

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 ¹ | Styrene ² | Vinyl toluene ² | t-Butyl styrene ² | Monochloro-Styrene ² |
|--|----------------------------------|----------------------|----------------------------|------------------------------|---------------------------------|
| 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 ³ | 0.070 | 0.037 | 0.039 | 0.052 |
| Vol. shrinkage on polymeri- zation, % | 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 |

¹ See Schildknecht 1952.² The Dow Chemical Company (literature).³ 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 refusal¹*

| 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 |

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

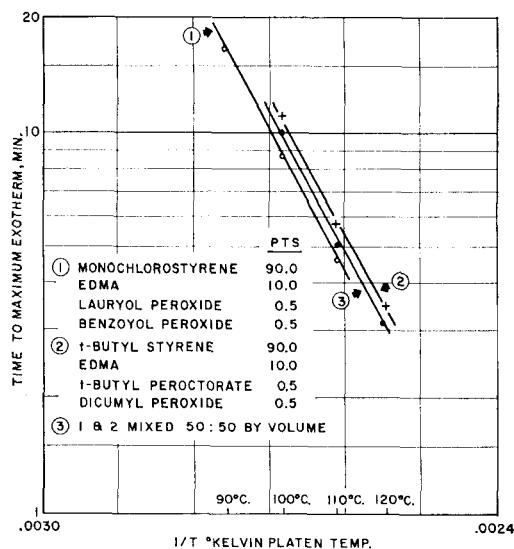


FIG. 1. Polymerization of styrene-type monomers in birch veneers.

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

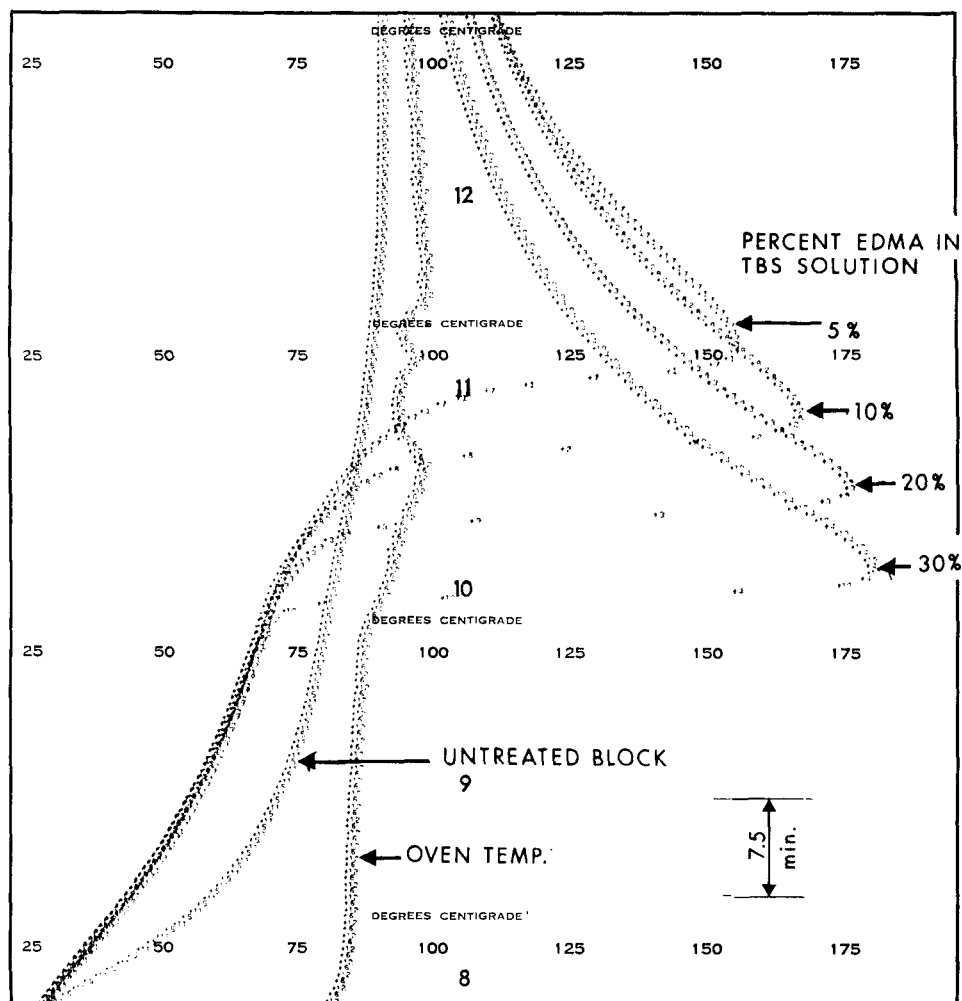


FIG. 2. Time-temperature record of effect of EDMA on the polymerization of TBS in basswood.

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 ¹ 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 ² | 5 | — | — | 53 | 148 |
| | 10 | — | — | 42 | 160 |

¹ Time to reach a maximum exotherm temperature.² 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 DERA-KANE® 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 DERA-KANE® 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 |
| | | 30.0 | 1.25 |
| VT | Trivinyl isocyanurate | 2.5 | 1.75 |
| | | 5.0 | 2.25 |
| | | 10.0 | 3.25 |
| | | 20.0 | 1.75 |
| TBS | Trimethylol propane triacrylate | 2.5 | 2.15 |
| | | 5.0 | 2.25 |
| | | 10.0 | 0.95 |
| | | 20.0 | 1.10 |
| | | 30.0 | 1.00 |
| TBS | Trimethylol propane trimethacrylate | 5.0 | 2.00 |
| | | 10.0 | 2.15 |
| | | 20.0 | 1.60 |
| TBS | Ethylene glycol dimethacrylate | 5.0 | 2.00 |
| | | | 2.55 |
| Untreated controls | | | 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 ¹ |
|---------|------------------|----------------------|---------------------------|
| 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 |

¹ 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 ¹ 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 |

¹ 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 | | Vazo ¹ -% | Exotherm | |
|-------------|---------|----------------------|-------------------|----------------|
| Type | Conc.-% | | Time ² | 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 |

¹ Concentration based on total weight of monomer and crosslinking agent.

² Time to reach maximum exotherm temperature.

containing various dyes impregnated in basswood blocks are given in Table 10. Amplast 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. ¹ 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+ |

¹ At 200+ temperature exceeded recorder maximum.

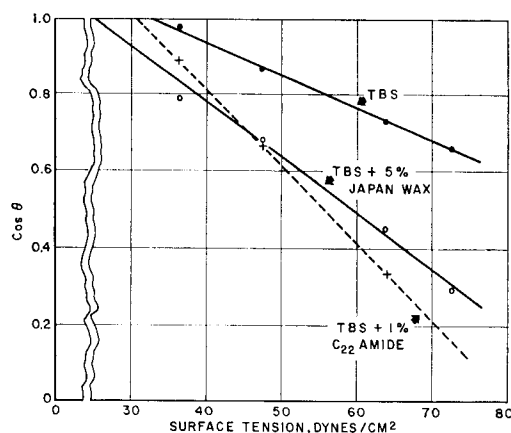


FIG. 3. Wettability of hard maple-poly-TBS composite (tangential face lightly sanded).

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/cm². Lightly sanded hard maple will have a critical surface tension of about 65 dynes/cm². 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:

TABLE 9. Cure of orthochlorostyrene solutions in Douglas-fir veneers containing various amounts of crosslinking agents¹

| Treatment | Crosslinker | | % Pickup | % Loss In Press | Cure Conditions | | | |
|-----------|-----------------|----|----------|-----------------|-----------------------|----------|----------|-----------------------------|
| | | | | | Platen Temp. Degree C | Time min | Exotherm | |
| | Type | % | | | | | Time min | Temp. ³ Degree C |
| Soak | None | — | 41.9 | 9.8 | 100 | 28.0 | 26.0 | 102 |
| Soak | EDMA | 5 | 37.5 | 13.9 | 100 | 17.5 | 15.0 | 102 |
| Soak | EDMA | 10 | 37.0 | 18.8 | 100 | 14.5 | 13.0 | 103 |
| Soak | EDMA | 20 | 32.4 | 17.0 | 100 | 12.0 | 9.5 | 106 |
| Soak | PE ² | 5 | 54.1 | 6.2 | 100 | 17.5 | 15.0 | 105 |
| Soak | PE | 10 | 51.9 | 6.6 | 100 | 12.5 | 10.5 | 111 |
| Soak | PE | 20 | 26.6 | 7.5 | 100 | 9.0 | 7.5 | 116 |
| Vacuum | None | — | 162.6 | 4.0 | 100 | 23.0 | 20.0 | 121 |
| Vacuum | EDMA | 5 | 115.8 | 5.3 | 100 | 14.0 | 11.0 | 149 |
| Vacuum | EDMA | 10 | 118.8 | 3.4 | 100 | 11.5 | 8.0 | 200+ |
| Vacuum | EDMA | 20 | 117.1 | 6.0 | 100 | 10.0 | 6.0 | 200+ |
| Vacuum | PE ² | 5 | 144.7 | 2.7 | 100 | 12.0 | 8.5 | 175 |
| Vacuum | PE | 10 | 133.0 | 3.0 | 100 | 10.5 | 7.0 | 178 |
| Vacuum | PE | 20 | 138.2 | 4.0 | 100 | 8.5 | 5.0 | 200+ |

¹ Added to the solutions: (based on weight of monomer plus crosslinking agent) 0.5% benzoyl peroxide, 0.5% dicumyl peroxide, 1.0% Tinuvin P.

² Polyester reaction product of dipropylene glycol and maleic anhydride (1 to 1.5 mole ratio).

³ At 200+ temperature exceeded recorder maximum.

Polyethylenimine Pretreatment

Hard maple poly-TBS composite boards were prepared for block shear tests. Prior to glue application, the surfaces were washed with toluene and treated with a 1% solution of polyethylenimine, PEI-50. Suitable controls were carried with the experiment. The blocks were assembled with D.E.R.[®] 334 epoxy resin and D.E.H.[®] 14 epoxy hardener, clamped at 200 psi for 24 hr, and tested in 7 days. Three shear blocks of 2 square inches in test area were prepared and tested. Table 11 indicates that both the toluene wash and PEI-50 improved the dry bond.

This work was extended to plywood panels. Birch poly-TBS veneer skins were glued to a 1/8" untreated Douglas-fir veneer core to produce a 3-ply crossbanded panel. Variables included pretreatment with a toluene wash and application of a 1% solution of PEI-50, three epoxy resins formulated with two epoxy hardeners, and hot and cold pressing. Dry shear strength data are given in Table 12. Pretreatment with PEI-50 improved the bond performance. The resin D.E.R. 331, used with

D.E.H. 52, appears most suited for this application.

In another panel test, various molecular weights of polyethylenimine were explored as pretreatments of birch poly-TBS skins. Resins D.E.R. 334 and 331 mixed with D.E.H. 52 were applied and cured by both hot and cold pressing. Shear test specimens were tested dry, after cold water immersion, and boiling (see Table 13). All specimens exhibited resistance to the cold water immersion test.

There appears to be little difference in the effect of molecular weight of polyethylenimine on performance of the glue bond. Resin D.E.R. 331 is somewhat superior to D.E.R. 334.

Simultaneous Cure of Monomer and Adhesive

It was previously shown that high boiling monomers can be satisfactorily polymerized in veneers in a press with little loss of impregnant. It is particularly advantageous to polymerize the monomer in an impregnated top veneer while simultaneously bonding a plurality of crossbanded veneers

TABLE 10. *Effect of one per cent dye on polymerization of TBS-DVB-55 (95-5) in basswood blocks treated to refusal (0.25% VAZO catalyst added)*

| Dye | Cure Temp. Degree C | Maximum Exotherm | |
|-----------------------|---------------------|-----------------------|----------------|
| | | Time Min ¹ | Temp. Degree C |
| Amaplast Black HY | 70 | 157 | 134 |
| American Aniline | 80 | 85 | 142 |
| | 90 | 57 | 147 |
| | 110 | 44 | 148 |
| Amaplast Blue OAP | 70 | 140 | 135 |
| American Aniline | 80 | 82 | 146 |
| | 90 | 51 | 150 |
| | 110 | 40 | 149 |
| Plasto Red B | 70 | 138 | 137 |
| Allied Chemical Corp. | 80 | 82 | 142 |
| | 90 | 59 | 152 |
| | 110 | 42 | 149 |
| Amaplast Yellow GHS | 70 | 132 | 136 |
| American Aniline | 80 | 78 | 147 |
| | 90 | 58 | 147 |
| | 110 | 40 | 151 |
| Anthraquinone Violet | 70 | 129 | 138 |
| N. C. Base | 80 | 76 | 148 |
| | 90 | 63 | 154 |
| | 110 | 39 | 159 |
| Oil Soluble Blue ZN | 70 | 115 | 142 |
| American Cyanamid | 80 | 78 | 150 |
| | 90 | 63 | 153 |
| | 110 | 38 | 159 |
| Sudan Irisol B4 | 70 | 132 | 137 |
| Pure (Blue-purple) | 80 | 77 | 144 |
| | 90 | 63 | 152 |
| | 110 | 43 | 156 |
| Calco Oil Red ZMQ | 70 | 115 | 141 |
| American Cyanamid | 80 | 76 | 148 |
| | 90 | 63 | 153 |
| | 110 | 45 | 160 |

¹ Time to reach maximum exotherm temperature.

to produce plywood with a composite face, or face and back.

Investigation indicates that conventional water-carried wood adhesives such as phenol formaldehyde, resorcinol formaldehyde, melamine formaldehyde, urea formaldehyde, and melamine fortified-urea formaldehyde resins are satisfactory for this use.

Table 14 gives results of shear tests on specimens cut from panels prepared from a 1/16" birch-polymer composite face veneer, and 1/8" crossbanded Douglas-fir core and

TABLE 11. *Glue block shear tests of maple-poly-TBS composites bonded with "D.E.R." 334 epoxy resin and "D.E.H." 14 epoxy hardener*

| Pretreatment | Dry Shear Strength, psi -Wood Failure, % Average of 3 |
|-----------------------|---|
| None | 1235-5 |
| Toluene wash | 2289-5 |
| PEI only - 1% | 2043-10 |
| | 2802+ ¹ |
| Toluene wash + 1% PEI | 2832+ ² |

¹ Two of these specimens (somewhat less than 2 square inches each) exceeded range of test machine and did not break. Maximum load when machine shut off is given.

² All specimens exceeded range of test machine. Average of maximum load when machine shut off is given.

bottom veneer. A urea formaldehyde resin was fortified with 20% melamine and formulated with 25% walnut shell flour (on basis of the urea formaldehyde resin). Both sides of the core veneer were spread with the adhesive. Press conditions were two panels per opening with impregnated faces nearest the platens at 175 psi, and 140 C for 20 min.

Typical test results for a variety of TBS-comonomer mixtures and crosslinking agents are given in Table 14. In general, wood failures in the Douglas-fir were high in both wet and dry tests, indicating satisfactory bonding of the composite face veneers to the core.

Similar panels were prepared with six different species of wood poly-TBS and poly-CLS composite faces, using phenol-resorcinol formaldehyde resin as the bonding adhesive. These panels were placed in exterior exposure for one year in the Midland, Michigan area. Only one minor delamination was noted among more than 100 panels placed in test.

ADDITIVES FOR MODIFICATION OF PROPERTIES

Slip Finishes

Certain end-use applications for wood-polymer composites may be improved by an additive that will reduce friction between the composite and a variety of materials moving in contact with it. Bowling alley approaches and pool cues are an example of such an application.

TABLE 12. *Shear tests of specimens from 3-ply panels with birch poly-TBS composite skins and Douglas-fir untreated core bonded with DOW epoxy resin*

| D.E.H. | Pretreatment | Time Prior To Test (Days) | Dry Shear Strength, psi | | | | | |
|--------|--------------|---------------------------|-------------------------|----------------|----------------|----------------|----------------------|----------------|
| | | | D.E.R. | | | | | |
| | | | 334 | | 331 | | 438/732 ¹ | |
| | | | H ² | C ³ | H ² | C ³ | H ² | C ³ |
| 52 | None | 1 | 178 | 133 | 185 | 211 | D | 191 |
| | | 7 | 184 | 162 | 200 | 202 | D | 198 |
| | PEI-50 | 1 | 173 | 164 | 194 | 220 | 162 | 215 |
| | | 7 | 206 | 220 | 227 | 206 | 170 | 219 |
| 14 | None | 1 | D | 168 | D | 200 | D | 123 |
| | | 7 | D | 194 | D | 187 | D | 130 |
| | PEI-50 | 1 | D | 138 | 152 | 184 | D | 90 |
| | | 7 | D | 215 | 178 | 232 | D | 164 |

¹ D.E.R. 438/D.E.R. 732 - 75/25 by wt.² Hot press - 2 panels/opening 200 psi - 100 C - 10 min.³ Cold press - 200 psi - 20 hours - room temp.

D Delaminate out of press.

It has been demonstrated that critical surface tension is related to coefficient of friction (Owens 1964). The lower the critical surface tension, the less friction encountered. The critical surface tension of a surface was defined in the discussion under adhesion. Note that for good adhesion, a high critical surface tension is desired, but for good slip, a low critical surface tension is required.

Figure 3 illustrates how addition of 5%

Japan wax and 1% erucyl amide (from C₂₂ fatty acid) added to TBS impregnating solution reduces the critical surface tension and thus imparts a slip finish to the hard maply poly-TBS composite.

Fire Retardants

Fire retardants may be added to impregnating monomer solutions to give a measure of fire retardancy to the composite. Table 15 lists several fire retardants containing

TABLE 13. *Effect of various molecular weights of polyethyleneimine conditioners for gluing birch-poly TBS skins to a Douglas-fir core¹*

| Conditioner | M.W. | Test | Shear Strength - psi | | | |
|---------------------------------|-----------|------------------|-------------------------|----------------|-------------------------|----------------|
| | | | D.E.R. 334 ² | | D.E.R. 331 ² | |
| | | | H ³ | C ⁴ | H ³ | C ⁴ |
| PEI 50 in H ₂ O | 30-50,000 | Dry | 166 | 166 | 184 | 224 |
| | | Wet ⁵ | 94 | 50 | 118 | 197 |
| PEI 18 in H ₂ O | 1,800 | Dry | 197 | 251 | 225 | 247 |
| | | Wet ⁵ | 72 | 209 | 132 | 203 |
| PEI 100 in H ₂ O | 100,000 | Dry | 197 | 251 | 225 | 247 |
| | | Wet ⁶ | 72 | 209 | 132 | 203 |
| PEI 18 in methylene chloride | 1,800 | Dry | 196 | 206 | 167 | 189 |
| | | Wet ⁵ | 56 | 174 | 87 | 124 |
| None | | Dry | D ⁶ | 122 | 86 | 170 |
| | | Wet ⁵ | D ⁶ | 70 | 34 | 144 |

¹ Both skins and core brushed with 1% PEI and dried prior to bonding.² Used with D.E.H. 52.³ Hot press - 100 C - 10 min - 200 psi.⁴ Cold press - 16 hrs - 200 psi.⁵ Immersed in cold water and subjected to 25" Hg vacuum for ½ hour and 65 psi pressure for ½ hour and tested wet.⁶ Delaminated from press.

TABLE 14. *Adhesion studies of 3-ply panels produced by simultaneously polymerizing monomers in situ in birch faces, and bonding to Douglas-fir crossbands using a melamine fortified urea formaldehyde resin*

| Monomer | Comonomer and/or Crosslinker | Conc. % | Shear Strength | | | |
|------------------|-------------------------------------|---------|----------------|--------------|-----|--------------|
| | | | Dry | | Wet | |
| | | | psi | %WF | psi | %WF |
| TBS ¹ | Diethyl fumarate | 0.0 | 119 | 85 | 128 | 95 |
| | | 10.0 | 140 | 80 | 106 | 100 |
| | | 20.0 | 233 | 100 | 184 | 100 |
| | | 30.0 | 246 | 50 | 154 | 60 |
| TBS ¹ | Acrylonitrile | 0.0 | 160 | 90 | 136 | 100 |
| | | 10.0 | 150 | 100 | 119 | 100 |
| | | 20.0 | 208 | 100 | 205 | 100 |
| | | 30.0 | 175 | 95 | 135 | 100 |
| TBS ¹ | Diethyl maleate | 0.0 | 169 | 95 | 99 | 100 |
| | | 10.0 | 219 | 100 | 187 | 100 |
| | | 20.0 | 136 | 90 | 120 | 95 |
| | | 30.0 | 165 | 90 | 108 | 100 |
| TBS | Trivinyl-isocyanurate | 2.5 | 133 | 90 | 110 | 100 |
| | | 5.0 | 183 | 60 | 80 | 95 |
| | | 10.0 | 131 | 80 | 132 | 95 |
| | | 20.0 | 233 | 90 | 204 | 90 |
| | | 30.0 | 221 | 65 | 190 | 40 |
| TBS | Trimethylol propane triacrylate | 2.5 | 187 | 40 | 178 | 70 |
| | | 5.0 | 137 | 85 | 104 | 98 |
| | | 10.0 | 161 | 70 | 144 | 95 |
| | | 20.0 | 166 | 75 | 107 | 100 |
| | | 30.0 | 250 | 85 | 203 | 95 |
| TBS | Trimethylol propane trimethacrylate | 5.0 | 225 | 90 | 203 | 70 |
| | | 10.0 | 224 | 80 | 181 | 70 |
| | | 20.0 | 141 | 85 | 125 | 100 |
| VT | Trimethylol propane trimethacrylate | 5.0 | 194 | ² | 194 | ² |
| | | 10.0 | 204 | ² | 147 | ² |
| | | 20.0 | 92 | ² | 94 | ² |
| | | 30.0 | 235 | ² | 223 | ² |

¹ Contains 5% ethylene glycol dimethacrylate.

² Wood failure not read.

bromine and phosphorous that were added to certain TBS solutions for impregnation. Tests for fire retardance were made by the Forest Products Laboratory fire tube method. Tris (2, 3-dibromopropyl) phosphate appears to perform the best (see Table 15) and results in less loss in physical strength such as modulus of rupture, as given in Table 16. Analysis of variance of the strength data indicates that this factor is highly significant. Tris (2, 3-dibromopropyl) phosphate is commercially available.

The use of these fire retardant materials in CIS monomer should provide even better

fire retardancy because of the increase in total halogen content.

CONCLUSIONS

High boiling styrene-type monomers have several advantages for the preparation of wood-polymer composites by heat-catalyst techniques. Rate of cure, monomer loss, and the composite physical properties can be varied by the appropriate selection and concentration of catalyst, comonomers, and crosslinking agents. Additives for modification to provide reduced friction and fire retardants are available.

Adhesion of these composites with epoxy

TABLE 15. Effect of concentration of fire retardants in basswood-poly-TBS composites when tested by the Forest Products Laboratory fire tube method

| Fire Retardant | Conc. ¹ % | Weight Loss ² by Fire-% |
|---|-------------------------|---------------------------------------|
| Tris (2, 3 di-bromo propyl) phosphate | 0 10 20 30 | 94.1 78.8 75.3 58.1 |
| Bis (2 bromo-ethyl) 2 bromo ethane phosphonate | 0 10 20 30 | 94.7 82.6 79.4 79.9 |
| Bis (2 bromoethyl) vinyl phosphonate | 0 10 20 30 | 93.3 83.0 81.1 74.8 |
| Bis (1, 3 dibromo-propyl) 2, 3 di-bromo propane phosphonate | 0 10 20 30 | 95.1 81.8 77.9 61.5 |

¹ Conc. in treating solution—wood treated to refusal ~140% weight increase.

² Total weight loss of wood—polymer composite.

resins is promoted by preconditioning with polyethyleneimine. Simultaneous polymerization of monomer *in situ* in veneers and bonding to a plurality of untreated cross-banded veneers to produce a plywood panel with wood-polymer composite faces is considered an advantage not available by other means.

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