

FATTY ACID MONOMER AS A REPLACEMENT OF STYRENE IN BIO-BASED POLYMERS



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THERMOSETTING POLYMERS

Applications

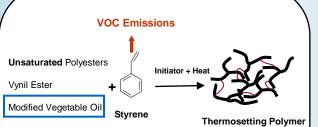
- Boating industry
- Automotive industry
- Aerospace
- Sporting goods
- Civil infrastructure
- Many other commercial applications









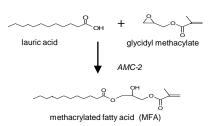


Liquid resins used in molding are a significant source of VOC emission

Federal Environmental Protection Agency introduced legislations to limit styrene emissions

MODIFIED VEGETABLE OILS AESO CH,O-C-(CH,),-HC-CH-(CH,),-CH, (acrylated H₃-(CH₂),-HC — CH-CH₂-HC — CH-(CH₂),-C-O II epoxidized CH,O-C-(CH,),-HC - CH-(CH,),-CH soybean oil) C-CH= CH2 **MAESO** CH.O-C-(CH.) -- HC -- CH-(CH.) -- CH (Maleinated CH₃-(CH₂)_cHC AESO) CH2O-C-(CH2)7-HC -CH-(CH2)7-CH3 C-CH = CH. SOMG/MA (Maleinated CH3 (CH3) 4 HC = CH-CH2+HC = CH-(CH3) 7 C-O 10 sovbean oil monoglyceride) COMG/MA (Maleinated castor oil monoglyceride)

MODIFIED FATTY ACID



- have very low volatilities
- reduce health and environmental risks
- increases renewable content in polymers

La Scala et al., Polymer, 2005

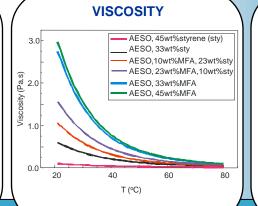
OBJECTIVES

Reduce styrene concentration because it is a hazard air pollutant (HAP) and a volatile organic compound (VOC).

Employ a fatty acid monomers as an alternative to styrene in the production of triglyceride-based polymers.

Produce a resin that can be employed in liquid molding (0.2 Pa.s < viscosity < 1 Pa.s).

Produce a polymer with good properties



Rheological measurements were performed employing a TA Instrument AR-G2 Rheometer.

The viscosity of all the samples decreased in an exponential way with the temperature. Without the addition of a comonomer the biobased resins doesn't fit the viscosity values required (0.2 and 1 Pa.s).

Because the viscosities of bio-based resins using MFA were fairly high; blends of MFA and styrene should be used as the reactive diluent to reduce the viscosity.







(Continued)

MECHANICAL PROPERTIES

	MFA (wt%)	Styrene (wt%)	Tg (°C)	E'at 30°C (MPa)	v (mol/m³)	Mc (g/mol)
AESO	35	0	26.84	128	526.7	2088.5
	23	10	38.13	423	1074.9	1023.4
	16.5	16.5	49.23	625	1719.8	639.6
	10	20	59.8	690	1934.8	568.5
	0	33	70.5	1084	2902.1	379.0
MAESO	20	0	41	270	510.1	2156.4
	15	15	72.9	1100	2856.5	385.0
	0	33	91	1700	4692.8	234.4

The mechanical properties were measured employing DMA Rubber elasticity theory: E' = $3vRT = \rho RT/Mc$

	MFA (wt%)	Styrene (wt%)	Tg (°C)	E'at 30°C (MPa)	v (mol/m³)	Mc (g/mol)
SOMG/MA	35	0	44.1	302	288.2	3816.8
	17.5	17.5	84.3	911	610.3	1802.4
	10	25	96.0	1100	847.6	1297.7
	0	35	114	1800	1271.4	865.2
COMG/MA	35	0	62	420	423.8	2595.5
	17.5	17.5	84	1020	720.5	1526.7
	10	25	101	1550	1186.7	926.9
	0	35	121	1955	1983.4	554.6

Tg and modulus both increase as the MFA content decreases because the fatty acid chain acts as plasticizer increasing the free volume of the polymer and increasing the effective molecular weight between cross-link.

MODIFIED LIGNIN

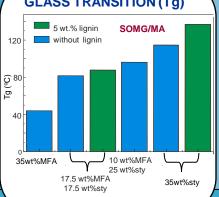
Modified Lignin as an Additive to Bio-based Thermosets Modified Lignin: butyrated kraft lignin 1

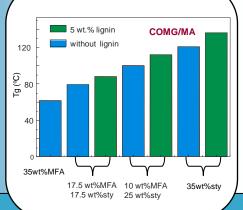
The addition of butyrated kraft lignin, as shown in the Figures (Tg and E' versus concentration of styrene and MFA) has a large effect in the polymer properties:

- 1) There is an increase in the Tg because the lignin has a high Tg of about 142 oC
- 2) Lignin acts as a plasticizers because it does not have double bonds that will participate in free radical polymerization so the storage modulus will decrease when lignin is incorporated to the matrix

¹Thielemans and Wool, Composites Part A: appl Sci Manuf, 2004







CONCLUSIONS

Modified fatty acids (MFA) can be employed to reduce styrene concentration, reducing VOC emissions, health and environmental risk.

Bio-based resins, specially SOMG/MA and COMG/MA, with blends of MFA and styrene (10wt% and 25wt%, respectively) were produced with acceptable viscosities and good polymers properties.

Chemically Modified lignin improved the biobased polymers properties.

ACKNOWLEDGEMENTS

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