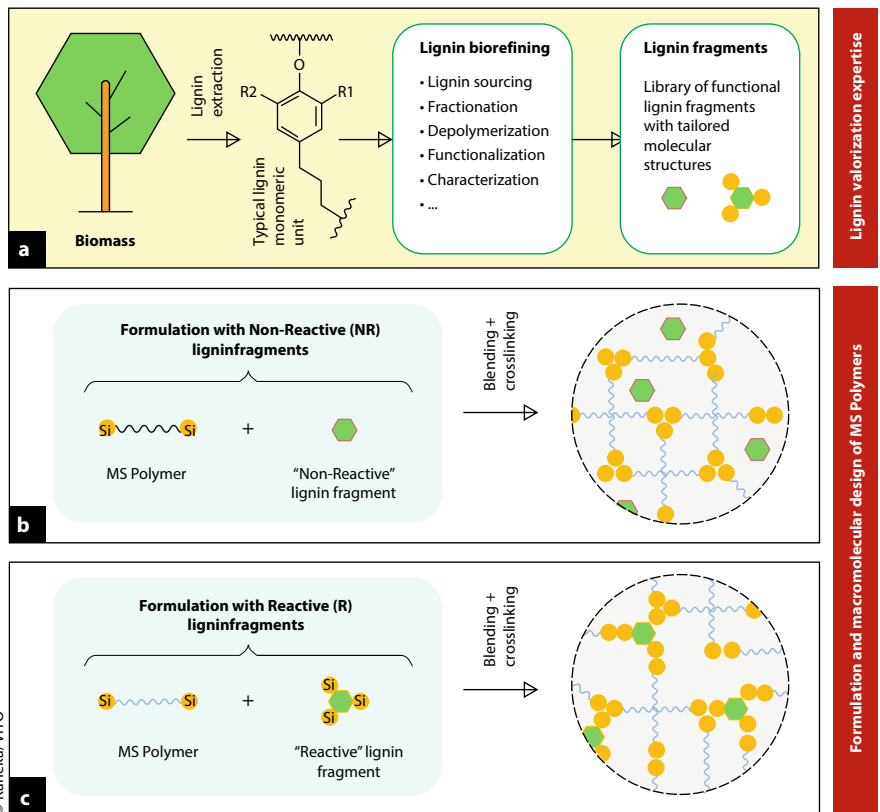


Improving the Thermal Stability of MS Polymers with Lignin Fractions

In this work, partly bio-based MS polymer products were developed by blending tailored lignin-based molecules into MS polymer. It is shown that not only the mechanical properties could be tuned by introducing these lignin fragments, but also the thermal stability of the polymer blends and the resulting adhesive formulations can be strongly improved.

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MS (Modified Silicone) polymer are a class of polymers exhibiting a long middle poly-ether section functionalized by silyl terminal groups. MS polymer are used in sealants, adhesives, or coatings with a variety of commercial applications, for example in the building and construction, transportation, do-it-yourself and flooring industry. In the presence of moisture and a catalyst, MS polymer cure at room temperature into a rubbery product by hydrolysis and condensation of the reactive silyl groups. MS polymer based sealants and adhesives have intrinsically good characteristics, such as adhesion on a wide range of substrates, flexibility, and ease of handling. In addition, MS polymer provide environmentally friendly alternatives to existing technologies, since they are solvent-, plasticizer- and isocyanate-free, and provide very low emissions.

A key trend in the industry is the growing demand for (more) eco-responsible materials, such as bio-based polymers, additives, or formulations [1] [2]. Lignin is a natural biopolymer, usually contributing to lignocellulosic biomass in a range of 20-30%. It is the second most abundant biopolymer on earth after cellulose. Lignin is available as a by-product of the pulping process of the paper industry, but is still

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Component		Formulation			
		1	2	3	4
Base polymer	MS Polymer	100	95	95	95
Bio-additive	Lignin monomer-NR		5		
	Lignin dimer-NR			5	
	Lignin oligomer-NR				5
M50	MPa	0.22	0.20	0.20	0.13
M100	MPa	0.34	0.31	0.31	0.20
Tb	MPa	0.42	0.40	0.44	0.39
Eb	%	143	148	166	262
ΔT_{onset} (DSC)	$^{\circ}\text{C}$	/	0	10	19

Table 1 > Tensile properties and thermal stability of MS Polymer and its blends with different non-reactive lignin fragments.

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too often insufficiently valorized [3] [4] [5] [6]. It is therefore not a surprise that the utilization of lignin as an alternative feed-stock in value-added applications such as bio-additives is attracting growing attention from both academia and industry.

Procedure

A key challenge to use lignin as additive is its notorious incompatibility with many common polymers such as nonpolar rubber matrices, forming large agglomerates due to strong lignin self-interactions [7] [8] [9] [10]. To obtain a good miscibility with MS polymer, the lignin was first fractionated or depolymerized into lower molecular weight fragments, which were then modified with different functional groups. The following two approaches were used for the modification (*Figure 1*):

1. Functionalization of the lignin fragments with non-reactive silyl groups. These fragments can be physically blended with MS polymer into a compound and will not react with the MS polymer during the curing process.
2. Functionalization of the lignin fragments with reactive silyl groups. After blending with MS polymer, these fragments can form crosslinks with it and will thus be chemically bonded to the MS polymer chains.

Blending of MS polymer with non-reactive (NR) lignin fragments

Three lignin fractions with different molecular weights were considered in this study: a lignin-based oligomer ($M_w = 1150\text{g/mol}$), a lignin dimer ($M_w = 330\text{g/mol}$), and a lignin monomer ($M_w = 166\text{g/mol}$). These three fractions were all silylated with non-

reactive silyl groups and blended with MS polymer in a weight ratio of MS polymer/lignin = 95/5.

The tensile properties of the MS polymer and the different blends are shown in *Table 1*. While the tensile properties remain similar after blending with the lignin monomer and dimer, blending with the lignin oligomer results in a decrease in modulus and increase in elongation. To evaluate the thermal stability, DSC measurements of the cured samples were performed and the temperature at which thermal degradation starts (T_{onset}) was determined. *Table 1* shows the increase in onset temperature (ΔT_{onset}) compared to pure MS polymer as a reference. Blending with both the lignin dimer and oligomer results in a significant increase in T_{onset} .

Blending of MS polymer with the non-reactive lignin oligomer has the positive effect of increasing the heat stability of a formulated sample, as confirmed by preparing a general purpose adhesive formulation. As shown in *Figure 2*, the decrease in hardness of the cured adhesive when stored at 120°C slows down when the lignin oligomer is present.

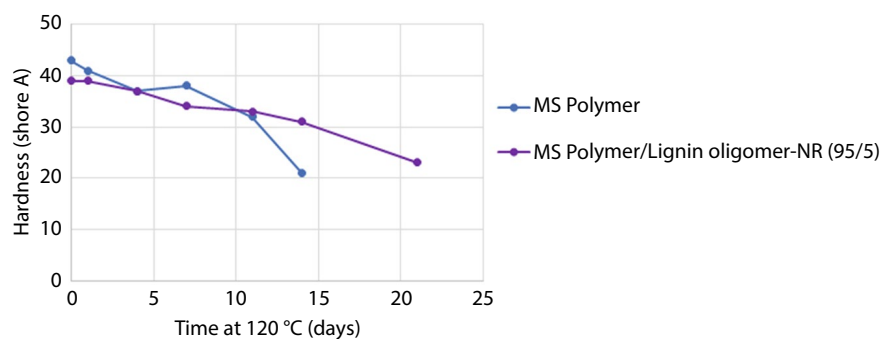


Figure 2 > Thermal stability at 120°C of a general purpose adhesive formulation based on MS polymer and its blend with a non-reactive lignin oligomer.

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Component		Formulation						
		1	2	3	4	5	6	7
Base polymer	MS Polymer	100	95	90	95	90	95	85
Bio-additive	Lignin monomer-R		5	10				
	Lignin dimer-R				5	10		
	Lignin oligomer-R						5	15
M50	MPa	0.22	0.18	0.12	0.19	0.16	0.28	0.35
M100	MPa	0.34	0.27	0.18	0.29	0.25	-	-
Tb	MPa	0.42	0.49	0.40	0.49	0.41	0.41	0.43
Eb	%	143	236	297	219	207	91	66
ΔT_{onset} (DSC)	°C	/	22	25	53	60	21	33

Table 2 > Tensile properties and thermal stability of MS Polymer and its blends with different reactive lignin fragments.

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with reactive lignin fragments results in a strong increase in thermal stability. The latter effect is clearly more pronounced with the reactive lignin fragments, compared to blending with non-reactive lignin fragments (Table 1).

A general purpose adhesive formulation was prepared with the blends to evaluate whether the reactive lignin fragments also show a stronger positive effect on the heat stability of a formulated sample. Figure 3 shows the decrease in hardness of the cured adhesive when stored at 120 °C. Although the reactive lignin monomer does not affect the thermal stability of the formulation after blending in a MS polymer/lignin ratio of 95/5, the formulations with the reactive lignin dimer and oligomer clearly show an improved thermal stability. When the MS polymer/lignin ratio is changed to 85/15, the thermal stability even becomes drastically better, certainly in case of the reactive lignin dimer.

To further clarify the potential for applications which require a high thermal stability, the thermal stability test was repeated at temperatures of 150, 180, 200 and 230 °C (Figure 4). The pure MS polymer

formulation was evaluated both with the standard quantity of Irganox 245 of 1 phr and with an increased quantity of 3 phr. This however has a negligible effect on the thermal stability. Also the blending of MS polymer with the reactive lignin oligomer does not show any significant effect on the thermal stability of the formulation at these higher temperatures. On the other hand, blending with the reactive lignin dimer generates a very temperature stable product. In a system with a blending ratio of 85/15 (MS polymer/reactive lignin dimer), the time for which the hardness remains stable at the different temperatures is, on average, even four times longer than in the pure MS polymer system.

Conclusions

High performance, partly bio-based MS polymer products can be obtained by blending MS polymer with molecularly-engineered lignin-based fragments. The lignin fragments can be functionalized to be either non-reactive or reactive with MS polymer. As shown in the data, the mechanical properties and thermal stability

of the products are influenced both by the molar mass of the lignin fragment and by the type of functionalization used. Particularly the reactive lignin dimer shows a high potential for strongly improving the thermal stability of MS polymer based systems, which results in the possibility to broaden the application area of MS polymer. In addition to the increased thermal stability, other functional advantages that could potentially be expected from tailored lignin additives include UV stability, anti-oxidant activity or even flame retardancy. //

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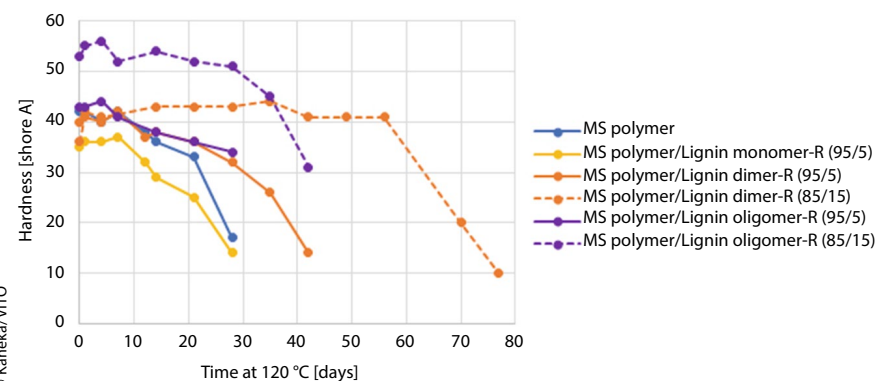


Figure 3 > Thermal stability at 120 °C of a general purpose adhesive formulation based on MS polymer and its blends with different reactive lignin fragments.

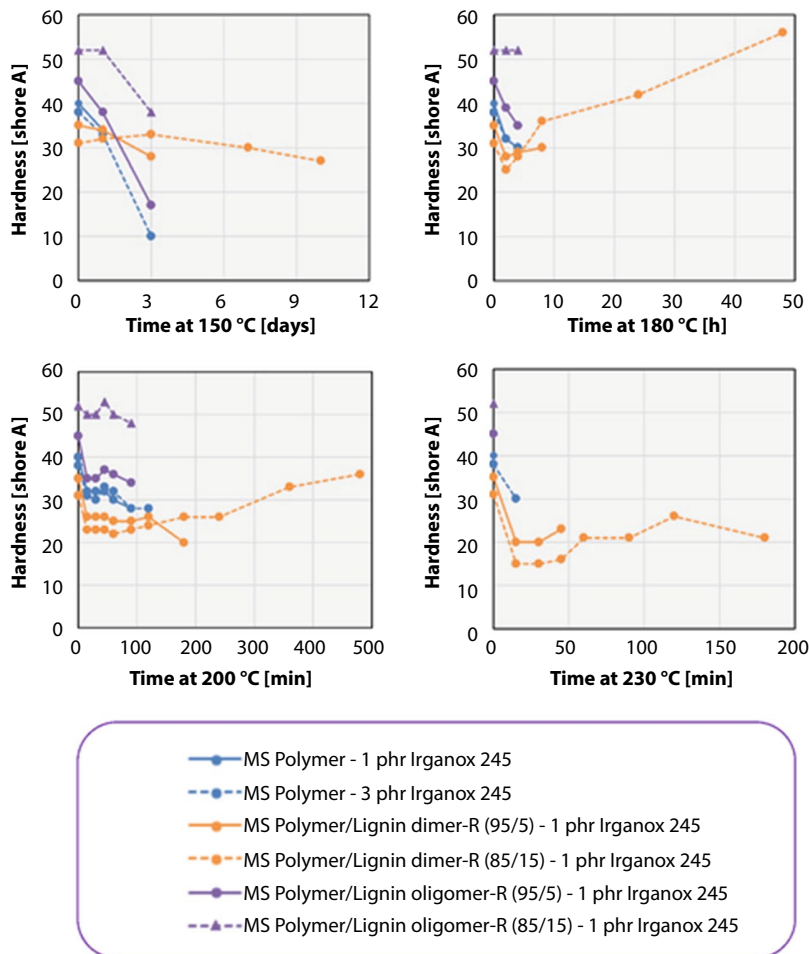


Figure 4 > Thermal stability at 150, 180, 200 and 230 °C of a general purpose adhesive formulation based on MS polymer and its blends with different reactive lignin fragments.

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