Furfural-Based Diols as Precursors for Vinyl Ester Resins

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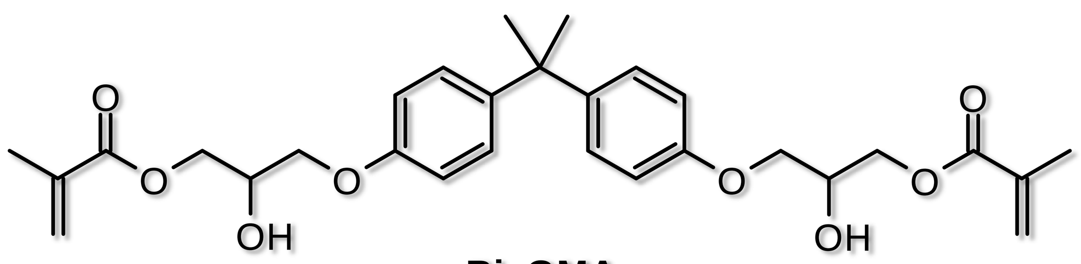
Introduction

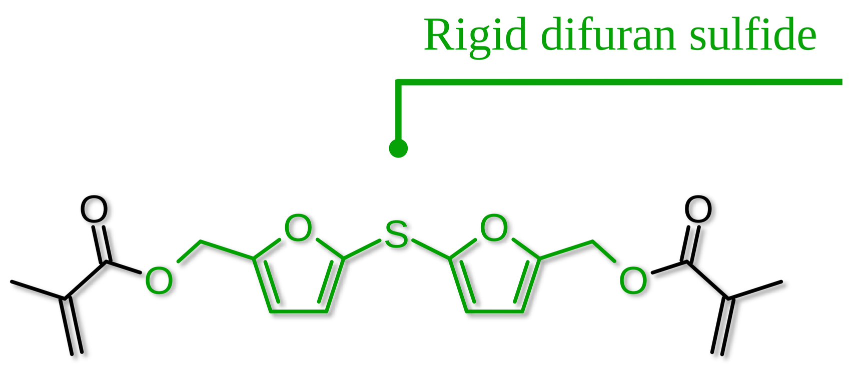
- Vinyl ester resins (VERs) are thermosetting polymers that mostly consist of oligomerized bisphenol A-glycidyl methacrylate (BisGMA).



BisGMA

- VERs show excellent mechanical and thermal properties, fast curing along with low volume shrinkage, corrosion resistance and low weight.[1]
- They can be used in composites, coatings, laminates, adhesives, etc.[1]
- One promising class of biomass-derived precursors for VERs are furans. Furfural is a versatile furan-derivative that is traditionally produced from pentosan-rich lignocellulosic side streams and leftovers of agriculture or forestry.[2]

Materials and Methods



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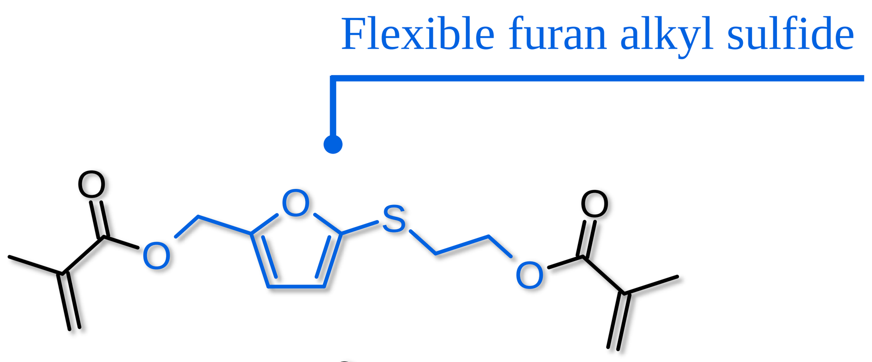

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- The properties of the two biobased dimethacrylates **1** and **2** were compared to those of BisGMA and its commercial oligomerized form, VER, containing 40 wt% of styrene.
- Biobased resins were thermally cured using *tert*-butyl peroxybenzoate as an initiator.
- VER was cured at room temperature using MEKP.

Figure 1. *Cured dogbone-shaped specimen of resin **2**.*

Results

- Monomer **1** is a waxy solid, but melts into a thin oil at ca. 50 °C. At 55 °C, it settled to a dynamic viscosity 40 times lower than that of BisGMA (Figure 2a).
- Monomer **2** remains as a slightly viscous liquid even at -18 °C. At higher shear rates and 25 °C, it had over 10 times lower viscosity compared with that of VER (Figure 2b).
- The lower viscosity of bioresins might be due to their smaller molecular weight and the absence of free hydroxyl groups that increase the intermolecular interactions between BisGMA molecules by forming hydrogen bonds.

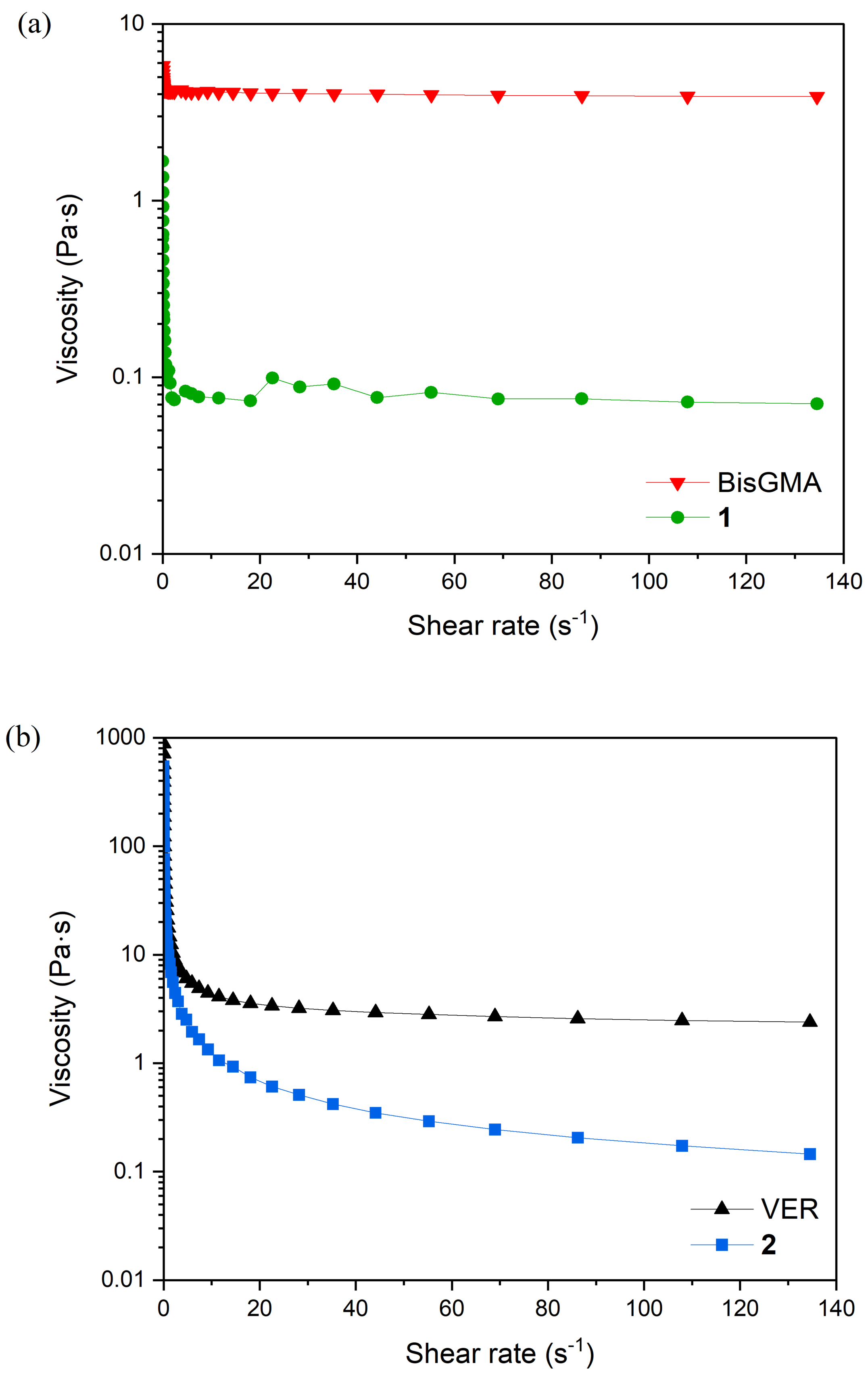

Figure 2. *Dynamic viscosities of (a) neat BisGMA and dimethacrylate **1** at 55 °C, and (b) commercial VER and neat dimethacrylate **2** at 25 °C.*

- Monomers **1** and **2** contain a sulfide functionality. Sulfides have previously been shown to inhibit the activity of peroxides used for radical curing of acrylates.[3]
- No significant interference from sulfide was observed during thermal curing of the dimethacrylates, though further studies and optimization may be required.

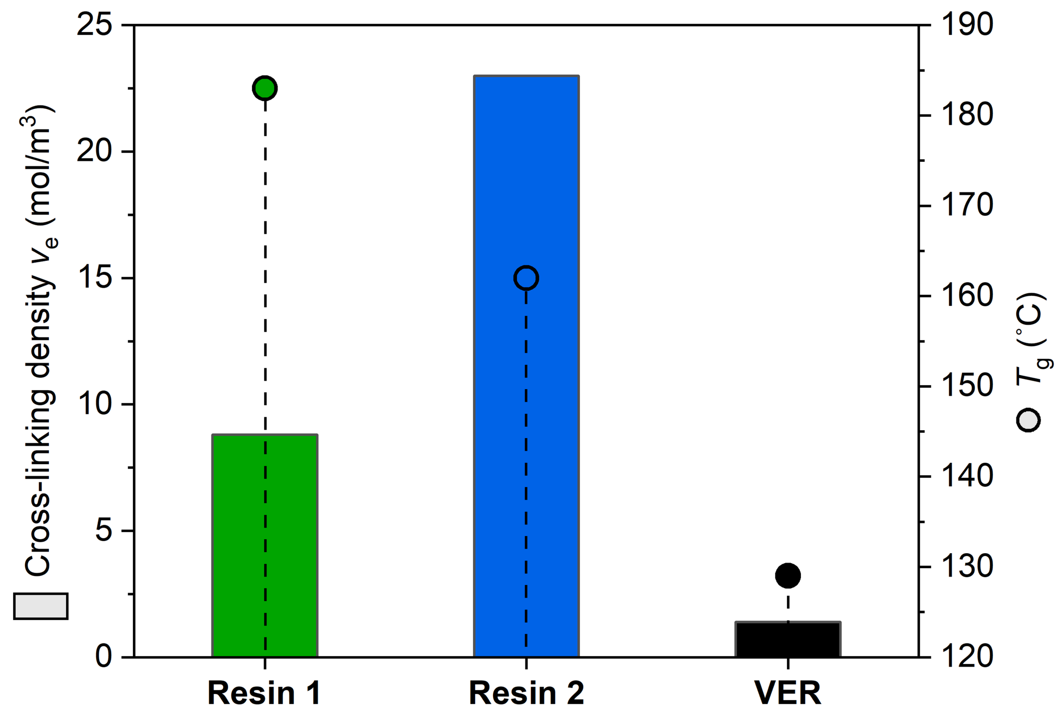

Figure 3. *Cross-linking densities and glass transition temperatures (peak of tan δ) of cured resins.*

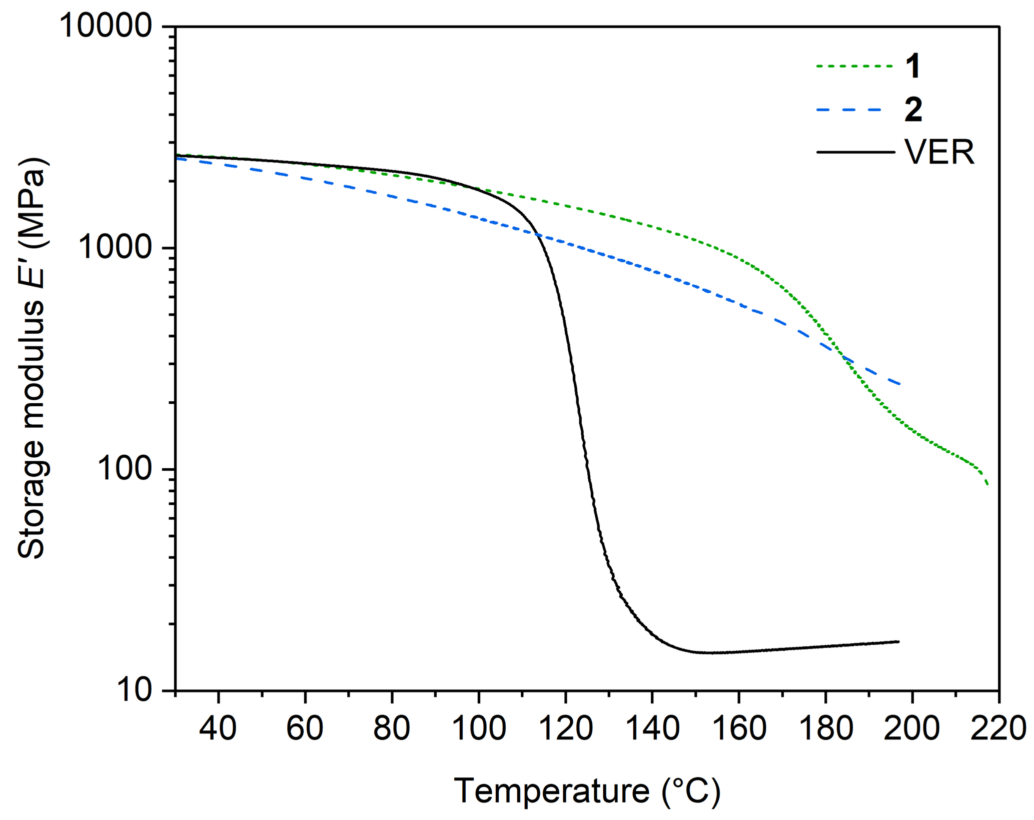

Figure 4. *Storage modulus of cured resins as a function of temperature.*

Conclusions

- Two novel furfural-derived sulfur-bridged dimethacrylates were successfully prepared in high yields and purity.
- Neat biobased monomers showed lower viscosities than BisGMA and VER.
- Both dimethacrylates were thermally cured into highly cross-linked specimens with T_g values of 183 and 162 °C.
- The storage modulus of both bioresins decreased much more slowly towards the end temperature than that of VER.
- The characterized dimethacrylates have a great potential as alternatives to commercial petrochemical VERs.

References

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(3) Ziegenbalg, N.; Gruschwitz, F. V.; Adermann, T.; Mayr, L.; Guriyanova, S.; Brendel, J. C. Vinyl Mercaptoethanol as a Reactive Monomer for the Preparation of Functional Homo- and Copolymers with (Meth)Acrylates. *Polym Chem* **2022**, *13*, 4934–4943.

Acknowledgements

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