

Interaction Between Wood and Polyvinyl Acetate Glue Studied with Dynamic Mechanical Analysis and Scanning Electron Microscopy

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ABSTRACT: The long-term properties of bonds are those that are of special interest. To achieve good bonds, the wood polymers and the adhering polymers must be compatible. This paper describes studies of the interaction of wood (*Pinus sylvestris*) with commercial polyvinyl acetate (PVAc) glue, polymethylmethacrylate (PMMA), and a more hydrophilic acrylate. Interaction was studied with a dynamic mechanical thermal analyzer (DMTA) operating in tensile mode in the tangential direction of wood. DMTA results were correlated with scanning electron microscopy (SEM) fractography studies of adhesion between polymers and wood on a cell wall level. The hypothesis put forward is that a good adhesion on the cell wall level results in a decrease in

the glass transition temperature (T_g) measured with DMTA. A decrease in T_g for the hydrophilic acrylate was shown when it was impregnated in wood. The decrease of T_g was correlated with good adhesion to wood on the cell wall level. For PVAc and PMMA no decrease in T_g was measured when glued or impregnated in wood. SEM study also showed that the adhesion on a cell wall level was poor. The results show that DMTA can be a useful technique to study adhesion between wood and glue on a molecular level. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3009–3015, 2004

Key words: viscoelastic properties; glass transition; compatibility; wood; glue

INTRODUCTION

The glue bond is a more and more common replacement for welds, riveted joints, joints with screws, etc. in products. This development is most visible in the automobile industry. Also in the wood working industry the direction is toward industrial use of glued materials and construction instead of nailing or screw joints. The most rapid development is taking place in the building product area, where a more efficient joining technique is needed. The use of glued-laminated timber (glulam), particle, and fiberboards (MDF, OSB) is becoming increasingly popular. Wood is also extensively used as curved laminated veneer in furniture.¹ The properties and durability of adhesives exposed to different climates² are becoming more and more important.

The long-term properties of bonds are those that are of special interest. If good bonds are achieved, the surface between wood and adherend is less susceptible to degradation. Many methods exist for testing the peel strength and adhesion of glue lines. However, the majority of these methods only indicate a good or

poor adhesion without the possibility of relating the test result to the properties of a specific glue or polymer. To achieve a good bond, the wood polymer and glue polymer must be compatible and thus decrease the energy in the interface. Wood and glue need to develop some kind of bonding force. To create secondary bonds between the glue polymer chains and molecule chains in the wood cell wall, the molecules must be able to come in close contact with one another and therefore the viscosity of the adhesive must be sufficiently low.

A method that can give a better basic understanding of adhesion between wood and polymers on the cell wall level is dynamic mechanical thermal analysis (DMTA). It is a common method used to measure relaxation temperatures, such as glass transition temperature (T_g) for polymers. Measurement with DMTA is a method extensively used to study compatibility in polymer blends. Only a few attempts have been made to use this type of technique to measure interaction between wood and adhesives or coatings.

Handa et al.³ showed that impregnating wood with polyoxyethyleneglycol methacrylate (PEGMA) lowered wood relaxation peak temperature from 230 to 200°C. With hydrophilic polyacrylic acid (PAA), the peak was lowered from 230 to 180°C. It was argued that the shift in peak temperature was due to the polymers interacting with the cell wall surface and disturbing the arrangement of wood polymers. A in-

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crease in of 2°C T_g of polystyrene (PS) was seen when wood flour was added. The T_g of PS moved toward the cellulose T_g peak.⁴ Grafting of maleic anhydride (MA) on styrene-ethylene/butylene-styrene (SEBS) increased the T_g of the EB part when mixed with wood flour. The SEBS-MA was used as a compatibilizer in polyethylene-wood flour composites, giving increased tensile strength of the composite.⁵

In an earlier work we studied the interaction between wood and four different polymers: two polyurethane alkyd lacquers and two different types of acrylates.⁶ The difference in T_g for pure polymer and polymer in contact with wood was measured with DMTA. A clear decrease of T_g was observed for the polyurethane alkyd lacquers and the more hydrophilic of the two acrylates. It was suggested that this change in T_g indicated a high degree of interaction (good bonding). The DMTA study was combined with scanning electron microscopy (SEM) investigation of fractured specimens. A correlation was found between a high degree of interaction and good adhesion on a cell wall level. With adhesion on a cell wall level, we mean the possibility for the polymer to adhere to the wood cell wall during fracture, examined at a magnification level of individual wood cells and wood cell walls.^{7,8}

It is of interest to investigate the interaction between wood and glues, but more data of different kinds of polymer systems are needed to determine the feasibility of this method for predicting the adhesion to wood. Polyvinyl acetate (PVAc) is an important type of industrial glue. The aim of the present article was to analyze the interaction of PVAc glue with wood by the use of DMTA and SEM fractography.

METHODS

Wood samples

For DMTA measurements, defect-free sapwood specimens of Scots pine (*Pinus sylvestris*) 36 mm long (tangential), 4 mm wide (radial), and 4 mm thick (longitudinal) were used. The wood had been dried from green without external heating and thereafter stored in a laboratory climate. The specimens were cut in the longitudinal direction with a razor into four pieces to be glued together later on.

Glue

The glue used was Cascol Trälim Inne no. 3304 (Casco Products, Stockholm, Sweden). The film-forming polymer PVAc was a dispersion in water. The density of the glue was $1,080\text{ kg/m}^3$ at a solid content of 50–60%, 30–40% PVAc, 1–5% butyl diglycol acetate (film-forming agent), and 50–60% water according to

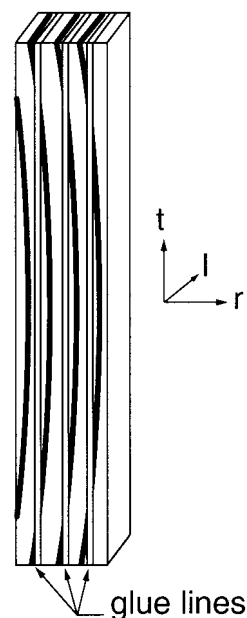


Figure 1 DMTA specimen with three glue lines. Measurement was made in tension in the tangential direction (t), radial and l , longitudinal directions of the wood.

the manufacturer. According to the manufacturer the glue also contained unspecified filler.

Gluing procedure

The wood pieces were freshly cut and the glue was applied within 10 min after cutting. PVAc glue was used and applied with three glue lines (Figure 1). After gluing the samples were kept under approximately 0.1 MPa pressure for 20 min. The glue spread was about 200 g/m^2 for each of the three glue lines. The glued wood specimens were dried in 33% relative humidity (RH) at room temperature for a total of 17 days before measurement in DMTA. Three days before measurement they were sanded to a thickness of 3 mm.

Preparation of PVAc films

Films of pure glue were used as reference. Films were made by casting glue on a flexible plastic sheet of polyester treated with a release agent. The film thickness obtained after drying for 8 days in room temperature was 0.3–0.4 mm. The remaining weight was 49% (compared to specified solid content of 50–60%). No further weight decrease was found after 4 months.

Impregnation and preparation of acrylic resins

Two types of acrylic resins were used, a methylmethacrylate resin and a more hydrophilic acrylic resin. The hydrophilic acrylic resin, Unicryl, was pur-

chased from British Biocell International (Cardiff, Wales, UK). Samples of impregnated wood (2 mm thickness in the longitudinal direction) and pure polymer were made. Wood was impregnated with Unicryl using vacuum impregnation and subsequently cured at 60°C for 48 h. Samples of pure polymer were produced simultaneously. Unicryl is normally used as an embedding resin in microscopy. The manufacturer states that Unicryl contains a mixture of four monomeric (meth)acrylate esters of unspecified composition premixed with a benzoyl peroxide catalyst. Unicryl is hydrophilic compared to methylmethacrylate.

Polymethylmethacrylate (PMMA) was made from methylmethacrylate resin with 1% benzoyl peroxide and polymerized at 65°C for 48 h. Samples of impregnated wood (2 mm thickness in the longitudinal direction) and pure polymer were made using vacuum impregnation and subsequently cured. Samples of pure polymer and impregnated wood were produced simultaneously.

Dynamic mechanical thermal analysis

Measurements were made in tension with a Dynamic Mechanical Thermal Analyser MkIII from Rheometric Scientific (Piscataway, NJ). Specimen size (length \times width \times thickness) in the DMTA was for pure PVAc film 12 \times 8 \times 0.3–0.4 mm. Wood specimens glued with PVAc were 23 \times 4 \times 3 mm. Acrylate and acrylate impregnated wood specimens were 20 \times 2–4 \times 1–2 mm. The clamps were applied on the transverse surface of wood specimens and measurement was made in the tangential direction. A minimum of two measurements were made on each type of specimen. Runs were made at 1 Hz with a heating rate of 2°C/min, and data were collected at intervals of about 1°C. The variation between runs for this particular DMTA is about 1°C. The dynamic average strain was 0.02–0.03%. When measuring in tension, a static force equivalent to about twice the force necessary for the dynamic amplitude was applied to prevent buckling.

Scanning electron microscopy on fracture surfaces

Fracture surfaces of wood glued with PVAc were studied with SEM. Wood pieces with a transverse surface cut by a sledge microtome were glued. The glue was applied to the microtomed wood surfaces and two specimens were then pressed together with a clamp for 2 h. The specimens were dried in air and then pulled apart. The fracture occurred in the glue line. The fracture surface had similar appearance after a drying time of 3 days as it did at 30 days. The SEM used was a Jeol 5200 and specimens were coated with gold.

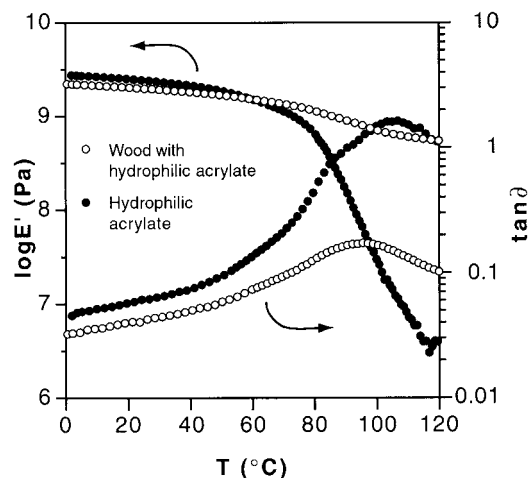


Figure 2 DMTA measurements on hydrophilic acrylate polymer and on wood impregnated with hydrophilic acrylate polymer. Polymer impregnated in wood had a T_g at 96°C and pure polymer had a T_g at 106°C.

RESULTS AND DISCUSSION

T_g as a tool to measure interaction between wood and polymers

In an earlier study⁶ results were obtained indicating that a good adhesion on a cell wall level between the wood and polymer resulted in a decrease in T_g . Two acrylate polymers were used as model polymers. For the more hydrophilic acrylate, a decrease in T_g with 10°C was shown when the polymer was impregnated in wood (Figure 2). The elastic modulus (E') corresponds with the curves decreasing with increasing temperature. The loss factor ($\tan\delta$) curves have a peak at 106°C for the pure polymer and at 96°C for polymer impregnated wood. SEM investigation of fractured specimens showed good adhesion on a cell wall level for this acrylate.⁶

A completely different behavior was observed for PMMA impregnated in wood. The SEM investigation of fractured specimens for PMMA showed poor adhesion on a cell wall level.⁶ The DMTA measurements on PMMA and PMMA impregnated wood showed no difference on the T_g for the PMMA. Both samples had similar glass transition temperatures (at 127 to 131°C) (Figure 3 and Backman and Lindberg⁶). This indicates a low degree of interaction between wood and PMMA.

The effect on T_g of adhesion on a cell wall level

Good adhesion on a cell wall level indicates interaction between the polymer and the wood cell wall, which implies some kind of bond formation. Adhesion on a cell wall level has been studied with microscopy,^{7,8} where poor adhesion was characterized by the

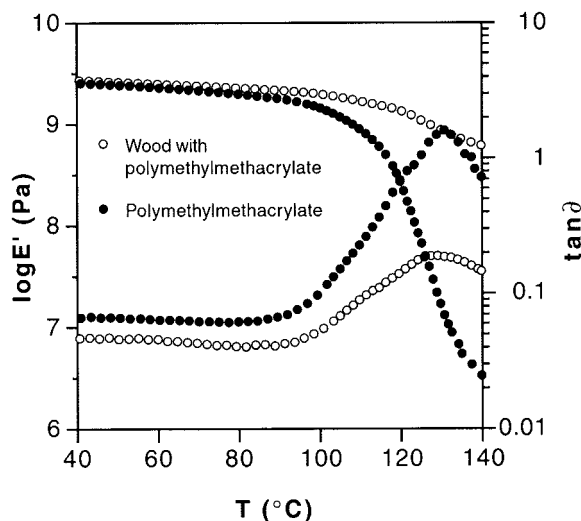


Figure 3 DMTA measurements on PMMA and wood impregnated with PMMA. PMMA in wood had a T_g at 127–129°C and pure PMMA had T_g at 129–131°C.

possibility to draw out rods of various polymers from the wood cell lumens. A polymer giving poor adhesion to wood as measured in this special way could very well give a good adhesion in a standard adhesion test due to the presence of mechanical interlocking, which is thought to be important in wood adhesion.⁹ Bond formation is difficult to differentiate from mechanical interlocking in standard adhesion tests.¹⁰

DMTA measurement of T_g is a method to study interaction on a molecular level of polymer chain segmental mobility. A decrease in the T_g is associated with an increase of free volume. Free volume is a concept used for polymers to explain the segment-size voids that exist between polymer chains, it is not related to the void volume in wood due to lumens and pores. The basic idea underlying the free-volume approach to relaxation phenomena such as T_g is that the molecular mobility at any temperature is dependent on the available free volume at that temperature.^{1,11,12} Figure 2 shows the decrease of T_g for the hydrophilic acrylate in contact with wood. The reason for this decrease is an increase in the free volume for the entire impregnated polymer volume. Such an increase in free volume could either be due to the presence of tensile forces^{4,13,14} and/or the presence of plasticizers.^{1,12}

Tensile forces acting on the polymer can be an indication of bonds between wood and the polymer. Tensile forces can result from shrinkage of the hydrophilic acrylate during polymerization in combination with the polymer adhering to wood on a cell wall level.

There could be a possibility that the decrease of T_g was due to the hydrophilic acrylate being plasticized by low molecular compounds from wood. To exclude this possibility the pure acrylate polymers and the

polymer-impregnated specimens were cured at the same time in the same container and were tested in the same way. If plasticizers were the cause of the T_g decrease, then the pure polymer polymerized in the same container as the wood impregnated specimen should also be plasticized and differ in T_g from polymer polymerized distant, or in the absence of wood. Experiments showed no such differences. This indicates the polymer was not plasticized by compounds originating from wood. The only externally available plasticizer was moisture, but it was also excluded since the specimens were stored together and tested in similar conditions.

The only reasonable explanation for the T_g decrease of the hydrophilic acrylate in contact with wood was tensile forces acting on the polymer. This decrease in T_g occurred when a polymer had a high degree of interaction with wood, which also previously has been shown for a polyurethane-alkyd lacquer.⁶ A polymer interacting with wood could have an increase in T_g due to a decreased mobility caused by the interaction with wood polymers.^{4,5} The decrease in T_g due to tensile forces could then be superimposed giving a total decrease in T_g . The origin of the tensile forces may be from shrinkage of the hydrophilic acrylate during polymerization in combination with the polymer adhering to wood on a cell wall level.

SEM fractography on wood glued with PVAc

To investigate the possibility of measuring the interaction between wood and glue, commercial PVAc glue was investigated. When studied in SEM the PVAc polymer showed no interaction with the wood cell wall. The microscopic pictures (Figures 4 and 5) show an abundance of rods of glue withdrawn from the inside of wood cell lumens. The fracture surface observed in SEM is from two transverse surfaces of

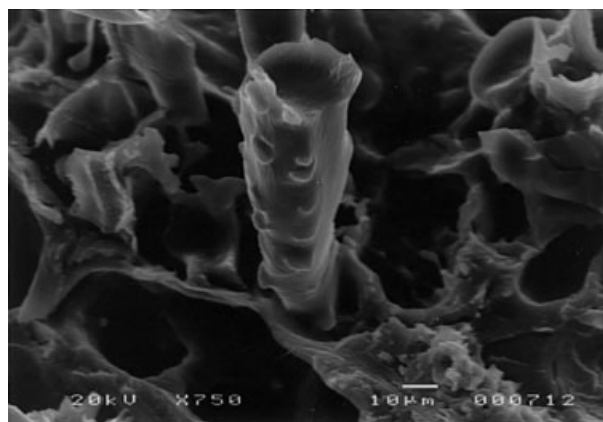


Figure 4 SEM micrograph of fracture surface of two transverse wood surfaces glued with PVAc, showing a protruding rod of glue.

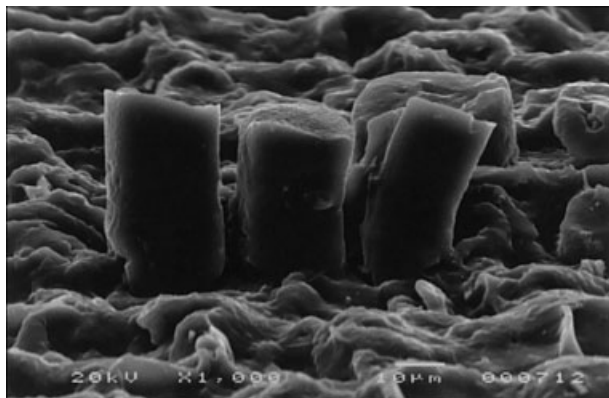


Figure 5 SEM micrograph of fracture surface of two transverse wood surfaces glued with PVAc, showing three protruding rods of glue.

wood that had been glued together and then fractured.

The viscosity of the glue was low enough for the glue to penetrate the cell lumens and to come close enough to the cell walls to render an offprint of the cell wall pits. Figure 4 shows a magnification of a rod of glue; the marks from pits between tracheids were clearly visible. The bond developed between the glue and wood cell wall, i.e., the interfacial adhesion, was, however, lower than the cohesion of the PVAc, and thus a rod of glue could be drawn out of the cell lumen.

Figure 5 shows three protruding rods of glue next to one another. The interaction between the glue molecules and wood molecules was so low that the cell wall previously located between these rods could be withdrawn. Similar behavior were shown for PMMA, where rods were drawn out of the cell lumen⁶, but no such rods could be observed for the more hydrophilic acrylate.⁶

DMTA measurements on PVAc

A film of pure PVAc with different drying times was tested in DMTA (Figure 6). T_g for PVAc is normally stated to be at 28°C,¹¹ but measurements in a DMTA normally render slightly higher temperatures.¹² Four specimens with drying times of 8 to 13 days gave T_g at $37.6 \pm 0.6^\circ\text{C}$. T_g was measured as the loss factor ($\tan\delta$) peak temperature. For the drying time of 8 days, a peak also appeared at about 70°C, but was missing for the longer drying time. The origin of this peak was unclear. We would like to emphasize that the PVAc glue used was a commercial system containing unknown additives and the origin of the peak was not investigated further. The longer drying time of 13 days in Figure 6 gave a significantly higher level of $\tan\delta$. It was probably related to the disappearance of the peak at 70°C, but, as stated above, the T_g peak

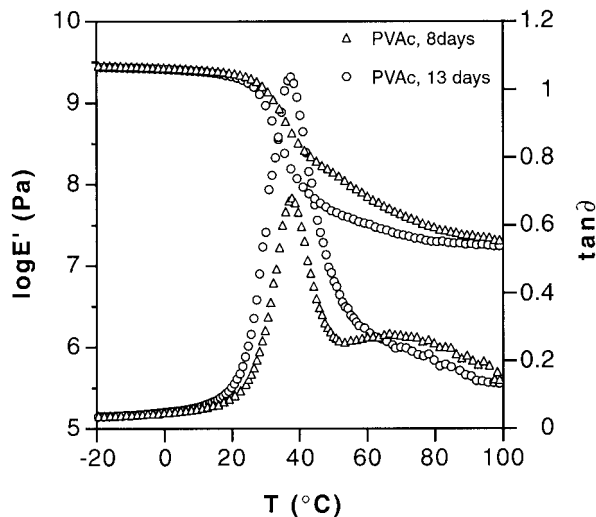


Figure 6 DMTA measurements of PVAc glue dried at room temperature for different drying times: 8 days and 13 days.

temperature did not change. A measurement on a PVAc glue specimen dried for a year (and previously subjected to drying for 48 h in 103°C) gave a T_g at 38.5°C.

DMTA measurements on wood glued with PVAc

Specimens of wood glued with PVAc were tested in the tangential direction of wood (Figure 1). Figure 7 shows the DMTA measurement of two specimens with glue dried for 17 days. They had a $\tan\delta$ peak between 39 and 40°C. If a specimen of wood is tested,

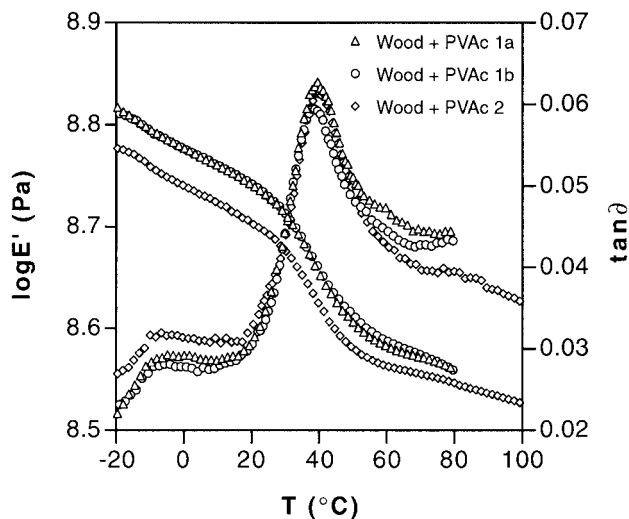
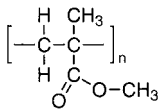
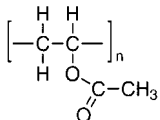
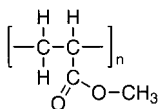


Figure 7 DMTA measurements of paired specimens of wood glued with PVAc. Specimen 2 and the first measurement of specimen 1 (1a) were made after drying for 17 days and measurement of specimen 1 was repeated the following day (1b).

TABLE I
Structure and Hansen Solubility Parameters of Polymers PMMA, PVAc, and PMA

Name	T_g (°C)	Structure	Hansen solubility parameters (MPa ^{0.5})			
			δ_D	δ_P	δ_H	δ
PMMA	105		18.64	10.52	7.51	22.69
PVAc	28		20.93	11.27	9.66	25.66
PMA	3		—	—	—	—

a $\tan\delta$ peak originating from wood polymer relaxation, probably from the wood polymer hemicellulose,¹⁵⁻¹⁷ can be found in the same temperature interval. In the tangential direction of *P. sylvestris*, this peak is at about $50 \pm 6^\circ\text{C}$ with a peak height at $\tan\delta = 0.04$.¹⁸ The peak height in Figure 7 was above 0.06 and the high temperature side of the peak showed a trace of the wood polymer relaxation. The peak at $39-40^\circ\text{C}$ in Figure 7 was attributed principally to the T_g of PVAc since the peak could not originate from wood. Specimen 1a in Figure 7, which was measured to an end temperature of 80°C , was tested again the following day and gave a T_g of 39°C with the curve of $\tan\delta$ and E' almost identical to the first run (Figure 7, 1b). The difference of the peak temperature for PVAc in wood ($39-40^\circ\text{C}$) from the peak temperature for pure PVAc ($37-38^\circ\text{C}$) was very small.

Both the microscopy study and DMTA measurements show that PVAc has low interaction at the cell wall level. This is in line with our hypothesis that only good adhesion on a cell wall level gives rise to a decrease of T_g as shown above for the hydrophilic acrylate.

Comparison of molecular structure between PVAc and PMMA

To further emphasize the similar behavior of adhesion on a cell wall level of PMMA and PVAc to wood, the molecular structures of their repeating units can be compared (Table I). PMMA has a T_g at 105°C , which is higher than polymethyl acrylate (PMA) with T_g at 3°C and PVAc at 28°C .¹¹ The three polymers have quite similar chemical structures. PMMA and PVAc also have relatively comparable Hansen solubility parameters,¹⁹ (Table I). PMA is only included in this discussion to show the similarities in chemical structure

between PMMA and PVAc. The structural unit of PMA is isomeric with that of PVAc, and the difference between PMA and PMMA is the presence of a methyl side group in PMMA. No solubility parameter for the polymer PMA could be found in the literature, but the solubility parameter δ (MPa^{0.5}) for the monomers of the above polymers (PMMA, PMA, and PVAc) all range from 18.0 to 18.4.¹⁹ Due to these similarities in molecular structure and solubility parameters, it was not surprising to find a similar behavior in interaction with wood for PMMA and PVAc.

CONCLUSION

The hypothesis put forward is that a good adhesion on the cell wall level, as measured with SEM fractography, results in a decrease in the T_g measured with DMTA.

- The T_g of pure PVAc and of PVAc in wood was the same, which indicated a low level of interaction between wood and PVAc. PVAc was shown with SEM fractography to have poor adhesion to wood on a cell wall level.
- A hydrophilic type of acrylate polymer showed a 10°C decrease in T_g when it was impregnated in wood compared with the T_g of pure polymer. It has in an earlier work⁶ been shown to have good adhesion to wood on the cell wall level.
- The polymer polymethylmethacrylate showed no difference in T_g as pure polymer or impregnated in wood. PMMA also showed poor adhesion to wood on a cell wall level. It was suggested that the similar behavior of PMMA and PVAc interaction with wood was a result of their similar chemical structures.

The decrease in T_g for a polymer adhering to the wood cell wall is due to an increase in free volume. The decrease in T_g as measured for the more hydrophilic acrylate was not due to increased amounts of plasticizer but was attributed most probably to be due to tensile forces acting on the polymer.

PVAc is an important type of industrial glue and obviously has relatively good adhesion to wood. It has been shown in this work that the presence of any kind of bond between wood and this PVAc glue has a very low probability. The adhesion as measured with a standard adhesion test would thereby mainly be due to mechanical interlocking between wood and PVAc.

The results show that DMTA can be a useful technique to study adhesion between wood and glue on a molecular level.

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