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EXPANDING THE LIMITS OF WOOD POLYMER COMPOSITES:
STUDIES USING DYNAMIC MECHANICAL THERMAL ANALYSIS

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ABSTRACT

Wood-Polymer Composites (WPC) are unique composite materials where a natural composite (wood) is impregnated with monomers that are then polymerized in the wood to tailor the material for special applications. The polymers are used to enhance specific properties of wood such as dimensional stability, hardness and abrasion resistance. The glass transition and secondary transition temperatures of the impregnated polymer are important parameters when considering the performance of polymer composites. In our experiments, using formulations of acrylic based polymers, the transition temperatures of WPC have been characterized using dynamic mechanical thermal analysis (DMTA). A combination of acyclic monomers and other components were used to make polymers having differing properties. The effects of these polymer systems on transition temperatures measured by DMTA of the composites are presented. The effects of the interaction of the polymers with wood (the interphase) are discussed. Dynamic properties of the composites are related to physical properties of the composites.

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1. INTRODUCTION

Dynamic Mechanical Thermal Analysis (DMTA) is a useful method of detecting relaxations in polymer molecules as the temperature is scanned over a range from subambient to above the material's glass transition. This method of analysis is much more sensitive than differential scanning calorimetry (DSC) for the detection of molecular relaxations at the glass transition temperature (T_g) and can detect and measure secondary transitions (Gearing and Stone, 1984) which are nearly impossible to detect using DSC. Viscoelastic relaxations of chemically treated wood have been studied using a dynamic viscoelastomer (Sugiyama, Obataya and Nonmoto, 1995). The polymerization of glycidyl methacrylate in wood has been studied, the course of the polymerization was followed by measurement of the $\tan \delta$ (Balaba and Subramanian, 1986).

We have studied the temperature dependence of the loss tangent $\tan \delta$ of wood polymer composites (WPC). WPC are solid wood impregnated with monomers subsequently polymerized in the wood. Our objective was to characterize the changes of $\tan \delta$ as affected by monomer combinations and by the interaction of monomers/polymers with the wood. Several factors can affect the interactions in the polymer impregnated wood. These include: 1. hydrogen bonding of the polymer with wood (hydroxyl groups) 2. covalent bonding to the wood 3. the presence of a surface can also result in different molecular weight distributions and crosslink densities in the interphase region of the interactions. In general, an increase in the transition temperature usually indicates the restricted mobility of the polymer molecules in the interphase region of the interface and is usually indicative of good interaction. Either one or a combination of any of the above factors can be contributing to this behavior. The use of DMTA as a technique for evaluating properties of WPC was explored by looking for relationships, if any, of $\tan \delta$ with the hardness of the WPC.

2. EXPERIMENTAL

2.1 Monomer solution preparation The monomers used to prepare specimens set 1 were isobornyl methacrylate (IBMA), glycidyl methacrylate (GMA), hydroxyethyl acrylate (HEA) and hexanediol dimethacrylate (HDDMA). The monomers were used individually and mixed in molar ratios for the preparation of specimens (Table 1). The base triethylamine (TEA) was used to catalyze the opening of the oxirane ring in GMA. Specimens for set number 2 were prepared using the monomers isobornyl methacrylate (IBMA) and neopentyl glycol diacrylate (NPGDA) mixed on weight to weight ratios (Table 2). All the monomer solutions contained Vazo 52, a free radical initiator.

Table 1. Monomers solutions used to prepare specimens for set number 1

Monomer	portion of solution
IBMA	100%
GMA	100%
IBMA/GMA	1 mole / 1 mole
IBMA/GMA/triethylamine	1mole/1mole/5% triethylamine
GMA/triethylamine	95% / 5% triethylamine
IBMA/triethylamine	95% / 5% triethylamine
HEA	100%
HEA/HDDMA	1 mole / 0.1 mole
IBMA/HEA	1 mole / 1 mole

Table 2. Monomers used to prepare specimens for set number 2

monomer	mix ratio
IBMA	100%
IBMA/NPGDA	1/1 by wt
IBMA/NPGDA	2/1 by wt
IBMA/NPGDA	1/2 by wt
NPGDA	100%

2.2 Specimen Preparation. Maple veneers about 1.0mm thick and 100mm by 100mm were impregnated with acrylate or methacrylate monomers subsequently polymerized in the wood. The untreated veneers were placed in a vacuum chamber, a vacuum applied, after 30 minutes of vacuum the monomer solution was drawn into the chamber to cover the wood. The chamber was then returned to atmospheric pressure. The veneers were soaked in the monomer solution for one hour then removed and the excess monomer wiped from the surfaces. The veneers were placed in a press heated to 100° C to polymerize the monomers. All specimens were post cured for 2 hours in an oven at 120° C. Excess polymer was removed from the surfaces of the veneers by light sanding. Specimens for DMTA were cut from the center section of the 100mm square veneers. They were cut 5mm wide by 20mm long and 1mm thick. These specimens were dried at 105° C then stored over a desiccant until analyzed.

2.3 Dynamic Mechanical Thermal Analysis. Specimens were analyzed using a Rheometrics model Wk III dynamic mechanical thermal analyzer. A small single cantilever holder was used to analyze the specimens in a bending mode. A frequency of 1 Hz and a strain of 1% was used. The temperature was programmed at 2 degrees C per minute from -50° C to 300° C.

3. RESULTS

Monomers were selected because of known properties of their polymers. 1. IBMA polymer has a high Tg relative to HEA polymer. 2. The hydroxyl groups of HEA polymer can potentially interact via hydrogen bonding with the constituents of wood. 3. The oxirane ring of GMA can make covalent bonds with groups in wood. 4. HEA polymer can be crosslinked with the dimethacrylate monomer HDDMA. IBMA can be crosslinked with the diacrylate NPGDA. The tan δ plot from DMTA was used to evaluate changes in transition temperatures (Tg) that could give some understanding of polymer-wood interactions.

3.1 Crosslinking within polymers. WPC specimens made using IBMA, GMA or NPGMA appear to have little or no molecular interactions with the wood to change the major transitions. The observed transitions are close to the known transitions of the bulk polymers. The difunctional acrylate NPGDA used to crosslink KBMA gives polymers with higher Tg than that of IBMA polymer. IBM/NPGDA mixed 2:1 and 1:1 by weight raises the Tg from 113° C for IBMA without NPGDA to 120° C and 126° C respectively (Table 3).

HEA polymer in wood has a Tg of 21° C, slightly higher than reported Tg of 15° C for bulk HEA polymer. This increase could be caused by the interaction of hydroxyl groups in the polymer with chemical constituents of the wood. We need to determine the Tg of bulk HEA polymer using conditions similar to our WPC analysis by DMTA before a more positive conclusion is made. An

increase of the Tg is seen when HEA polymer is crosslinked with 0.1 mole of the difunctional methacrylate HDDMA per mole HEA (Fig. 1). The resulting WPC specimen has a Tg of 38° C (Table 4).

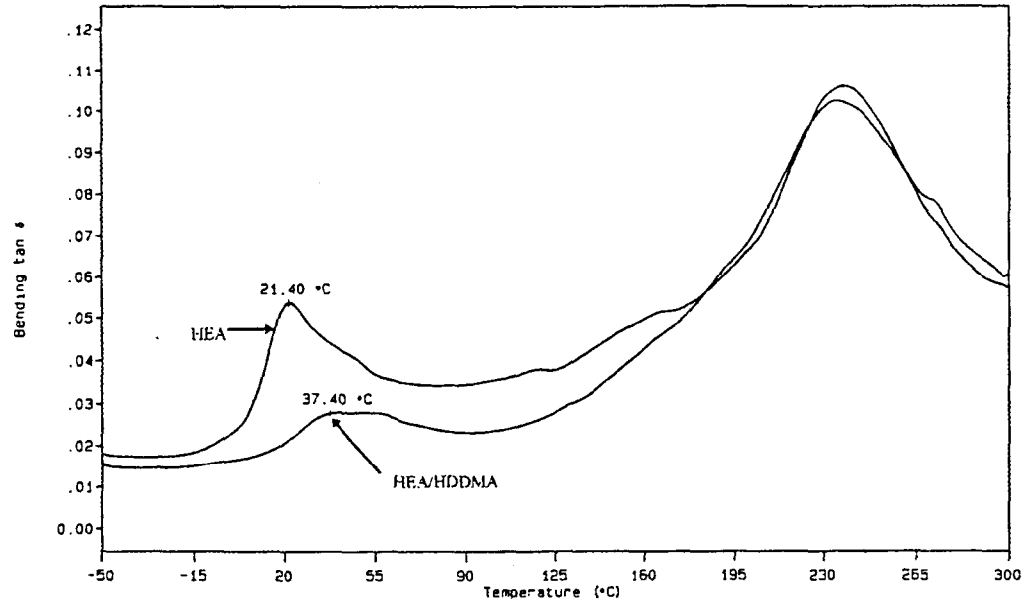


Fig. 1 DMTA of wood-HEA composites with and without crosslinking by HDDMA

Table 3. Specimen data for set 2.

Specimen	polymer loading percent	Rockwell hardness scale L	transition temperature degrees C
IBMA	61	34	113
IBMA/NPGDA1/1	64	37	126
IBMA/NPGDA1/2	66	41	107
IBMA/NPGDA2/1	69	39	120
NPGDA	65	39	80

3.2 GMA crosslinked polymer to wood. Relaxation in the polymers of WPC were observable as peaks in the $\tan \delta$ versus temperature plot using DMTA. The $\tan \delta$ Tg of 108° C for WPC prepared using IBMA was near the reported Tg of 111° C for IBMA. WPC prepared using IBMA/GMA and triethylamine to open and react the oxirane ring has the major transition 33 degrees higher than that of WPC specimens prepared using IBMA/GMA without triethylamine (Fig. 2). This increase of the transition temperature is seen as an indication GMA has attached (crosslinked) the polymer to the wood. WPC specimens prepared using GMA without triethylamine have a major transition at 89° C. WPC specimens prepared using GMA with triethylamine have no major transition peaks in the $\tan \delta$ plot until 243° C (Fig. 3) which is the point the wood begins to degrade. It appears the GMA polymer has crosslinked with the wood sufficiently that the transition has broadened so much it is no longer

easily detected on the $\tan \delta$ plot. We will do further experiments to confirm the attachment of polymer to the wood.

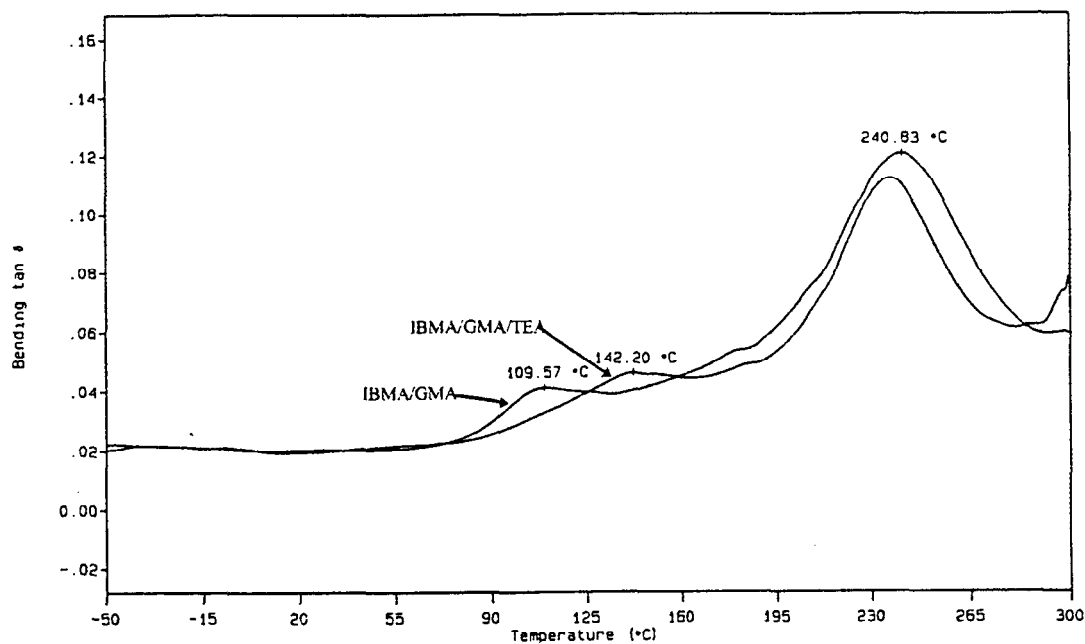


Fig. 2 DMTA of wood-polymer composites with glycidyl methacrylate's oxirane ring reacted and unreacted

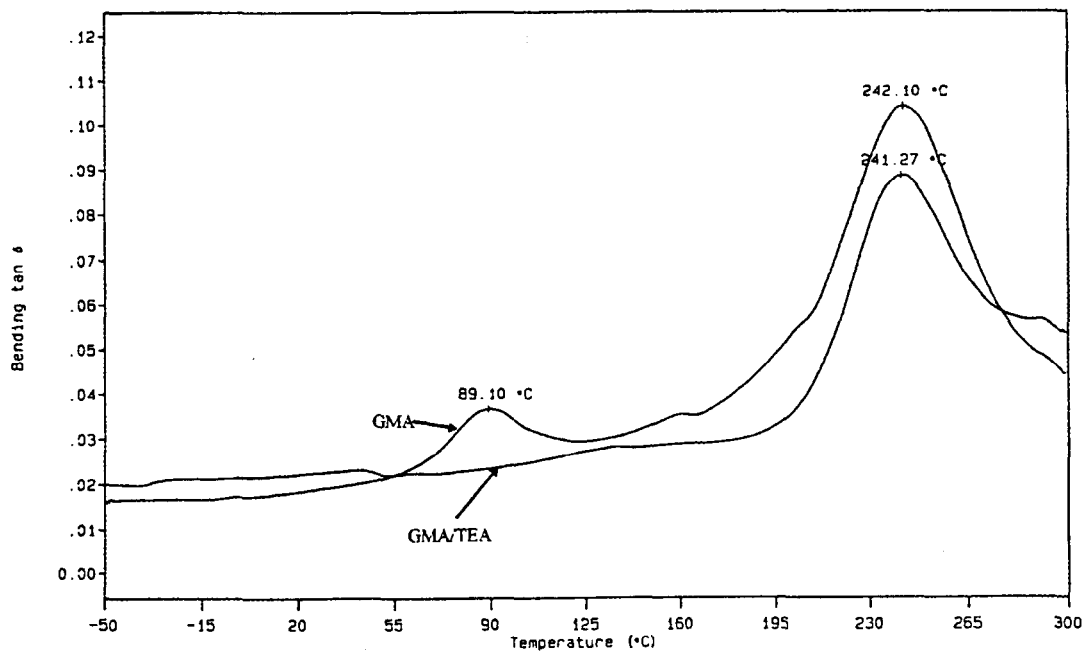


Fig 3. DMTA of wood-glycidyl methacrylate composites having oxirane ring reacted and unreacted

3.3 Transition temperatures related to hardness of WPC. The Rockwell hardness(scale L) of WPC specimens is generally greater for the specimens having higher transition temperatures (range from 89° C to 142° C) than for the specimens having lower transition temperatures (range from 210 ° to 96° C). The WPC specimens made with HEA in the monomer solution had lower hardness and lower transition temperatures than those of other WPC specimens (Table 4). The hardness of WPC is generally related to the hardness of the polymer but might also be affected by polymer-wood interactions.

Table 4. Specimen data for set 1.

Specimen	polymer loading percent	Rockwell hardness scale L	transition temperature degrees C	secondary transition degrees C
IBMA	61	36	108	252
GMA	68	41	89	241
IBMA/GMA	60	44	109	241
IBMA/GMA/triethylamine	63	45	142	236
GMA/triethylamine	72	44	none	243
IBMA/triethylamine	57	-	97	247
HEA	72	24	21	238
HEA/HDDMA	68	31	38	235
IBMA/HEA	64	34	96	233
control	0	-9	none	252

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