

# THE HEAT CURE OF HIGH BOILING STYRENE-TYPE MONOMERS IN WOOD

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## ABSTRACT

The advantages of high boiling styrene-type monomers for preparation of wood-polymer composites by heat-catalyst polymerization are discussed. The effect of crosslinking agents, some comonomers and catalyst concentrations, on the polymerization is noted. Adhesion problems and some solutions are presented. Simultaneous polymerization of monomer in impregnated veneers and bonding to other veneers to produce a panel with wood-polymer composite faces is presented as one solution. Additives for modification, such as fire retardancy, are discussed.

## INTRODUCTION

The heat-catalyst cure of methyl methacrylate and styrene in wood has been discussed by several authors (Beall, Meyer, and Skaar 1966; Burmester 1967; Czvikorsky 1968; Kenaga 1969; Langwig 1968; Meyer 1965; Miettinen 1967; Raff, Herrick, and Adams 1965; Siau, Meyer, and Skaar 1966; Young and Meyer 1968). In most cases the monomer-impregnated wood is enclosed in a container or wrapped with aluminum foil to prevent loss of monomer from the surface. An inert atmosphere to reduce monomer inhibition is advocated. Certain European investigators have used low molecular weight polyesters to reduce monomer loss and lower the temperature of the exotherm (Burmester 1967; Czvikorsky 1968; Miettinen 1967).

Recently two developmental monomers, t-butyl styrene and monochlorostyrene, have become available. These styrene-type monomers offer good potential for wood-polymer composites because of their low volatile characteristics. As will be demonstrated, these monomers can be cured in wood with very little surface depletion without wrapping or using an inert atmosphere. In addition, they can be polymerized *in situ* in veneers in a press while simultaneously bonding crossbanded veneers to produce plywood with wood-polymer composite faces.

## MONOMER PROPERTIES

The physical properties of methyl methacrylate (MMA) and four styrene-type monomers are given in Table 1. Methyl methacrylate imparts good properties to wood-polymer composites on polymerizing *in situ*. However, it boils at 101 C at 760 mm Hg, is soluble at about 1.5% by weight in water, and shrinks about 20.6% by volume on polymerization. It must generally be cured in an inert atmosphere. The four styrene-type monomers, styrene (St), vinyl toluene (VT), t-butyl styrene (TBS), and monochlorostyrene (ClS), have particular advantages for the production of wood-polymer composites based on monomer properties and end use of the composite. As shown in Table 1, St boils at 145 C at 760 mm Hg., VT boils at 170 C., TBS boils at 219 C, and ClS boils at 185 C. Thus, the volatility dictates the conditions under which these monomers can be cured in wood. For instance, wood impregnated with ClS or TBS can be cured in an oven without substantial monomer loss. Note, also, that TBS shrinks only 7% on polymerization. Thus, low density with high bulk and minimal dimensional distortion can be achieved as compared with the other monomers. Distortion of the cell wall is a function not only of shrinkage during polymerization, but also a function of moisture in the cell wall. The low solubility of ClS,

TABLE 1. *Monomer properties*

	Methyl Methacrylate <sup>1</sup>	Styrene <sup>2</sup>	Vinyl toluene <sup>2</sup>	t-Butyl styrene <sup>2</sup>	Monochloro-Styrene <sup>2</sup>
Molecular weight	100	104	118	160	139
Approx. isomer ratio					
- para			40	95	33
- meta			60	5	
- ortho					67
Density g/cc 20 C	0.94	0.91	0.90	0.88	1.09
Boiling point degrees C @ 760 mm Hg.	101	145	172	219	177-185
Solubility monomer in water % @ 25 C	1.55	0.032	0.0089	0.00053	0.0064
Water in monomer % @ 25 C	1.25 <sup>3</sup>	0.070	0.037	0.039	0.052
Vol. shrinkage on polymerization, %	20.6	17.0	12.6	7.0	13.0
Density of homopolymer g/cc	1.18	1.09	1.03	0.95	1.25

<sup>1</sup> See Schildknecht 1952.

<sup>2</sup> The Dow Chemical Company (literature).

<sup>3</sup> See Simonds and Church 1967.

TBS, and VT in water results in less distortion of the wood during polymerization (Siau 1969).

An example of the polymerization characteristics of the styrene-type monomers is given in Table 2. Basswood blocks, 1¼" × 1¼" × 4" longitudinally, were impregnated to about 120% weight pickup of 95% plant grade monomer (containing inhibitor) and 5% crosslinking agent, and 0.25% VAZO azobisisobutyronitrile catalyst. The impregnated blocks were placed in an oven without wrapping. A thermocouple inserted in each block indicated when the exotherm peak was reached. As shown, 30% of the more volatile styrene was lost. Only 7% of TBS was lost, and most of this loss was due to exudation as a result of thermal expansion rather than to evaporation. The time to reach maximum exotherm temperature reflects the reactivity of these four monomers: ClS>TBS>VT>St.

In another study of the cure of TBS and ClS, birch veneers were impregnated at approximately 100% loading with solutions

of the monomers containing 10% ethylene glycol dimethacrylate (EDMA) crosslinking agent. The veneers were cured in a press at various temperatures, as given in Fig. 1. The plot indicates the time to reach maximum exotherm temperature for both monomer solutions and a 50-50 mixture of the two. Loss of TBS and ClS monomer during cure under these conditions is

TABLE 2. *Polymerization characteristics of styrene-type monomers in basswood blocks impregnated to refusal<sup>1</sup>*

Monomer	Cure Temp. Degree C	Monomer Loss on Cure -%	Time to Exotherm Hr: Min
Styrene	75	31.6	3:16
Vinyltoluene	75	20.1	2:13
Monochlorostyrene	75	9.5	1:35
t-Butylstyrene	75	7.1	1:50
Styrene	95	29.7	1:21
Vinyltoluene	95	15.7	1:12
Monochlorostyrene	95	8.8	0:45
t-Butylstyrene	95	7.0	0:53

<sup>1</sup> Monomer solution contains 5% DVB-55 (55% divinylbenzene) and 0.25% VAZO catalyst. Blocks cured in an air atmosphere with no wrapping.

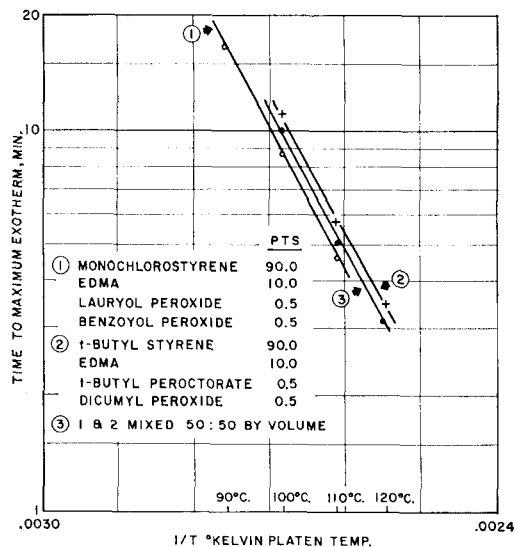


FIG. 1. Polymerization of styrene-type monomers in birch veneers.

less than 6%. Loss of St under similar conditions will amount to 30% to 50%, with considerable residual monomer remaining or not polymerized.

#### EFFECT OF CROSSLINKING AGENTS

Crosslinking agents are added to the monomers to increase reaction rate and improve the physical properties of the wood-polymer composite.

Studies of crosslinking agents were conducted with basswood blocks  $1\frac{1}{4}'' \times 1\frac{1}{4}'' \times 4''$  longitudinally. The blocks were impregnated with the appropriate solution and placed in an oven at 90 C. A thermocouple was inserted in the end of each block to follow the temperature change. Figure 2 indicates the type of data obtained for each crosslinking agent. This figure is the trace of temperature data obtained for various additions of EDMA to TBS. Table 3 lists the results obtained for several crosslinking agents used at various concentrations with TBS. In some cases, temperatures of 170 to 180 C were recorded. Obviously the heat buildup indicated by such exotherm temperatures could be injurious to the

physical properties of the wood-polymer composite since this heat is not quickly dissipated. However, this information was important for developing formulations for veneer treatments, where the mass of monomer is not as great and the heat accumulation is less.

As shown in Table 3, the most reactive crosslinking agent among those tested is trimethylol propane triacrylate. Several dimethacrylates are shown to be very reactive, such as ethylene glycol dimethacrylate (EDMA). Monomer DVB-55 contains 55% divinyl benzene and is quite reactive. However, DVB-55 contains a small amount of saturates (i.e. diethyl benzene) that remain trapped in the wood-polymer composite and that may cause an odor problem.

The effect of various crosslinking monomers on abrasion resistance of yellow birch polymer composites is noted in Table 4. For this test  $\frac{1}{16}''$  face veneers were impregnated and simultaneously cured and bonded to untreated Douglas-fir veneers in a 3-ply assembly by a method to be described later. Abrasion resistance of the treated surface ply was determined by measuring the depth of wear, after 1,000 revolutions, in a Taber Abrader using CS-17 wheels. Up to 10% or more crosslinking agent may be required to give best improvement in abrasion resistance. However, this appears to vary with the crosslinking agent. Trivinyl isocyanurate appears to decrease the abrasion resistance at 10% concentration as compared to additions of lesser or greater quantities.

#### EFFECT OF COMONOMERS

Diethyl maleate, diethyl fumarate, and acrylonitrile are known to provide improved solvent properties and hardness in various copolymer systems. Their effect on the polymerization characteristics of TBS in basswood is shown in Table 5. The TBS-acrylonitrile system had a very high exotherm temperature. In addition, about 10% monomer was lost during the cure cycle.

The effect of these comonomers on abrasion resistance of birch polymer composites

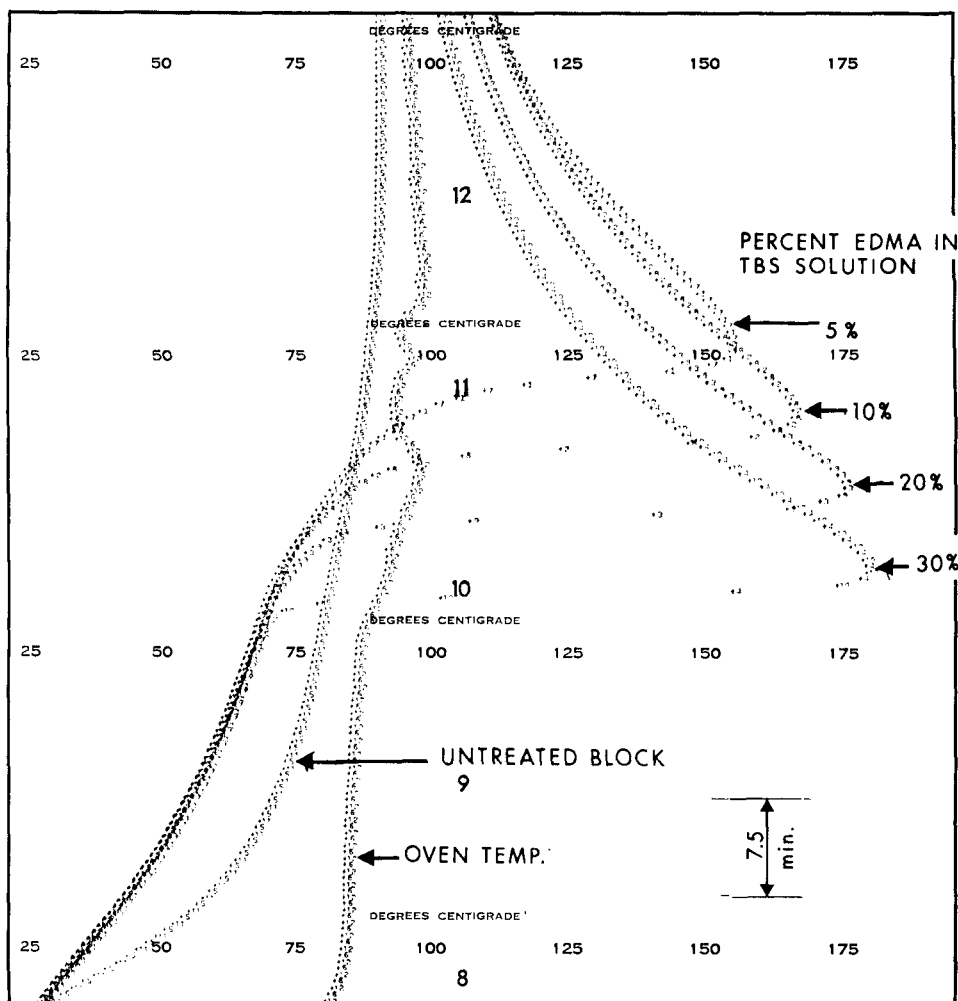


FIG. 2. Time-temperature record of effect of EDMA on the polymerization of TBS in basswood.

of TBS and VT are given in Table 6. These composites were prepared and tested as given in the preceding section. Diethyl fumarate appears to give improvement in abrasion resistance in the TBS and VT systems.

EFFECT OF CATALYST CONCENTRATION

Studies similar to the preceding work on crosslinking agents, using basswood blocks, were made to determine the effect of cata-

lyst concentration (see Table 7). As would be expected, the greater the concentration of VAZO, the larger the exotherm temperature, and the shorter the time to reach exotherm temperature. Strength properties were not determined, but high catalyst concentration leads to short polymer chains and generally inferior polymer properties. The catalyst VAZO is used in preference to various peroxides because it is compatible with dyes in the monomer systems.

TABLE 3. Effect of crosslinking agents on polymerization of TBS in basswood blocks in air at 90 C (0.25% VAZO® added)

Crosslinking Agent	Conc. %	Loading %	Loss during cure %	Exotherm	
				Time <sup>1</sup> Min.	Temp. Degree C
Trimethylol propane triacrylate	10	134	5.0	34	176
	20	138	4.1	36	182
	30	106	1.8	25	184
Trivinyl isocyanurate	10	117	7.3	51	140
	20	139	5.5	51	141
	30	141	4.0	49	146
Trimethylol propane trimethacrylate	5	135	6.3	50	145
	10	139	6.3	48	155
	20	131	4.7	40	165
	30	142	2.3	37	163
Ethylene glycol dimethacrylate	5	125	6.5	52	154
	10	133	5.9	46	166
	20	134	5.5	40	175
	30	135	7.0	34	179
Triethylene glycol dimethacrylate	5	117	6.0	36	151
	10	132	5.4	34	164
	20	129	4.9	30	159
	30	138	5.0	27	174
Tetraethylene glycol dimethacrylate	5	128	5.8	40	150
	10	140	5.0	35	157
	20	130	4.6	34	162
	30	126	3.8	27	165
Polyethylene glycol dimethacrylate	5	128	5.8	43	151
	10	128	5.3	37	169
	20	131	4.4	30	159
	30	137	4.1	28	172
DVB-55 <sup>2</sup>	5	—	—	53	148
	10	—	—	42	160

<sup>1</sup> Time to reach a maximum exotherm temperature.

<sup>2</sup> 55% Divinylbenzene.

#### EFFECT OF POLYMERS IN MONOMERS

Wood can be impregnated with low molecular weight polymer dissolved in monomer as demonstrated by various European investigators (Burmester 1967; Czvikovsky 1968; Miettinen 1967). The following work illustrates some of the possibilities imparted by this approach.

Various concentrations of the low molecular weight DERAKANE® 114 vinyl ester resin were prepared in 95 parts styrene and 5 parts EDMA, impregnated in basswood blocks, and polymerized as described previously. Results shown in Table 8 indicate that the loss in weight of monomer during cure and the time of cure are materially

reduced with up to 15% addition of DERAKANE® 114. The exotherm temperature was very high, and the heat caused much degrade in the center of the block. However, it is stressed again that veneer treatments do not reach such temperatures on cure and the above method of study of cure is of value to determine the kinetics involved.

The effect of polymer in monomer polymerized *in situ* in veneer is further illustrated in Table 9. In this study a polyester reaction product of 1 mole dipropylene glycol and 1.5 moles of maleic anhydride was compared to EDMA at additions of up to 20% by weight in orthochlorostyrene (not

TABLE 4. *Effect of crosslinking monomers on abrasion resistance of birch polymer composites*  
Mils removed per 1000 revolutions of Taber Abrader using CS-17 Wheels.

Monomer	Crosslinker	Conc. of Crosslinker %	Mils Removed
TBS	Trivinyl isocyanurate	2.5	2.25
		5.0	2.30
		10.0	3.10
		20.0	1.60
VT	Trivinyl isocyanurate	30.0	1.25
		2.5	1.75
		5.0	2.25
		10.0	3.25
TBS	Trimethylol propane triacrylate	20.0	1.75
		2.5	2.15
		5.0	2.25
		10.0	0.95
TBS	Trimethylol propane trimethacrylate	20.0	1.10
		30.0	1.00
		5.0	2.00
		10.0	2.15
TBS	Ethylene glycol dimethacrylate	20.0	1.60
		5.0	2.00
Untreated controls			2.55
			2.52

the mixture of ortho- and para-chlorostyrene used previously). Douglas-fir veneer was impregnated with the various solutions, and polymerization was effected in a press. As shown in Table 9, the polyester resulted in somewhat shorter cure time and less loss of monomer during cure.

TABLE 6. *Effect of comonomer on abrasion resistance of birch polymer composites*  
(All comonomer solutions contained 5% EDMA and 0.25% Vazo)  
Mils removed per 100 revolutions of Taber Abrader using CS-17 Wheels.

Monomer	Comonomer	Conc. of Comonomer %	Mils Removed <sup>1</sup>
TBS	Diethyl fumarate	0	2.00
		10	1.45
		20	1.52
		30	1.35
VT	Diethyl fumarate	0	2.10
		10	2.05
		20	1.95
		30	1.95
TBS	Acrylonitrile	0	1.75
		10	2.90
		20	2.30
		30	2.20
VT	Acrylonitrile	0	1.80
		10	2.25
		20	1.75
		30	2.35
TBS	Diethyl maleate	0	2.00
		10	3.65
		20	3.20
		30	3.25

<sup>1</sup> Average of two specimens and four readings per specimen.

EFFECT OF DYES ON CURE

The use of dyes in wood-polymer composites is important for various end uses. However, many dyes are known to inhibit polymerization. Test results of cure of TBS

TABLE 5. *Effect of comonomer on polymerization of TBS in basswood blocks in air at 90 C*  
(Comonomer solution contains 5% EDMA and 0.25% VAZO)

Comonomer	%	Loading %	Loss during cure %	Exotherm	
				Time <sup>1</sup> min.	Time Degree C
Diethyl maleate	0	128	5.9	50	148
	10	143	6.4	49	151
	20	129	6.2	52	141
	30	150	6.4	55	140
Diethyl fumarate	0	141	6.0	48	161
	10	132	5.6	45	159
	20	129	5.6	44	159
	30	148	5.0	41	164
Acrylonitrile	0	135	6.1	49	162
	10	100	5.8	41	163
	20	128	7.0	40	192
	30	124	9.9	42	182

<sup>1</sup> Time to reach maximum exotherm temperature.

TABLE 7. Polymerization of TBS at 90 C in basswood as influenced by amount and type of crosslinking agent and concentration of catalyst

Crosslinker			Exotherm	
Type	Conc.-%	Vazo <sup>1</sup> -%	Time <sup>2</sup>	Temp. Degree C
EDMA	10	1	27	172
		0.5	31	167
		0.25	33	162
		0.125	39	157
EDMA	5	1	28	165
		0.5	33	159
		0.25	36	154
		0.125	44	155
DVB-55	10	1	35	172
		0.5	39	168
		0.25	42	160
		0.125	68	132
DVB-55	5	1	35	162
		0.5	41	158
		0.25	53	148
		0.125	70	131

<sup>1</sup> Concentration based on total weight of monomer and crosslinking agent.

<sup>2</sup> Time to reach maximum exotherm temperature.

containing various dyes impregnated in basswood blocks are given in Table 10. Amaplast Black HY dye causes a significant reduction in the rate of cure at 70 C. This difference tends to disappear at higher cure temperature. Oil Soluble Blue ZN and Calco Oil Red ZMQ do not cause such inhibition.

TABLE 8. Effect of DERAKANE® 114 vinyl ester resin on cure of styrene-EDMA (95-5) in basswood. Approx. 130% Monomer-Polymer Pickup

Oven Temp.	Vinyl ester Resin % Solids	Monomer Loss On Cure %	Cure Time Minutes	Exotherm Temp. <sup>1</sup> Degree C
95	0	38.1	76	162
	1.5	27.3	78	165
	3.0	23.2	74	180
	7.5	14.8	62.5	200+
	15.0	10.2	58	200+
75	0	29.2	126	137
	1.5	20.8	136	152
	3.0	20.0	131	161
	7.5	11.4	103	200+
	15.0	7.4	91	200+

<sup>1</sup> At 200+ temperature exceeded recorder maximum.

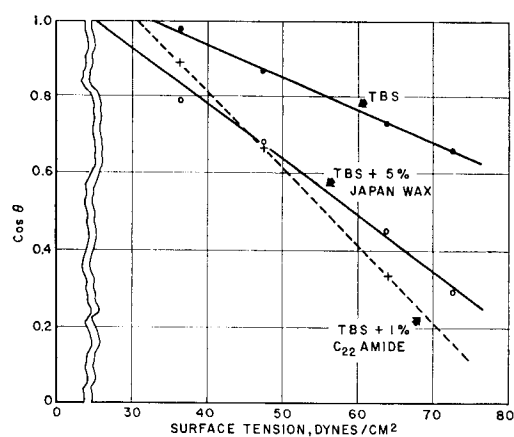


FIG. 3. Wettability of hard maple-poly-TBS composite (tangential face lightly sanded).

#### ADHESION OF TBS-WOOD COMPOSITES

The glueability of polymethylmethacrylate-wood composites has been reported by Loos (Loos and Kent 1968). His work indicates some difficulties in obtaining good bonds with some of the conventional wood adhesives. Poly-t-butylstyrene, which is highly hydrophobic, could be expected to cause even more difficulties.

Critical surface tension is regarded as a measure of wettability of a polymer surface, and this can be related to adhesion (Gray 1962). In other words, an adhesive must satisfactorily wet the surface of an adherent if a good bond is to be obtained. Critical surface tension is defined as that surface tension of a liquid that has zero contact angle or complete spreading when in contact with a surface. It is determined by extrapolation of a plot of the surface tension and the cosine of the contact angle of various liquids that are placed in contact with a surface (Gray 1962).

Figure 3 shows that the critical surface tension of a lightly sanded poly-TBS-hard maple composite is about 33 dynes/cm<sup>2</sup>. Lightly sanded hard maple will have a critical surface tension of about 65 dynes/cm<sup>2</sup>. Obviously, the wood poly-TBS composite is very difficult for a conventional water-carried adhesive to wet.

Methods to aid this problem are described as follows:











