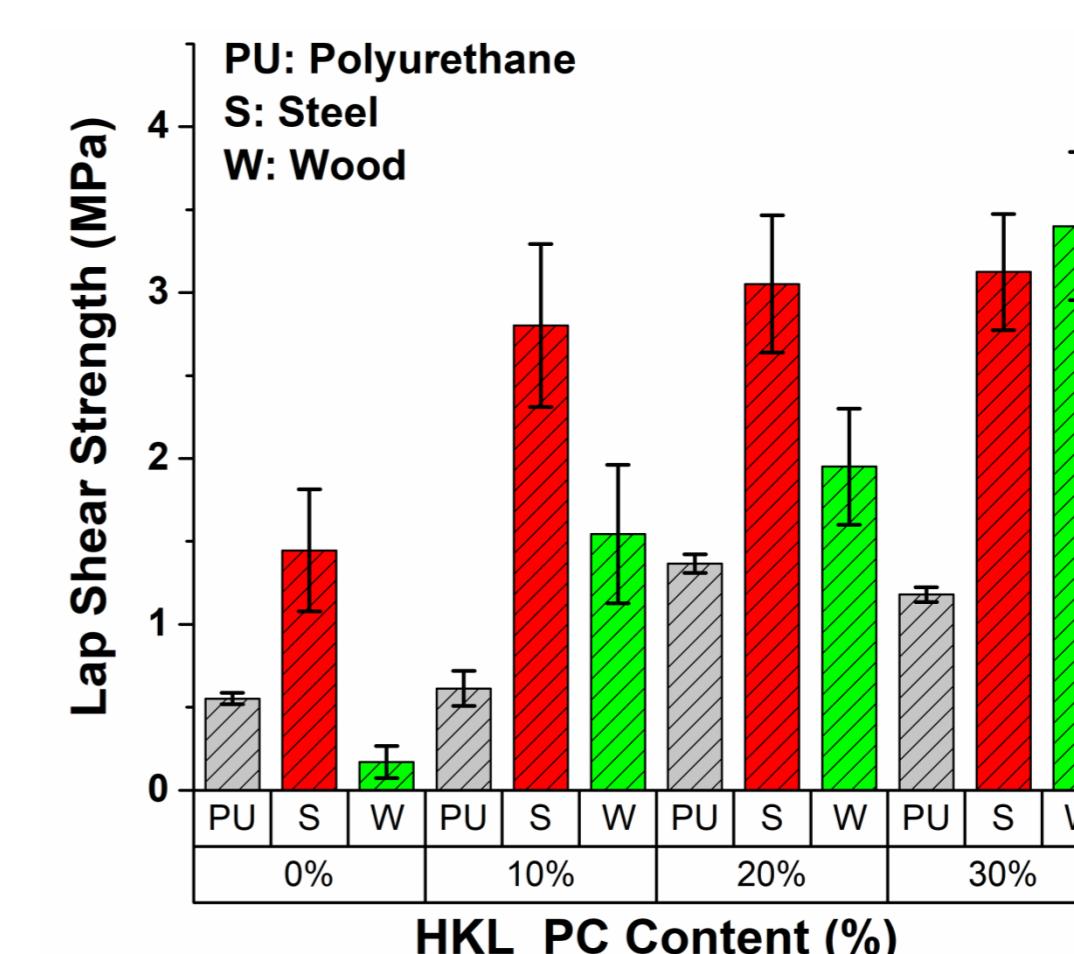
### Curing kinetics:



### Thermomechanical properties:



### Practical adhesion:



## Conclusions

- Kraft lignin was successfully modified;
- Lignin-based PU adhesives were successfully synthesized;
- Addition of lignin oxypropylated with propylene carbonate: no changes in adhesives curing kinetics, ↑ T<sub>g</sub>, and improved mechanical properties and adhesion performance;
- ↑ wt% lignin ⇒ ↑ T<sub>g</sub>, ↑ Young's modulus, ↑ UTS\*, ↑ Elongation at break\* and ↑ adhesion performance\* ; (\*except for 30 wt% formulations)
- > 20 wt% ⇒ Phase separation ⇒ ↓ UTS, ↓ Elongation at break and ↓ adhesion performance (PU and steel).

## References

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