Application Development for Kraft Lignin and Waste Cooking Oil-Based Epoxy Asphalt

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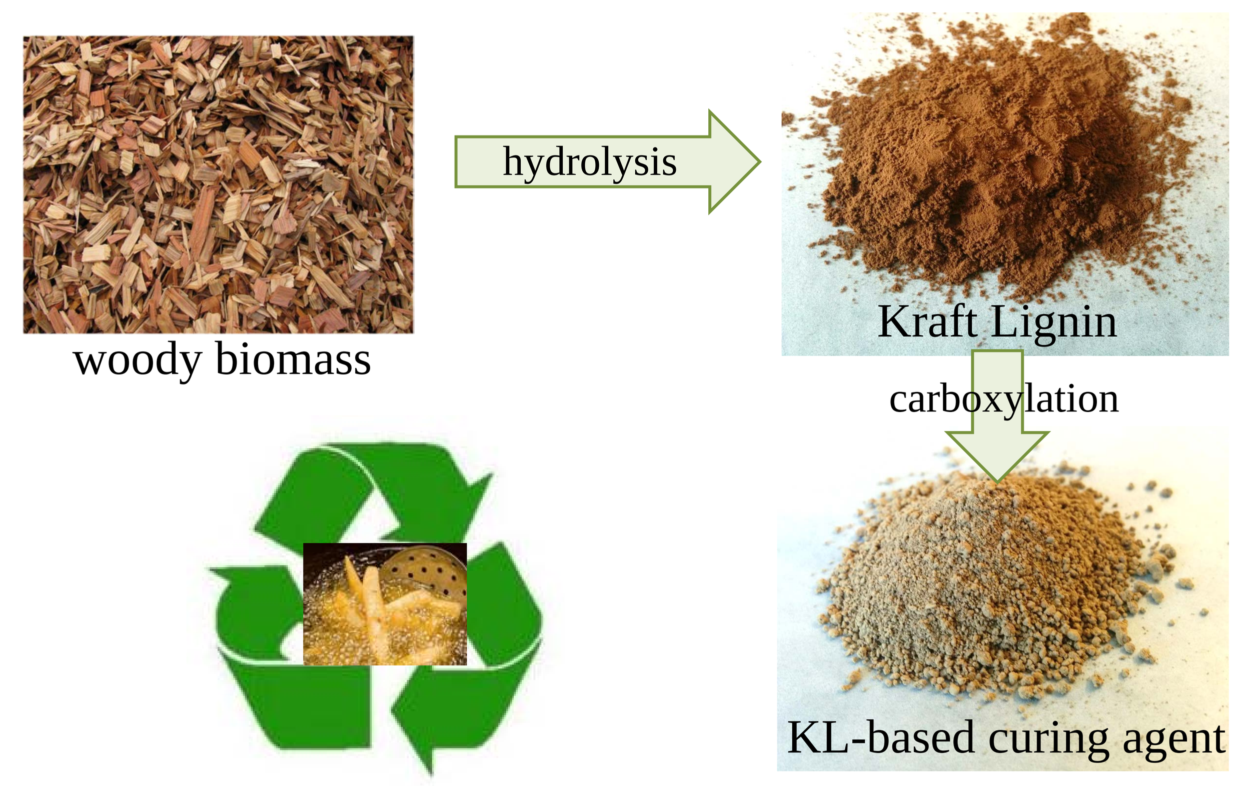
Introduction



In this project, asphalt was modified with Kraft lignin (KL) and waste cooking oil (WCO) based epoxy resin.

Procedure

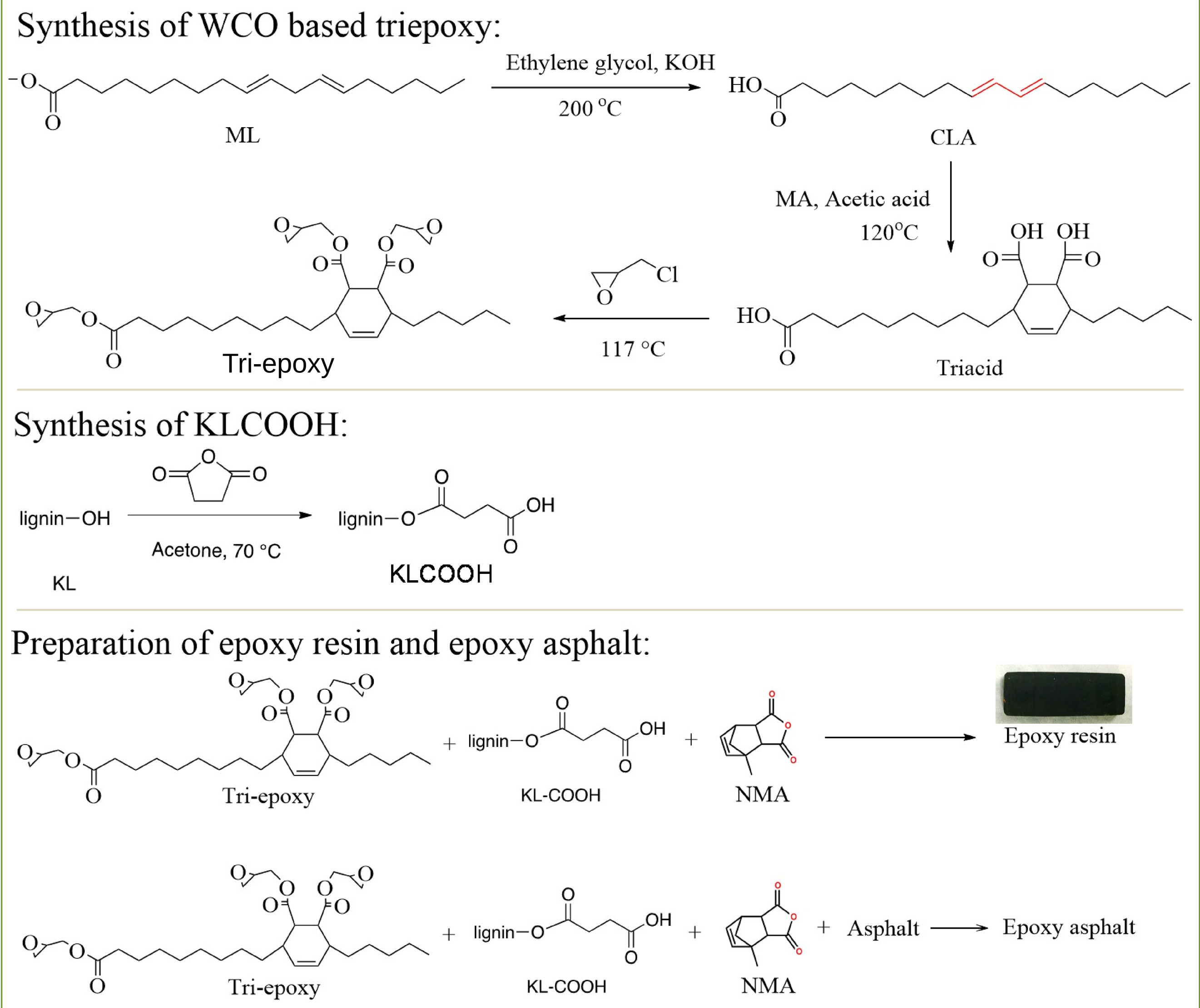


Figure 1: Reaction scheme for preparation of WCO-based epoxy, KLCOOH, epoxy resins, and epoxy asphalt binders.

1. The WCO based triepoxy and Kraft lignin based curing agent (KLCOOH) were prepared according to the reaction scheme shown in Figure 1.
2. The triepoxy and curing agent (KLCOOH and co-curing agent NMA) were combined in a 1/1 molar ratio and cured at 150 °C for 2 hrs., then 200 °C for 1 hr. 2-ethyl-4-methylimidazole was added as a catalyst. Different molar ratios of KLCOOH to NMA (0/1 and 2/1) were investigated.
3. The cured epoxy resins were analyzed with differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and thermogravimetric analysis (TGA) to evaluate the non-isothermal curing behavior, dynamic mechanical properties, and thermal stability, respectively.
4. Epoxy asphalt binders were prepared with different epoxy resin content: 7.5% or 15% by weight.
5. Epoxy asphalt binders were analyzed with a parallel plate rheometer. Frequency sweep tests and temperature sweep tests were conducted.

Results

Table 1: Hydroxyl values of KLCOOH and KL determined by ^{31}P NMR.

	Hydroxyl value (mmol/g)		
	Aliphatic	Aromatic	Carboxylic
KL-COOH	0	0.89	3.30
KL	2.45	5.14	0.51

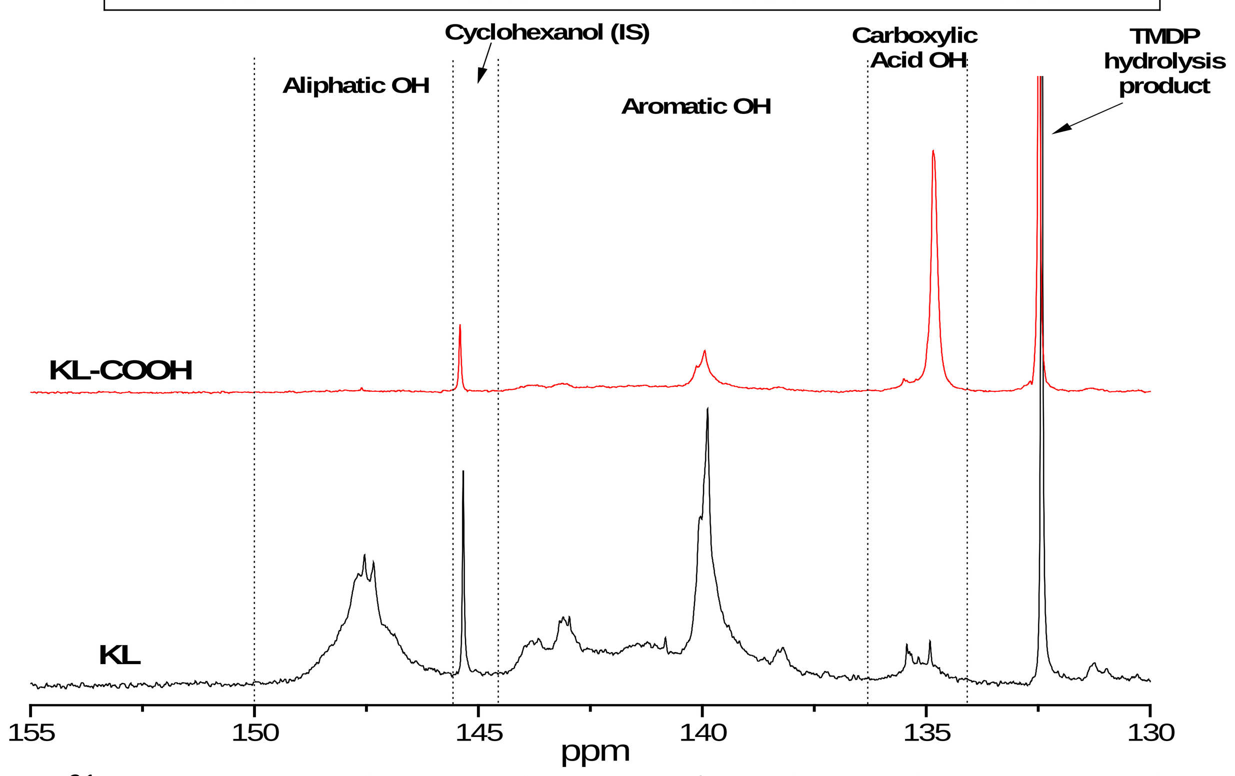


Figure 2: ^{31}P NMA spectra for KL and KLCOOH (cyclohexanol as an internal standard).

KL primarily contains aliphatic and aromatic hydroxyl groups, while KLCOOH primarily contains carboxylic hydroxyl groups. The carboxylation reaction successfully converted most of the hydroxyls in KL into carboxyl groups in KLCOOH.

Table 2: Fatty acid content of WCO, and theoretical and experimental epoxy values for WCO-based triepoxy.

Fatty Acid Content (%)					Epoxy Value (mmol/g)	
C16:0	C18:0	C18:1	C18:2	C18:3	Theoretical	Experimental
12.82	5.52	33.46	43.26	4.94	4.13	3.32

Linoleic acid (C18:2) and linolenic acid (C18:3) compose approximately 50% of the WCO fatty acid content. Only these fatty acids can be converted into triepoxy because the Diels-Alder reaction step in the triepoxy synthesis requires conjugated double bonds. The experimental epoxy value indicates 80.4% conversion of fatty acids to triepoxy.

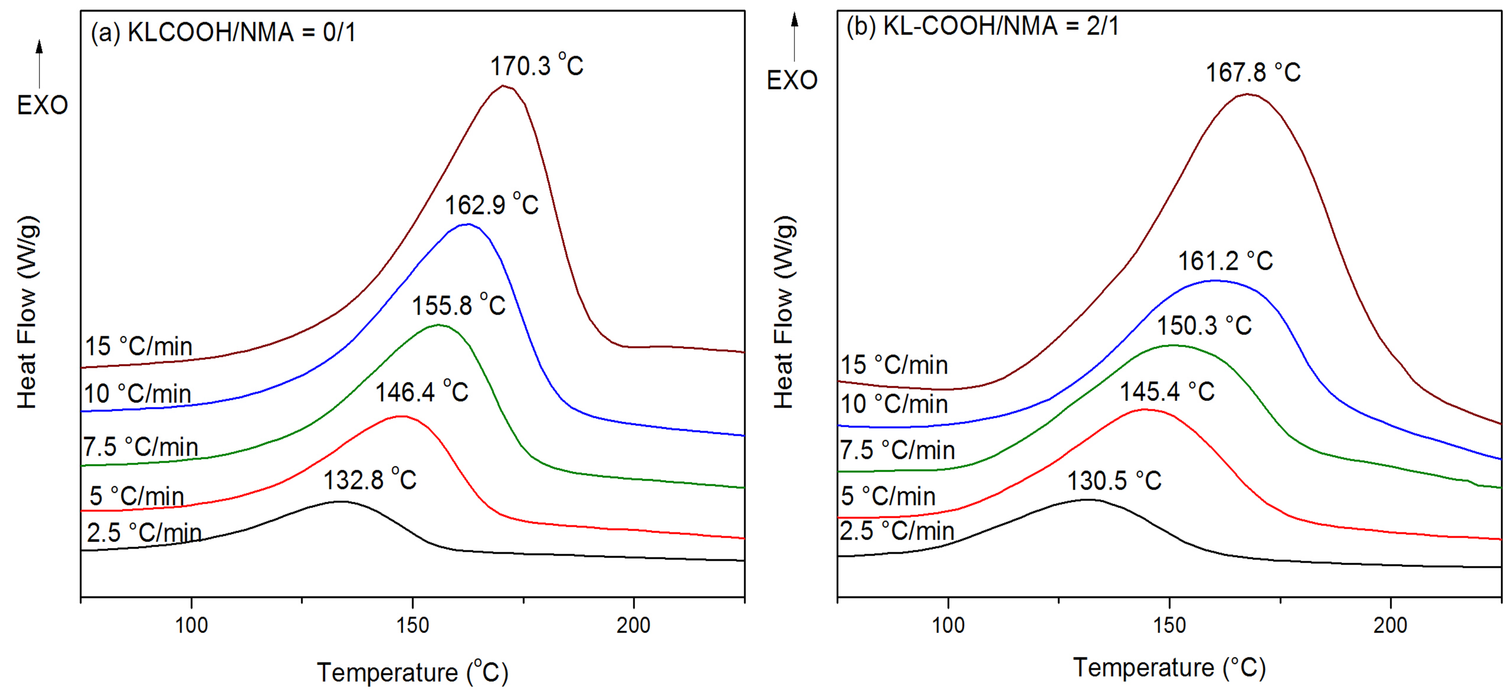


Figure 3: DSC heating curves for epoxy resin samples.

Each heating curve exhibits a single exothermic peak. For each sample, the peak temperature increases with higher heating rate. For each heating rate, the peak temperature is lower for epoxy resin with KLCOOH compared to epoxy resin with NMA only. This suggests that KLCOOH has greater reactivity with triepoxy than NMA.

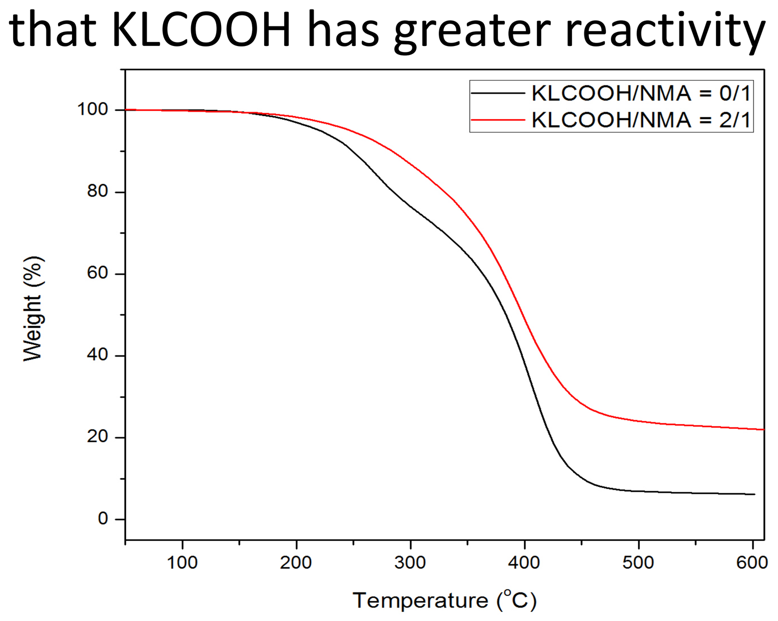


Figure 4: TGA curve illustrating changes in weight loss with temperature.

Compared to epoxy resin cured with only NMA, epoxy resin with a 2/1 ratio of KLCOOH to NMA exhibits less weight loss over a wide range of temperatures.

1. Xin, J.; Li M.; Li R.; Wolcott, M. P.; Zhang, J. Green Epoxy Resin System Based on Lignin and Tung Oil and Its Application in Epoxy Asphalt. *ACS Sustainable Chem. Eng.* **2016**, *4*, 2754-2761.

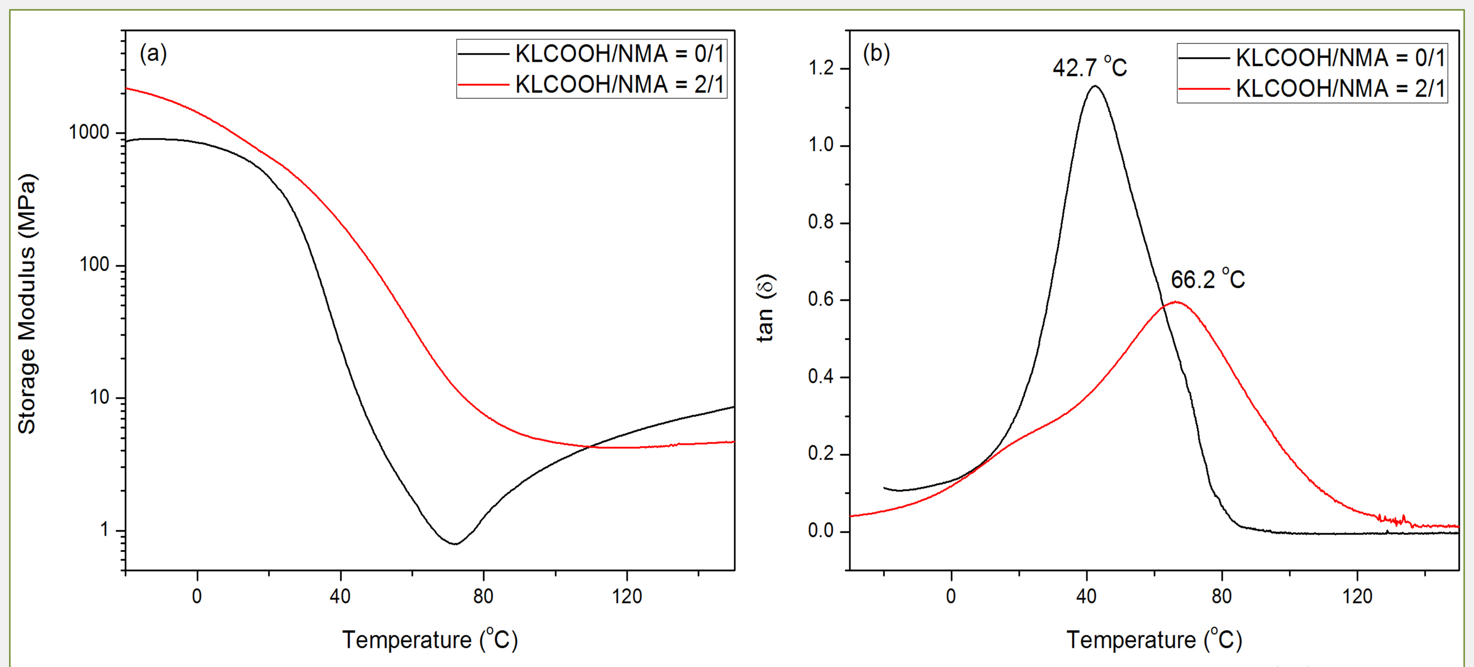


Figure 5: DMA curves for epoxy resin samples. Peaks of the tan(δ) curves correspond to the glass transition temperatures (T_g).

At normal operating temperature, the storage modulus increases with the addition of KLCOOH in epoxy resin. In addition, the T_g of 2/1 KLCOOH/NMA is higher than of 0/1.

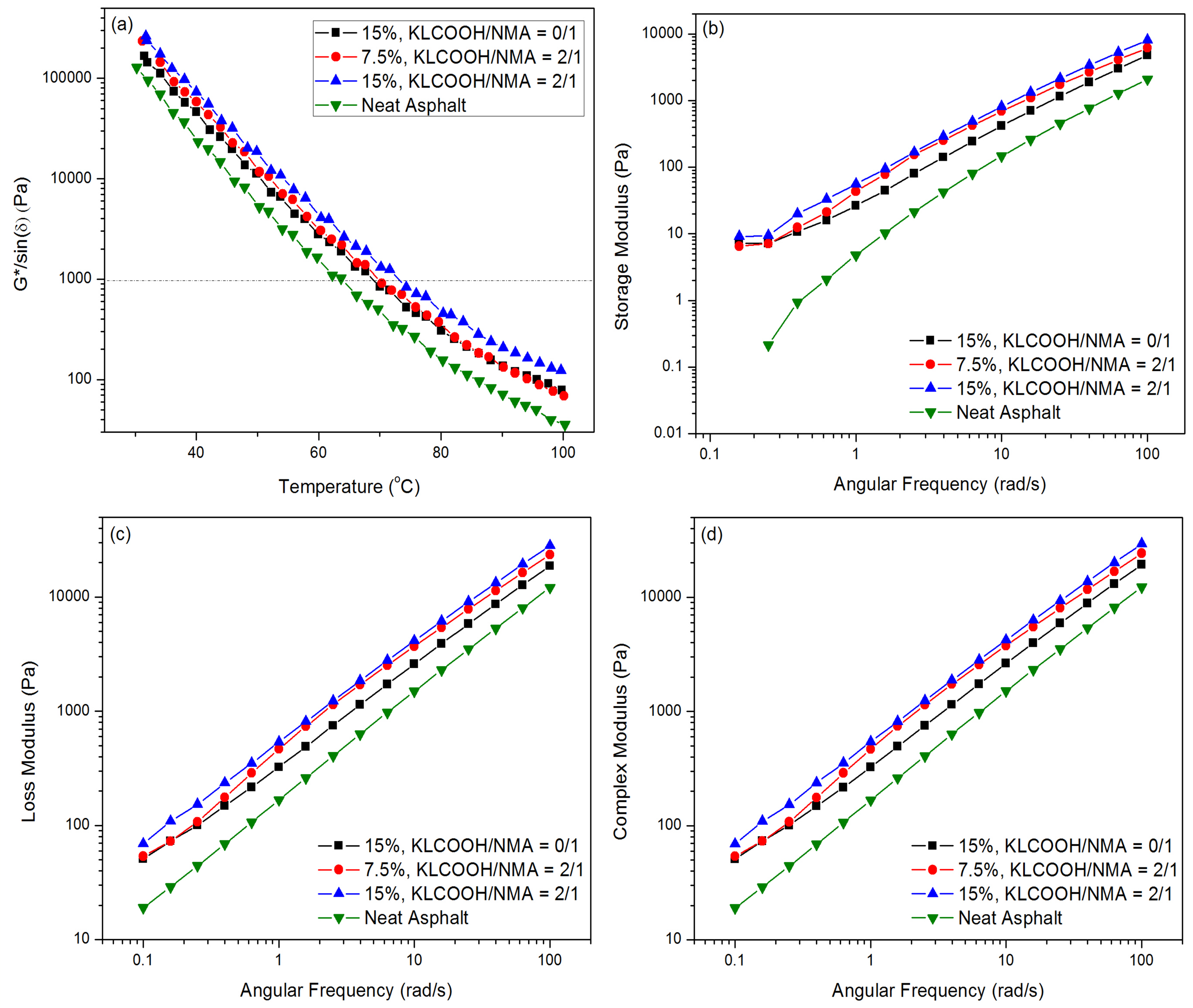


Figure 6: Rheological properties of neat asphalt and epoxy asphalts.

The temperature at which $G^*/\sin(\delta)$ = 1 kPa is the maximum temperature for effective asphalt performance. Higher epoxy resin and lignin content increase the maximum temperature, from 64 °C for neat asphalt up to 72 °C for 15% epoxy resin with KLCOOH/NMA = 2/1.

The storage, loss, and complex moduli are lowest for neat asphalt, and increase with higher epoxy resin and lignin content. This reflects improvement in viscoelastic behavior and material strength for angular frequencies between 0.1 and 100 rad/s, which is the normal range for vehicle traffic.

Conclusion

Curing with KLCOOH improves the thermal stability and mechanical properties of epoxy resins. For asphalt binders, higher KLCOOH content and epoxy resin weight composition improve maximum operating temperature and rheological properties. Further research may include the examination of different curing agent molar ratios and epoxy asphalt weight compositions, as well as direct comparison to commercial epoxies.

Acknowledgements

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