New Lightweight Materials: Balsa Wood–Polymer Composites Based on Ethyl α-(Hydroxymethyl)acrylate

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SYNOPSIS

It is clearly demonstrated here that ethyl α-(hydroxymethyl)acrylate (EHMA) is a unique monomer for increasing the dimensional stability and physical properties of balsa wood. Copolymers containing EHMA, and especially EHMA–styrene mixtures, were shown to improve the dimensional stability (water soak test) and the absolute mechanical properties of balsa wood. Improvements in *specific* modulus and *specific* toughness (absolute properties divided by specific gravity) were achieved using an EHMA–styrene monomer mixture with polybutadiene diacrylate as cross-linker and toughening agent, with the best results obtained at low (10–40%) weight gain. This is the first report that we are aware of describing specific property improvement greater than expected based on density increase. These improvements in modulus and toughness were ascribed to efficient penetration of monomers into the cell walls. Solid-state NMR and scanning electron microscopy confirmed strong interaction of the copolymers generated *in situ* with wood cell wall components, consistent with the property improvements obtained. The combination of a light-weight, renewable wood precursor with synergistic reinforcement by this combination of monomers offers unique opportunities for increased use of wood–polymer composites in a wide variety of structural and insulating applications. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The name "balsa" is applied to the low-density wood species of the genus *Ochroma*, which are trees commonly found in tropical America. Their range extends from the West Indies, through Central America, to the northern regions of South America.[1] Over 90% of the world's supply of balsa wood comes from *Ochroma grandiflora* in Ecuador. Wood from the *Ochroma* is considerably lighter than cork, with specific gravity varying between 0.05 and 0.41, the mean value being about 0.14.[2] This represents the greatest *range* in density for any tree species and encompasses the lightest commercial whole wood available. Balsa has the additional distinction of being one of the fastest growing timber trees in the world, attaining growth rates of 15–26 ft per year.[3] The tree matures in about 10 years, at which time it is 60–90 ft in height and 30–45 in. in diameter. Balsa wood has been used commercially as sound insulation, heat insulation in refrigerators, core material in boat hulls, vibration insulation for machinery and in aircraft panels to provide light, strong insulation and support in internal walls.[4]

Described here is an extension of work previously carried out in our laboratories on Southern pine whole wood–polymer composites (WPCs) to the formation of composites from balsa wood. In this paper, we use the acronym WPC to refer to wood–polymer composites formed by monomer impregnation of whole wood followed by *in situ* polymerization. Balsa wood was chosen because of the combination of properties discussed above and its potential for use in lightweight composites with high specific strength. The previous paper in this journal gives an overview of tests used for characterization of wood and wood–polymer composites including our Southern pine results.[5] Data in various graphs and tables in that paper are valuable for comparison to results discussed here.

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EXPERIMENTAL

Materials

V-30 azo initiator was donated by Wako Chemical Co. 2,2-Azobisisobutyronitrile (AIBN) was obtained from Polyscience and purified by recrystallization from methanol. Both azo initiators were stored in a freezer at −10°C. Ethyl α-(hydroxymethyl)acrylate (EHMA) was synthesized by reaction of ethyl acrylate and paraformaldehyde in the presence of 1,4-diazabicyclo-[2,2,2]-octane (DABCO).[6] Styrene (ST) and methyl methacrylate (MMA) were purchased from Aldrich Chemical Co. p-Acetoxystyrene monomer (ASM) was donated by Hoechst-Celanese. Poly(butadiene diacrylate) (pBDDA) was synthesized by reacting hydroxyl-terminated polybutadiene (Polyscience) with acryloyl chloride in the presence of triethylamine and 4-dimethylaminopyridine (DMAP). Balsa wood strips with the initial dimensions $\frac{1}{16} \times \frac{1}{2} \times 5.0$ in. were cut in half (perpendicular to the long axis) to give matched pairs of samples. One-half of each pair was treated and the other half was used as the control for physical property measurements. Coefficients of variation (standard deviations divided by mean value times 100) ranged from 22 to 35% for the physical property data given below.

Impregnation and Curing

Wood samples, previously dried 12 h at 105°C, were placed in a vacuum chamber (< 3 mmHg) for 20 min. The samples had a metal weight on them to keep them submerged during the next step. While the samples were still under vacuum, the comonomer mixture containing cross-linker and initiator was introduced into the vacuum chamber via a syringe until the samples were completely submerged. The vacuum was then slowly released and the samples were allowed to soak for 18–24 h at 65–70°C. After impregnation, samples were placed in separate test tubes that were subsequently fitted with septa. Each test tube was then purged with nitrogen and the samples were thermally cured in a conventional oven or oil bath for 24–36 h. The thermal cure temperature was 55°C for systems containing AIBN initiator and 80°C for those containing V-30 initiator. Alternatively, samples were cured in a Cober LBM 1.2A microwave/convection oven for 2 h at 120 W, then 2–4 additional hours at 240 W.

RESULTS AND DISCUSSION

The NMR spectra in Figure 1 confirm the presence of EHMA polymer within the balsa wood. Although the spectrum of the wood–polymer composite clearly displays a combination of the peaks found in the individual spectra of poly(EHMA) and untreated balsa wood, the spectral subtraction (WPC minus wood) does not remove all the wood peaks nor is the difference spectrum identical to that of poly-(EHMA). These differences indicate strong interaction between the polymer and wood components, causing chemical shift changes for groups that do not cleanly subtract or correlate with neat component spectra. These interactions appear to involve both intermolecular hydrogen bonding and transesterification of pendent ethyl ester groups of the vinyl polymers with cellulose alcohol moieties, for example. Further support for cell wall penetration is provided by antiswelling data and physical property measurements.

The dimensional stability of the WPCs is illustrated in Figure 2. This bar graph displays the amount of volume increase for various samples due to water uptake after soaking for 5 days at 23°C. The sample containing pure EHMA polymer demonstrated the greatest dimensional stability, similar to what was observed with pine WPCs.[7] In general,
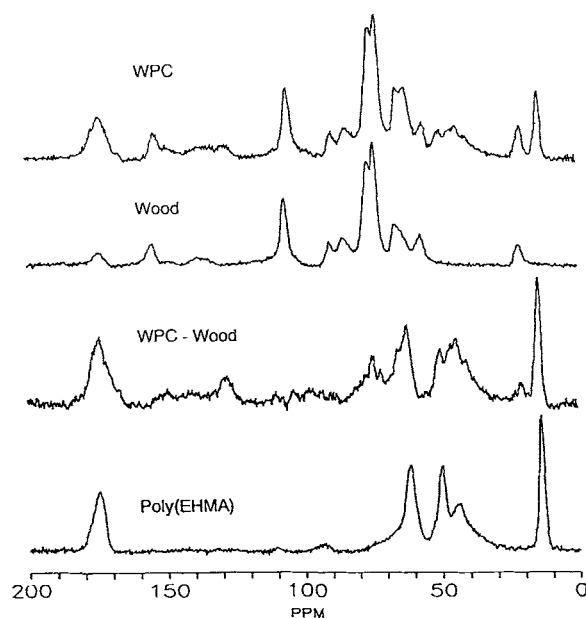
Figure 1 ^{13}C-CP/MAS spectra (from top to bottom) of balsa/poly(EHMA) WPC, whole balsa wood, difference spectrum (WPC minus wood), and pure poly(EHMA).
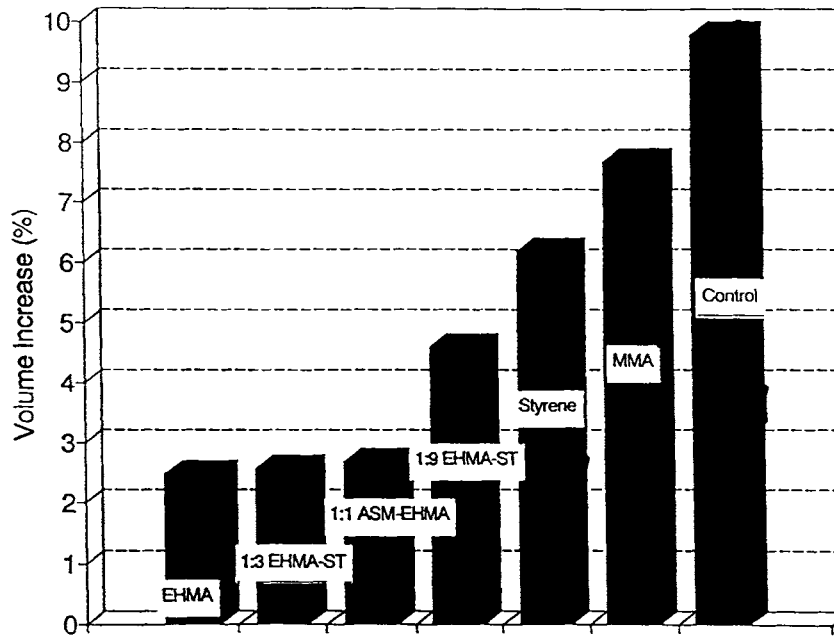
Figure 2 Dimensional stability of balsa WPCs given as % swelling due to water uptake after 5 days soaking.

as the concentration of EHMA in copolymers decreased, the dimensional stability of the WPCs decreased. This is probably due to a lower percentage of total polymer being incorporated into the cell walls, which increases the amount of water uptake possible; further work is needed, however, with regard to interdependent variable effects such as differential monomer sorption and the effect of total weight gain on dimensional stability. Qualitatively, it is striking that styrene-impregnated samples swelled more than twice as much as did the EHMA-impregnated samples, whereas MMA samples swelled more than three times as much as did the EHMA WPCs. It is clear that EHMA is an outstanding monomer for obtaining dimensional stability in WPCs.

Table I shows the results of the buckled plate test[8] for various sets of different WPCs. In general, a greater improvement in mechanical properties was seen for wood samples with less than 0.2 g/cm^3 initial density than for the samples having greater initial specific gravity (density and specific gravity are used synonymously in this paper). A large range of different monomer mixtures giving *in situ* polymer formation were examined in this study; however, emphasis here is on WPCs containing EHMA-ST copolymers, which gave the greatest improvements in modulus and toughness of those evaluated. Although the ASM homopolymer did improve mechanical properties, the ASM WPCs were not as

dimensionally stable as were the EHMA-ST WPCs and ASM is much more expensive than are ST and EHMA. Thus, the EHMA-ST WPCs demonstrated the most desirable combination of properties at a reasonable cost.

For balsa WPCs to compete with other composites, the *specific* properties of the material should be improved by the treatment. The specific modulus (or specific toughness) is the modulus (or toughness) divided by the specific gravity. For the whole wood control samples, the densities of the dried wood samples were used, whereas the total densities of the WPC samples were used for these samples. Specific properties give a qualitative indication of component synergism and mutual reinforcement. Few literature reports give specific properties for WPCs, probably because, for virtually all systems studied to date, the specific properties are less (often dramatically less) than those of the untreated wood.

In the balsa WPCs, improvements in *absolute* mechanical properties were achieved for all treatments (Table I). Although these results appear very encouraging and are certainly as good as or better than previous literature reports on WPCs in general, it must be noted that the *specific* mechanical properties decreased for all but one type of treatment (see Table II). Only for the balsa-EHMA-ST-pBDDA WPCs was there a substantial improvement in the specific modulus and specific toughness. To our knowledge, an improvement in specific proper-

Table I Modulus and Toughness Data (from Buckled Plate Test[7]) for Balsa Wood–Polymer Composites

Treatment	No. Tested	Average SG[a]	Average Δ Modulus (%)	Average Δ Toughness (%)
EHMA only	12	0.268	+7.5	−6.0
MMA only	6	0.266	+9.7	+16.1
1 : 3 EHMA–MMA	12	0.214	+22.3	+2.5
EHMA–MMA–pBDDA	6	0.191	+40.0	+52.8
ASM only	6	0.184	+68.5	+75.4
1 : 1 ASM–AN	6	0.189	+26.3	+17.0
1 : 1 ASM–EHMA	6	0.192	+21.4	+12.9
1 : 1 ASM–ST	6	0.090	+180.5	+135.8
EHMA–ST–pBDDA	36	0.219	+32.6	+15.0
9 : 1 EHMA–ST	6	0.316	+28.2	+5.9
3 : 1 EHMA–ST	6	0.309	−1.3	+25.7
1 : 1 EHMA–ST	18	0.256	+43.4	+64.6
1 : 3 EHMA–ST	6	0.177	+85.2	+61.8
1 : 9 EHMA–ST	24	0.206	+34.8	+91.2
Styrene only	6	0.316	+28.2	+5.9

[a] SG is the specific gravity (density) of the wood sample *before* polymer impregnation.

ties of wood on WPC formation has never been reported previously. In Table II, these results for our best system are compared to the few specific property values reported in the literature.[9,10] For the two sets of MMA-impregnated wood samples, there was a *decrease* in specific properties from 8.4 to 48.1%. These decreases are similar to those that we obtained for analogous treatments. In contrast, the average

specific modulus and specific toughness improved by 27.4 and 6.7%, respectively, for the three sets of samples impregnated with EHMA–ST–pBDDA. Final weight increases for these three sets of samples ranged from 10 to 40%.

We were surprised to find that a major criterion for specific property improvement is control of the amount of weight gain due to impregnation. As

Table II Comparison of As-measured Properties and Specific Properties (Measured Divided by Density) from Literature Data vs. Our Data for Balsa Impregnated with EHMA–ST–pBDDA

Wood/Treatment	No. Samples	Average Toughness (kJ/m^2)	Average Δ Toughness (%)	Average Specific Toughness	Average Δ Specific Toughness
Basswood/PMMA[8]	14	8.1	+50.0	8.1	−44.5
Basswood/control[8]	14	5.4		14.6	
Sugar maple/PMMA[9]	9	30.9	+43.1	27.2	−8.4
Sugar maple/control	10	21.6		29.7	
Balsa/EHMA–ST–pBDDA	18	8.9	+21.9	27.1	**+6.7**
Balsa/control	18	7.3		25.4	

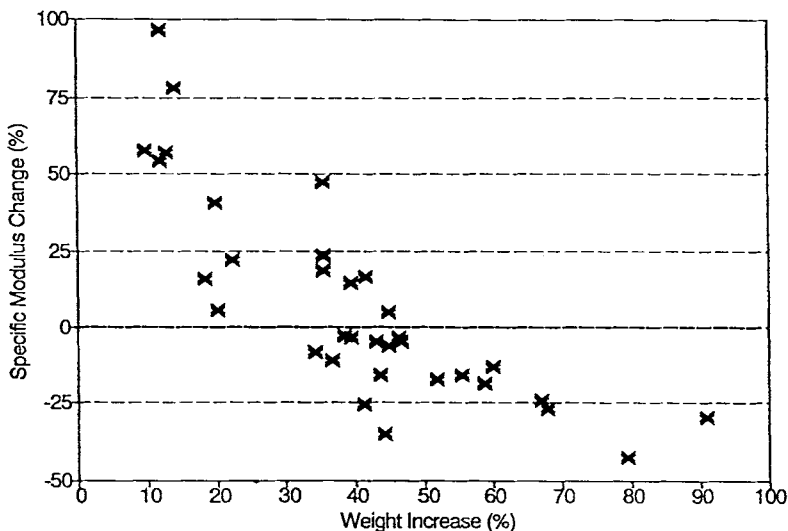| Wood/Treatment	No. Samples	Average Modulus (GPa)	Average Δ Modulus (%)	Averag Specific Modulus	Average Δ Specific Modulus
Basswood/PMMA[8]	14	11.6	+48.7	11.6	−45.0
Basswood/control	14	7.8		21.1	
Balsa/EHMA–ST–pBDDA	18	10.7	+32.1	32.1	**+27.4**
Balsa/control	18	8.1		25.2	

Figure 3 Effect of weight gain due to monomer uptake on % specific modulus change.

demonstrated by Figure 3, most of the EHMA–ST–pBDDA WPCs with improved specific properties had weight gains no greater than 30–40%. Beyond a certain value, the increase in density actually causes a decrease in *specific* mechanical properties. To control the weight gain, the samples were weighed before and after impregnation. If the weight gain was acceptably low, the samples were cured at atmospheric pressure under N_2. If the weight gain was too high, the samples were cured under high vacuum ($\cong$ 1 mmHg) to remove the excess co-monomer mixture from the cell lumens. Polymer-filled lumens are *not* necessary for strength improvement since the major increase in strength
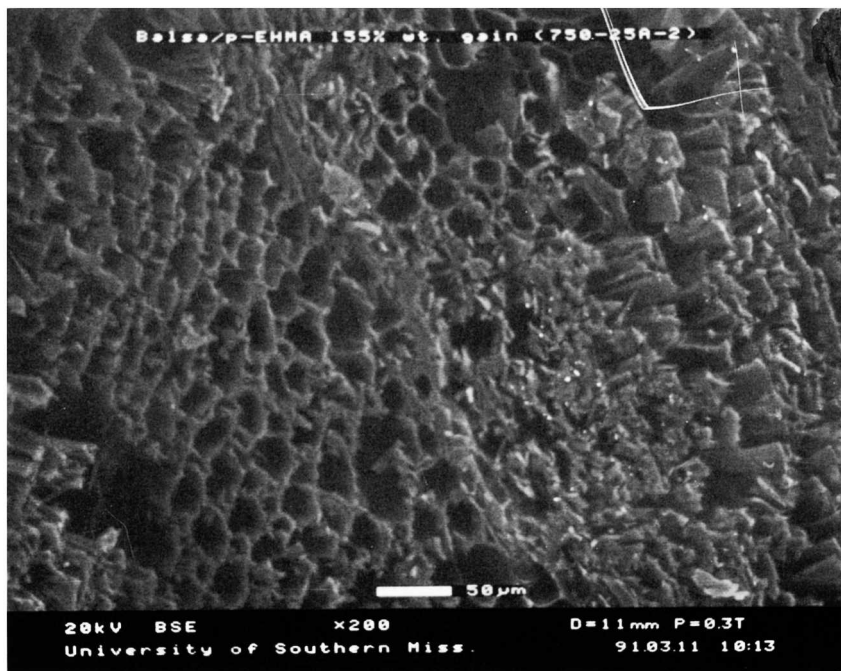

Figure 4 SEM micrograph of cross section of a fractured balsa wood–polymer composite containing 55 wt % poly(EHMA).
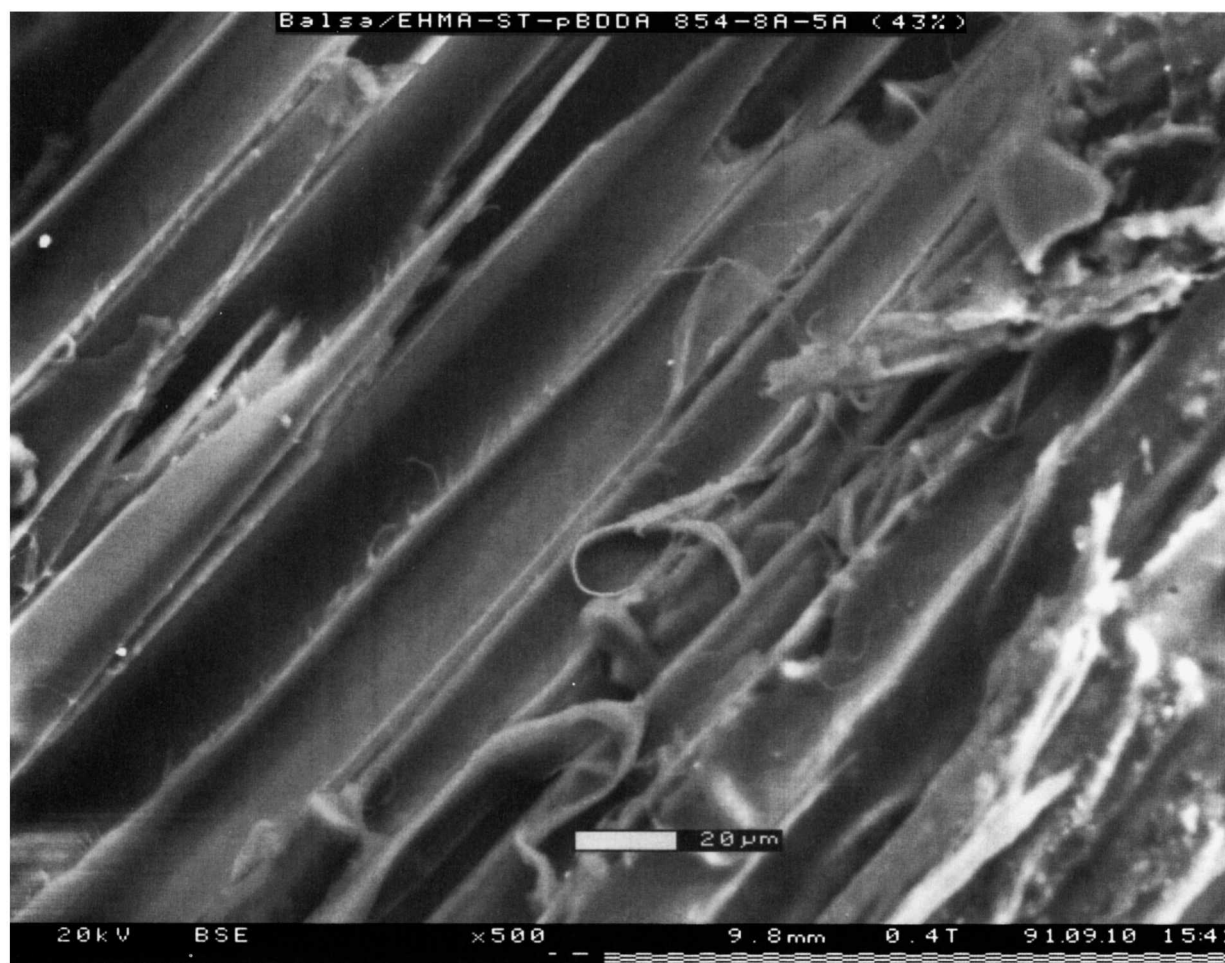
Figure 5   SEM micrograph of split radial section of a balsa wood–polymer composite containing EHMA–ST–pBDDA.

comes from cell wall reinforcement with polymer. However, if the lumens *are* filled with polymer, the cell walls must also contain that polymer for attaining maximum property improvement. In other words, the polymer located in the lumens should adhere to and penetrate the cell walls. Lumen filling is important, for example, when hardness is a major criterion for the application of interest.

Scanning electron microscopy (SEM) was used to examine polymer distribution within the WPCs and to confirm polymer–cell wall interaction. Figure 4 gives a micrograph of a typical cross section of a balsa/EHMA composite. This WPC is 55% polymer by weight with most of the cell lumens empty. This indicates that most of the polymer is contained within the wood cell walls. This intimate relationship between poly(EHMA) and the cell wall materials is further demonstrated in Figure 5. Good penetration and adhesion of the polymer to the cell

wall is indicated by the wood fibrils that remained attached to the cell wall after fracture, indicating wood cohesive failure rather than adhesive (interfacial) failure. EDAX results in the SEM (see the previous paper in this journal for details[5]) further confirmed good penetration of, and interaction with, the wood cell walls by these comonomer mixtures. Overall, this system (EHMA–ST–pBDDA) represents the most conclusively demonstrated example to date of monomer and polymer impregnation and reinforcement of whole wood cell walls. This intimate chemical and physical interaction results in wood–polymer synergism that is unique in giving *specific* property enhancements.

REFERENCES

1. S. Greenhouse, *Wood Products,* **46,** 870 (1941).
2. A. H. Stang, *Trop. Woods,* **14,** 12 (1928).
3. J. L. Stearns, *South. Lumberman Mag.,* **Dec. 15,** (1943).
4. J. Kohn, *Forest Prod. J.,* **8,** 27-A (1958).
5. J. R. Wright and L. J. Mathias, *J. Appl. Polym. Sci.,* **48,** 2225 (1993).
6. J. R. Wright and L. J. Mathias, *Polym. Prepr.,* **30,** 233 (1989).
7. J. R. Wright and L. J. Mathias, *Polym. Compos.,* **32,** 370 (1992).
8. R. L. Brady and R. S. Porter, *J. Mater. Sci.,* **24,** 4138 (1989).
9. J. E. Langwig, *Forest Prod. J.,* **18,** 33 (1968).
10. M. H. Schneider, *Forest Prod. J.,* **39,** 11 (1989).