

Interaction Between Wood and Polyurethane-Alkyd Lacquer Resulting in a Decrease in the Glass Transition Temperature

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ABSTRACT: The long-term properties of paint and glue are of great interest to both manufacturers and users of these materials. If a good bond is achieved, the surface between the wood and the paint or glue will be less susceptible to degradation. Thus, the wood and polymer must be compatible and develop some kind of bonding force between them. A high degree of interaction between wood and commercial polyurethane-alkyd lacquer was shown as a decrease by 10°C of the glass transition temperature (T_g) for the lacquer on wood compared to the pure lacquer. The lacquer also demonstrated good adhesion to wood at a microscale. The interaction was investigated with dynamic mechanical thermal analysis and scanning electron microscopy fractography. The reason for the decrease in T_g is probably because of the lacquer having a higher free volume when applied to the wood, most likely due to it being subjected to tensile forces developed during the drying of the lacquer. Results from investigations of wood impregnated with two different acrylates, a polymethylmethacrylate and a more hydrophilic acrylate, support the suggestion that a decrease in T_g will occur if the polymer adheres to wood, but that poor interaction with little or no adhesion will result in no decrease in T_g . This article also presents results of the dynamic mechanical behavior of Scots Pine in the tangential direction. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 595–605, 2002

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

INTRODUCTION

The use of gluing as a joining method is becoming more and more commonplace in many products as a replacement for welding, riveting, use of screws, and so forth. This development is probably most visible in the automotive product sector, but

many other industry branches are moving in the same direction. For wooden products, the shift is clearly toward the use of glued materials and constructions instead of nailing or screw joints. The area of most rapid development is in building products, where more up-to-date and efficient joining techniques are needed. Buildings are usually painted in colors and a long life between repair or recoating is, naturally, desirable. A similar requirement exists for lacquered furniture and other expensive wood products.

Interfaces exist in all paint/wood, lacquer/wood, and glue/wood systems. The weakest part

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of these interfaces is always the bond. Many demands must be satisfied for a long-lasting interface. First, the contact area must be as large as possible, following surface roughness of the substrate down to molecular dimensions. Second, there must be a perceivable compatibility between molecules in order for bonds to occur.

It is seldom that these requirements are fulfilled. It has been shown that the glue in boards is very unevenly distributed and actually covers a very small part of the total surface.¹ Even for a relatively controlled gluing of surfaces which appear smooth, the interface strength varies considerably over small local areas.² This can even be seen under microscopy after a peel-off method.³ The bonds between wood and polymers are much more complicated than bonds between glued, painted, or lacquered metals or polymers because of the unavoidable roughness of any wooden surfaces. Östman⁴ showed that the surface roughness, R_a , for wood is about 10 μm ; although the method used was relatively crude because the needle jumps and make impressions on the wood surface.⁵ This R_a is around the same size as the cell lumen size, or of a double cell-wall thickness in latewoods.⁶ Also, if the lateral resolution of the surface roughness measurements is increased, a fractal-like surface roughness is observed extending down to molecular dimensions. A molecule, monomer, or oligomer in a paint, lacquer, or glue has a cross-sectional size of only parts of a nanometer. At that size, even small drying cracks found in wood⁷ can add significantly to the interaction area. For this reason, it is clear that a paint, lacquer, or glue should have sufficiently low viscosity to fill up the surface roughness and penetrate small cracks.

The bond between wood and a polymer can be modeled as several volumes interacting in different ways (Fig. 1): (1) a volume of pure polymer in the middle of a glue bond and in the outer part of a surface treatment; (2) as a composite of polymer and wood close to the wood surface; and (3) at the wood surface where the wood and polymer can form primary or secondary bonds.

The material in the first volume, (1), would not interact with wood because of the relatively long distance between them. However, this volume can be affected by forces such as internal tensile or compressive forces resulting from shrinkage and swelling of both wood and polymer. The next volume can be considered a composite in the classic sense, with the polymer acting as matrix and the wood fibers as reinforcement or filler. Because of

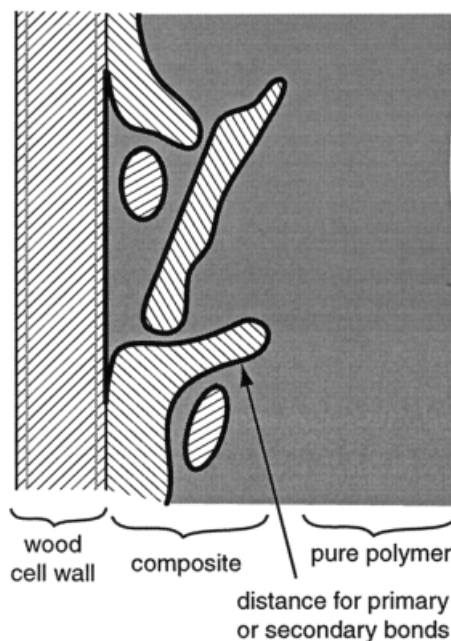


Figure 1 Model of interaction volumes.

the relatively short distances between the polymer in this composite and the wood polymers, of the order of a few micrometers, some interaction can be expected. Many studies have investigated the interaction between filler and polymer in filled polymer systems.^{8,9} It was shown that these interactions can shift the glass transition temperature (T_g) of the polymer and that the interaction length can be treated as an interphase.¹⁰

The layer closest to the wood has a very large area and although the interaction distance is small, it accounts for a considerable proportion (volume percentage) of the adherent. In this volume, the interaction occurs for small segments with interaction lengths from about 1 nm up to 100 nm.¹⁰

The long-term properties of paint and glue systems are of most interest to both users and manufacturers. If good bonds are achieved, the surface between wood and adherent is less susceptible to degradation. Many methods exist for testing the peel strength and adhesion of these bonds. However, the majority of these methods only indicate a good or a poor adhesion without the possibility of relating the test result to the properties of a specific glue or lacquer. To achieve a good bond, the wood and polymer must be compatible and develop some kind of bonding forces. The viscosity of the adherent must also be sufficiently low so as to allow the polymer chains to fill the wood's surface features at a microscopic scale.

The work presented in this article was an investigation into the interaction of two commercial polyurethane-alkyd lacquers and two acrylate polymers with wood by the use of a dynamic mechanical thermal analyzer (DMTA) and scanning electron microscopy (SEM) fractography. The level of interaction is measured by the change in relaxation speed for the main chain movements (T_g). Two different acrylate polymers were used as references: one interacted poorly with the wood, whereas the other interacted well. The aim of this work was to show a connection between good microscopic adhesion, and therefore, a high degree of interaction, with a decrease in T_g for a polymer adhering to wood. The influence of the viscosity of the lacquer and acrylates was not investigated.

METHODS

Material

The two polyurethane-alkyd lacquers used were Deluxe (YVA213) from International (hereafter PUR1), and Celco Golvlack (10133) from Nordsjö (hereafter PUR2). Films of the two lacquers were made by applying a total of 19 layers of lacquer with a brush on a metal plate treated with a release agent, Marbocote 445 from Montoil AB. The drying period used between applying layers of paint was that recommended by International for the PUR1 lacquer: min/max, 24 h/4 days at 5°C; 6 h/2 days at 23°C; and 4 h/1 day at 35°C. After the final layer had been applied, the film was dried at 35°C for 1 week and thereafter stored in a laboratory climate.

Plasticized specimens of PUR1 were made by immersing a specimen cut from the films in aliphatic white spirit for 26 h at room temperature (RT).

The solvent used in both polyurethane-alkyds is white spirit. The dry weight of PUR1 was stated to be 44% in the data sheet obtained from the manufacturer. A steel plate was painted with one layer of PUR1 and the applied mass of lacquer established by weighing after 20 s. After a 40-min drying period [$T = 23^\circ\text{C}$, 40% relative humidity (RH)], some 58% of the mass of paint remained. Under these conditions, there was no further weight loss. However, after thermal treatment at 80°C for 4 days, the mass had been reduced by a further 4% of original mass to 54%. When painting lacquers on a wooden substrate,

similar behavior was seen with about 60% of the original paint mass remaining after 1 h and with very little further decrease in sample weight after 7 h.

Polyurethane lacquers exist in many different formulations and also as polyurethane-alkyd lacquers. These lacquers are analogues of unsaturated alkyd resins in which parts of the chain were replaced by a diisocyanate; with wood, toluene diisocyanate (TDI) is often used. The resin cures by autooxidation with atmospheric oxygen of the double bonds in the fatty acid portion.¹¹

The wood used in the present study was clear sapwood from Scots Pine (*Pinus Sylvestris*), which had been dried from green without external heating and thereafter stored in a laboratory climate. DMTA measurements of samples cut in the tangential direction were made. The samples had been preconditioned in 11 and 33% RH at RT over saturated solutions of LiCl and MgCl₂,¹² giving about 3 and 7% moisture content (mc), respectively.¹³

Wood specimens treated with either PUR1 or PUR2 lacquer were made for DMTA measurements by using two different methods.

(1) Wood slices with a thickness of 3.5 mm were sawed perpendicular to the longitudinal direction. From these slices, smaller specimens with a width in the radial direction of 2–3 mm were cut using a razor blade and finally smoothed using 150-grade sandpaper. Both tangential surfaces were painted with three layers of lacquer (according to the schedule given above) and then either dried at RT or dried at 35°C for 1 week and thereafter stored at RT. The amount of lacquer applied was ~ 80–100 g/m². The transverse direction was then sanded until the sample thickness was about 2 mm. This procedure was used to minimize the amount of lacquer penetrating from the transverse direction.

(2) Wood slices with a thickness of about 2.5 mm were painted once on the sawed transverse surface, dried at 35°C for 1 week, and then stored at RT. Specimens were then made by cutting the slice with a razor blade and sanding all surfaces except the painted one with 150-grade sandpaper. The lacquer fills the wood cell cavities (lumens) close to the surface. The thickness of the resulting lacquer layer on the transverse surface is very thin, even though the lacquer was applied at ~ 135 g/m².

A hydrophilic embedding acrylic resin, Unicryl (from British Biocell), was impregnated into the wood by using a slight vacuum and subsequently

cured at 60°C for 48 h. Pure polymer was produced simultaneously. The uncured resin is a mixture of four monomeric (meth-) acrylate esters of unknown composition. The resin was bought premixed with a benzoyl peroxide catalyst. Pure polymer and impregnated wood specimens were made in the same way by using methyl methacrylate with 1% benzoyl peroxide. The methyl methacrylate was polymerized at 65°C for 48 h.

METHODS

DMTA of specimens with a free length of 12–20 mm were made in tension by using a dynamic average strain of 0.03–0.04%. The frequency was 1 Hz and the heating rate 2°C/min. Analysis was made with a DMTA MkIII from Rheometric Scientific. Specimens of treated or untreated wood were measured in the tangential direction with the mounting clamps pressed against the transverse plane. Specimen thickness in the longitudinal direction was 1–2 mm and the width in the radial direction 2–3 mm. The pure acrylate specimens had the same dimensions. The polyurethane-alkyd specimens used were 5 mm wide and 0.3 mm thick.

The SEM used was a Jeol 5200, and specimens were coated with gold. Surfaces for the two acrylate-impregnated materials were created by loading the specimens in tension in the longitudinal direction until fracture occurred. Three layers of polyurethane-alkyd were applied on a microtome-cut transverse surface. After drying, the specimens were cut in the longitudinal direction toward the lacquer surface to create a notch, after which the fracture surface to be studied was created by tearing the wood chips apart.

RESULTS AND DISCUSSION

Dynamic mechanical measurements for untreated wood samples cut in the tangential direction and initially conditioned to 3 and 7% moisture content are presented in Figure 2. The modulus can be seen to decrease from 1.2 GPa at –120°C to 0.6 GPa at 80°C with only slight differences between the 3 and 7% moisture content samples. At around –80°C, a loss factor ($\tan \delta$) peak associated with the movement of methylol groups coupled to water molecules can be seen.^{14,15} When the moisture content increases, the peak temperature decreases. At about 50°C, a

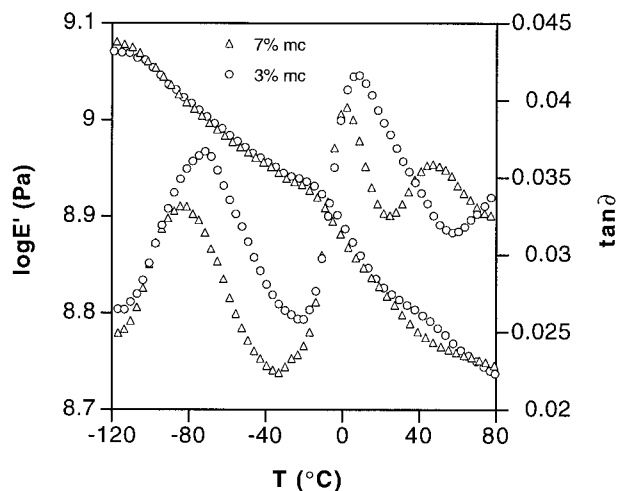


Figure 2 DMTA measurements in the tangential direction of wood with different moisture contents.

hemicellulose (HC) glass transition peak^{16,17} is visible for samples with 7% moisture content. For a moisture content of 3%, the peak temperature increased to above 80°C. The movement of the peak for the 3% moisture content sample is also seen in the elastic modulus (E'), which does not decrease in quite the same way for the 3 and 7% moisture content samples at about 40°C. The loss factor peak observed for both samples between –1 and 8°C¹⁸ has not clearly been assigned to any molecular movement.^{15,19,20} This peak also decreases in height with increasing moisture content.

The damping peak usually associated with the hemicellulose T_g was not easily interpreted. The wood used in these tests is subjected to drying at elevated temperatures because the experiments were made without climate control. This means that the location of the HC T_g peak is a poor indicator of the interaction of HC with polymers (i.e., it is not possible to recognize movements of HC peaks because of HC interaction with polymers). However, it is necessary to understand the dynamic mechanical behavior of the untreated wood to distinguish wood polymers from the applied lacquers and acrylates. The interaction between the wood and the coating polymers was studied by observing changes in the lacquer and acrylate polymer loss factor peaks.

Acrylate

Polymethylmethacrylate (PMMA) is a polymer known to interact poorly with wood.²¹ However, it

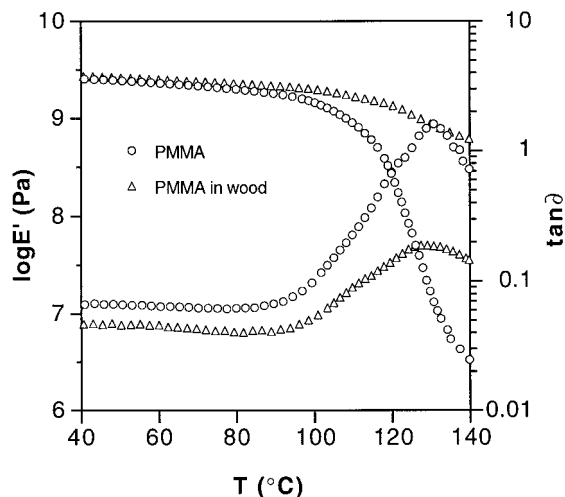


Figure 3 DMTA measurements of pure polymerized methyl methacrylate (PMMA) and PMMA impregnated in wood.

is widely used as a stabilizing polymer for wood; in fact, it is one of the most common stabilizing chemicals quoted in the literature (articles, patents, etc.) from 1926 to 1997, reported in Wallström.²²

In Figure 3, the tensile dynamic modulus and $\tan \delta$ for pure PMMA and PMMA-impregnated tangential wood are shown. The pure polymer and PMMA in wood have virtually the same T_g peaks, 129–131°C for pure polymer and 127–129°C for PMMA in wood. The much lower peak height for PMMA in wood reflects the relative amount of PMMA in the impregnated wood. The tensile modulus of the impregnated samples is considerably higher than that of the untreated wood. For the impregnated wood, a slight shoulder can be seen from 80°C and down. This shoulder is not seen in the pure PMMA curve and is believed to be due to wood polymer relaxation.

The dynamic measurements do not indicate any molecular interaction between the PMMA and the wood. To support these findings, a fractography investigation of specimens broken in tension was carried out. In Figures 4 and 5, SEM micrographs of the fracture surfaces are shown. The adhesion between the wood and the PMMA can be seen to be very low. In Figure 4, a rod of PMMA about 0.7 mm long which has been pulled from within a cell can be seen. The PMMA surface is smooth, with no cell-wall debris adhering to it. At the tip of the rod, a cast of the window like pits common in Scots pine can be seen. In addition, the fracture surface shows several empty cells,

where it is believed that polymerized PMMA was drawn out. Shorter rods of PMMA (see Fig. 5), all showing smooth surfaces, can be seen in abundance on the fracture surface. The gap seen between the wood and PMMA in Figure 5 is also a remarkable feature. This low adhesion, together with the DMTA graph showing the same peak temperature for the pure PMMA and the impregnated wood, clearly indicates very low interaction between the wood polymers and PMMA.

Results from DMTA tests on a hydrophilic acrylate polymer (more hydrophilic than PMMA) and samples of wood impregnated with the polymer are shown in Figure 6. A clear difference in loss factor peak temperature can be seen. The hydrophilic acrylate-impregnated samples show a

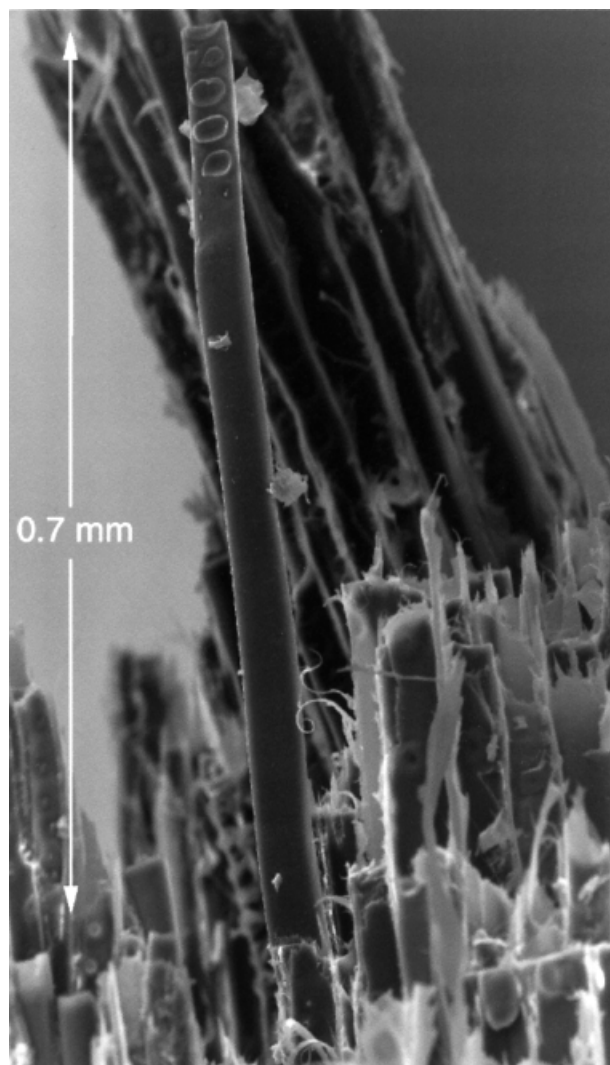


Figure 4 SEM micrograph of longitudinal fracture of composite showing a rod of PMMA.

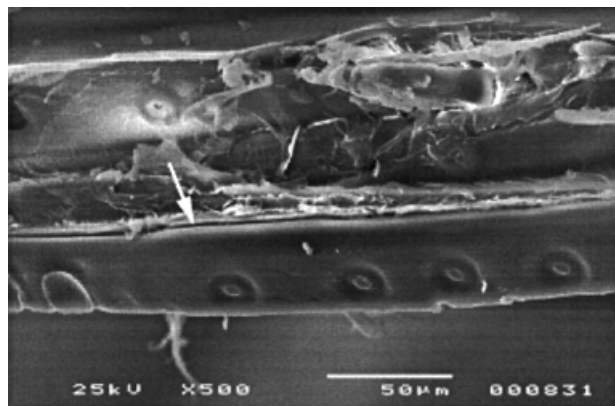


Figure 5 SEM micrograph of longitudinal fracture of composite showing poor adhesion between wood and PMMA. The arrow indicates a clear gap between wood and PMMA.

loss factor peak at 96°C, whereas the pure polymer has a peak at 106°C, a decrease in peak temperature in the impregnated specimen. The change in peak temperature is an indication of changes in molecular mobility in the hydrophilic acrylate. In Figure 7, a fracture surface of the hydrophilic acrylate-impregnated wood is shown. The lumens in the micrograph are filled and the hydrophilic acrylate can be seen to adhere to the wood extremely well compared to PMMA. No pulled out rods of the hydrophilic polymer could be found. The fractures in the wood and hydrophilic acrylate occur mostly in the vicinity of each other. In Figure 7, three cells filled with polymer can be observed where the fracture occurred in

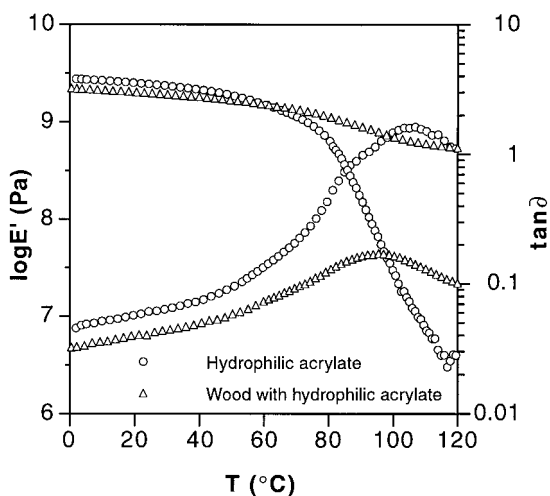


Figure 6 DMTA measurement of hydrophilic acrylate, pure and impregnated in wood.

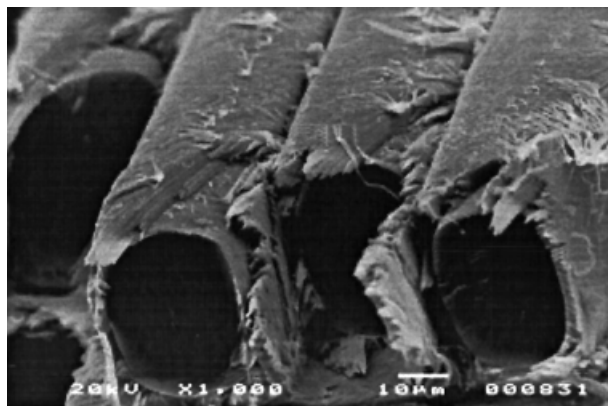


Figure 7 SEM micrograph of longitudinal fracture of composite showing good adhesion between wood and hydrophilic acrylate; the lumens are filled.

the wood cell wall. Figure 8 is a magnification of Figure 7 where the cell-wall layers can be discerned. On the hydrophilic acrylate surface, either layer S3 or an impression of S3 can be seen. The thick layer is S2 and traces of the layer S1 are seen in the left-hand part of the figure.

When two miscible homopolymers are blended, the T_g of the blend is a weighted average of the T_g of the two components.²³ A polymer which is compatible with the wood it impregnates should show an increase or decrease in T_g due to its interaction with wood polymers. However, it is only the impregnated polymer closest to wood that experiences this interaction. It should therefore be possible to see a double T_g peak with the superimposed relaxation from the pure polymer far from the wood surface and that from the polymer interacting with the wood and wood polymers (see Fig. 1). However, this is not the case for the hy-

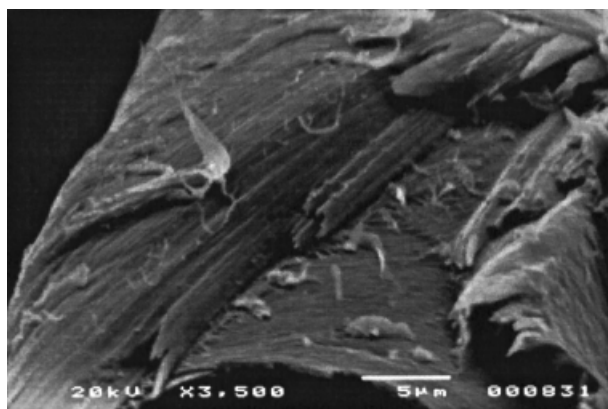


Figure 8 SEM micrograph, showing magnification of Figure 7.

drophilic acrylate-impregnated wood, as only one T_g peak is visible (see Fig. 6). The reason for this is that the polymer in the center of the cell lumens is far from the cell walls. The average lumen size is 10–30 μm , which is far greater than the possible interaction length of 1–100 nm. The 10°C decrease in the T_g peak for the impregnated hydrophilic acrylate cannot be due to the effects of the very small volume of the polymer closest to the cell wall and the interaction with the wood polymer. The decrease in T_g must be due to the entire polymer volume obtaining a higher free volume.

An increased free volume, and resulting decrease in T_g , could be the result of the presence of plasticizers or tensile forces.^{24,25} The pure polymer samples were polymerized, stored, and tested in exactly the same way as the impregnated samples, even as far as being polymerized in the same container at the same time. The only external plasticizer available is moisture, but because samples were stored together, they should have the same moisture content, so it is possible to rule out the presence of a plasticizer as the reason for the decrease in T_g . This leaves the only reasonable explanation for the decrease in T_g for the hydrophilic acrylate in wood as being tensile forces developed in the impregnated polymer during polymerization. The PMMA impregnated into wood is not subjected to these tensile forces because the polymer exhibits very low adhesion to the wood and is subsequently free to shrink unhindered during polymerization. The hydrophilic acrylate, however, adheres well to the wood, and after polymerization, the entire polymer volume will be subjected to tensile forces.

In ref. ²⁶, it was shown that impregnating wood with polyoxyethylene glycol methacrylate (PEGMA) lowered one peak temperature in

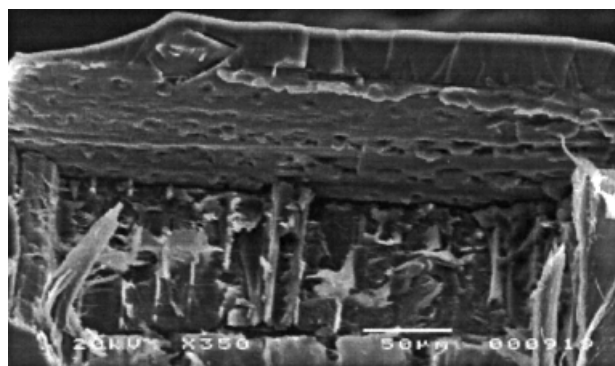


Figure 9 SEM micrograph of wood painted with polyurethane-alkyd (PUR1).

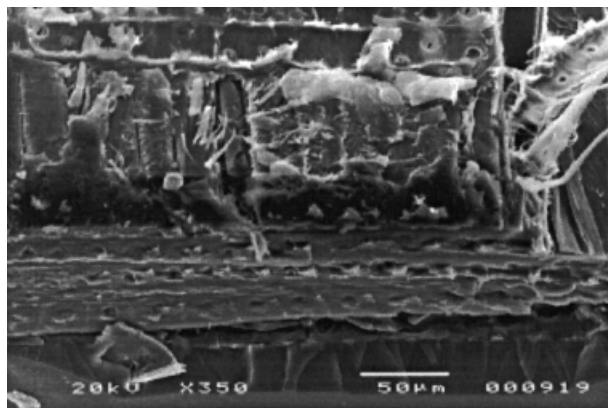


Figure 10 SEM micrograph of wood painted with polyurethane-alkyd (PUR1).

wood from 230 to 200°C. The presence of a glass transition at 130–230°C in wood is usually related to amorphous components in cellulose.²⁷ It was argued that the shift in this T_g peak was due to the PEGMA interacting with the cell-wall surface and disturbing the arrangement of lignin, cellulose, and hemicellulose by extending the intermolecular distance. The use of a hydrophilic polyacrylic acid (PAA) also decreased the wood T_g from 230 to 180°C. The authors did not attempt to explain why the molecular distance in wood increases, although they did speculate about the presence of PEGMA and PAA within the cell wall. It is quite possible that the decrease in cellulose T_g in that work was due to the same mechanism as observed in the present work, tensile forces resulting from the polymer shrinking during polymerization, but being constrained by its close interaction with the wood cell wall.

Polyurethane-Alkyd

To investigate whether it was possible to observe a decrease in T_g for polymers with good adhesion, tests with two commercial polyurethane-alkyd lacquers were carried out. When investigated in SEM, both lacquers showed good adhesion to the wood. Figures 9 and 10 show opposite surfaces of a fracture. In the upper part of Figure 9, a layer of lacquer has detached itself from the transverse surface of the wood. No rods of the polyurethane-alkyd are seen protruding from this detached lacquer. At the bottom of Figure 10, the pure lacquer is visible and the cell lumens are clearly filled with lacquer. Figure 11 show the transverse sur-

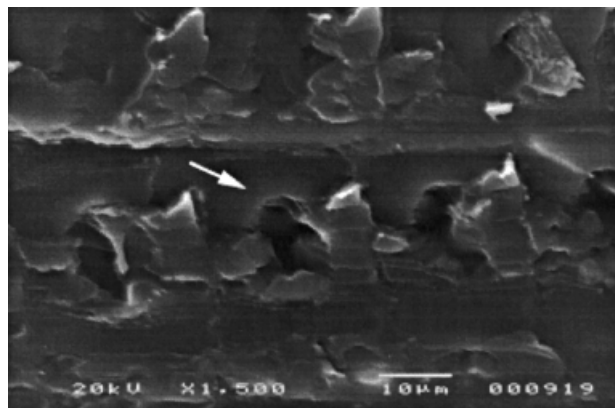


Figure 11 SEM micrograph of wood painted with polyurethane-alkyd (PU R1), a magnification of Figure 10.

face in Figure 10 magnified showing traces of the wood cell structure. The arrow indicates a possible interfacial fracture between the wood and polyurethane-alkyd, although most of the surface was characterized by cohesion failure in the lacquer.

The two polyurethane-alkyd lacquers used were from two different manufacturers and samples coated with these had very similar dynamic mechanical properties. In Figures 12 and 13, the elastic modulus and $\tan \delta$ for the lacquers are shown. These are designated as PUR1 (Fig. 12) and PUR2 (Fig. 13). The modulus can be seen to decrease from 2 GPa at -20°C to about 10 MPa after the transition, a drop in modulus of three

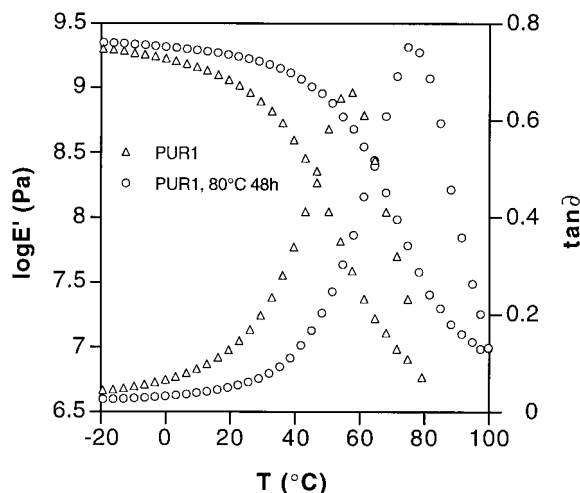


Figure 12 DMTA measurements of polyurethane-alkyd (PUR1) lacquer, with heat treatment at 80°C and without heat treatment (i.e., dried in 35°C for 1 week).

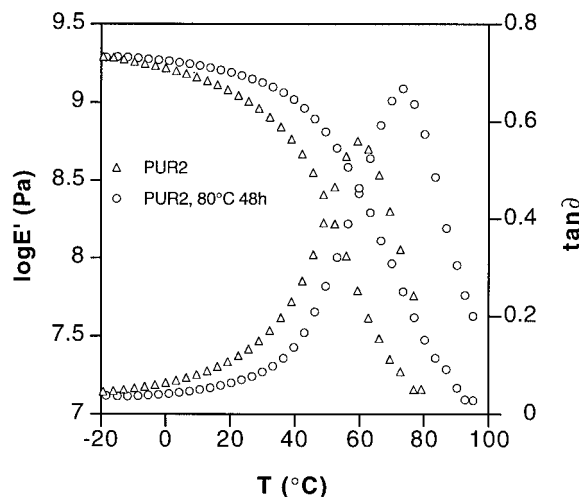


Figure 13 DMTA measurements of polyurethane-alkyd (PUR2) lacquer, with heat treatment at 80°C and without heat treatment (i.e., dried in 35°C for 1 week).

orders of magnitude. The glass transition temperatures for the two lacquer polymers were 57°C for PUR1 and 60°C for PUR2. Lacquer films stored at RT gave the same curves after 1 week, and after three months, the peak temperature for PUR1 had increased only slightly from 57 to 59°C . Dynamic measurements of alkyd and urethane coatings presented in ref. ²⁸ showed T_g 's of ~ 68 and 87°C , respectively, at 110 Hz. Both polymers are slightly crosslinked and the elastic modulus for the urethane coating fell from 2 GPa at 20°C to 30 MPa at 140°C , with a similar modulus as that given in the present study.

Heat treatment of the lacquers at elevated temperature increased the glass transition temperatures. The peak height increased and T_g increased to 76°C for PUR1 and 74°C for PUR2 after treatment at 80°C for 48 h (see Figs. 12 and 13). In both cases, the lacquer specimens decreased in weight by 5%. An additional heat treatment for another 48 h increased the T_g further, but by only 3°C . Following thermal treatment at 80°C for 4 days, the samples decreased in weight by 5–6%, but the color of the lacquer became rather yellow; indicating a slight degradation. A heat treatment at 120°C for 24 h resulted in a T_g at 94°C for PUR1 and 91°C for PUR2; in both cases the peak decreased in height compared to the samples treated at 80°C and was a little lower than the untreated samples. The full width half-height (FWHH) of the loss factor peaks from both lacquers increased slightly with longer thermal treatments and higher temperatures. The un-

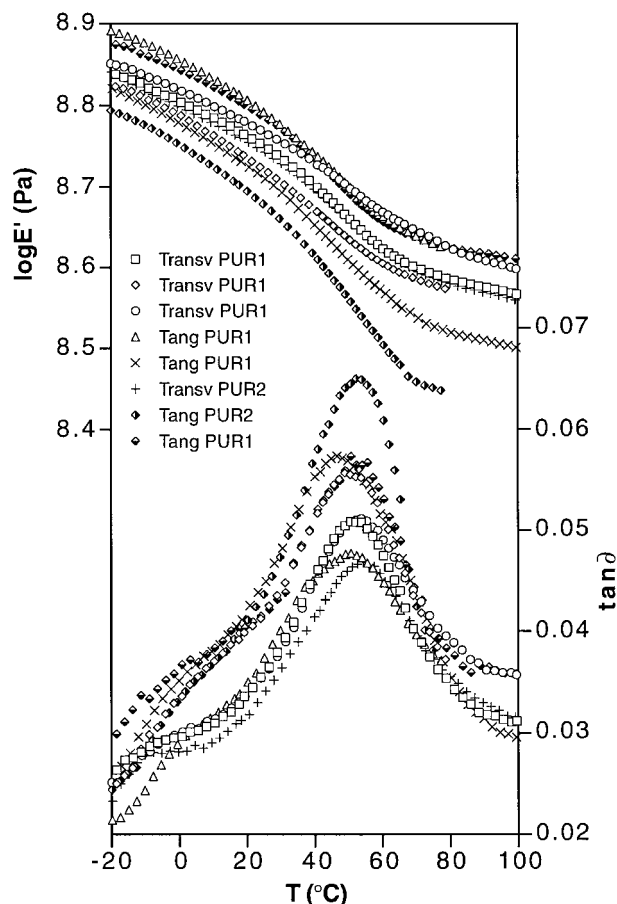


Figure 14 DMTA measurements of polyurethane-alkyd on transverse and tangential surfaces.

treated and thermally treated specimens had similar moduli above the T_g .

Tangential measurements of wood painted with lacquers are shown in Figure 14 with the $\tan \delta$ peak temperatures presented in Table I. The

two lacquers were again very similar in behavior, PUR1 showing a peak at 50–54°C and PUR2 at 52–54°C. Both tests had some scattering, although the resolution of these DMTA tests is about 1°C between measurements. Both types of specimens (e.g., painted on tangential or transverse surface) also behave similarly. Why one of the PUR1 samples showed a remarkably lower T_g at 47°C is unexplained. The lacquer painted on wood compared to the pure lacquer without thermal treatment showed a 3–7°C lower peak temperature for the PUR1 and 6–8°C lower for the PUR2.

Transversely painted specimens were treated at 80°C for 48 h. These showed an increase in the $\tan \delta$ peak temperature to 66°C for PUR1 and to 62°C for PUR2. Neither of these figures is even close to the peak temperatures of 76 and 74°C for the pure PUR1 and PUR2, respectively, treated in 80°C for 48 h. There is, in other words, a significant difference in the T_g for the pure lacquer and for the lacquer on wood and this difference increases following thermal treatment.

The reason for the increase in peak temperature for pure films with thermal treatment can be due to the increased amount of crosslinking^{29,11} or the decreased amounts of plasticizer.^{30,23} An increase in crosslink density is often associated with an increase in peak width³⁰; however, the width can also decrease.³¹ A broadening of a peak can also be due to the addition of plasticizers, where poor solvents for the polymer generally broaden the peak more than good solvents.^{30,23} An increase in peak height can be due to decreased amount of plasticizer³⁰; at low levels of crosslinking, the $\tan \delta$ level is not affected.³¹ Thermal treatment of lacquers at 80°C increased

Table I Thermal History and Peak Temperatures for PUR1 and PUR2 Lacquer Painted on Wood Before Measurement in DMTA

Painted on:	Lacquer	35°C (days)	RT (days)	$\tan \delta$ peak (°C)
Transverse surface	PUR1	7	1	50.5
	PUR1	7	7	53.8
	PUR1	7	21	52.1
	PUR2	7	21	53.5
Tangential surface	PUR1	7	2	53.3
	PUR1	—	6	50.7
	PUR1	—	13	46.7
	PUR2	—	6	52.3
	PUR2	—	13	52.3

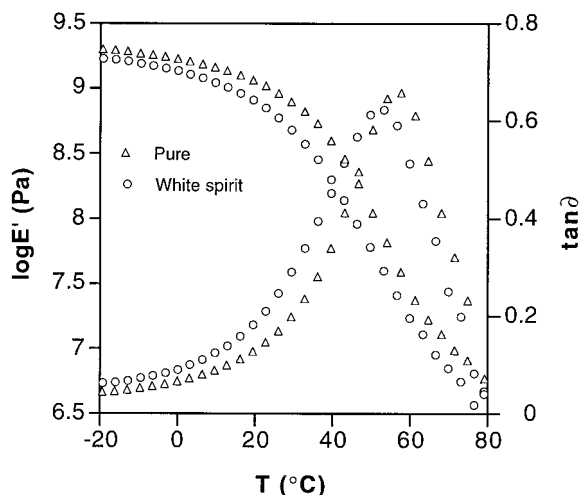


Figure 15 DMTA measurements of polyurethane-alkyd lacquer; white spirit content decreased from 4.4 to 3.2% during the experiment.

peak height and decreased weight but did not significantly alter FWHH. A specimen of PUR1 lacquer with 3–4% absorbed amount of white spirit decreased the T_g from 59 to 52°C and slightly increased the FWHH compared to untreated lacquer (see Fig. 15). The increase of T_g for PUR1 and PUR2 thermally treated at 80°C is due to decreased amounts of plasticizer.

Thermal treatment of wood samples painted with lacquer also increased the T_g . This should also be due to decreased amounts of plasticizer in the lacquer. No differences in the content of low molecular weight components such as white spirit should exist between the pure lacquer and the lacquer on wood. The drying schedule used was the same in both cases with about 60% of the lacquer mass applied remaining after 40 min. To test whether wood absorbed and retained white spirit, a DMTA wood specimen was soaked in aliphatic white spirit and increased in weight by about 30%. After exposing the specimen to normal atmosphere, almost all the absorbed spirit had evaporated after 1 h. A few hours later, the specimen did not even smell of white spirit and therefore the wood cannot be considered a barrier for aliphatic white spirit. Water, or moisture, is also a plasticizer for polyurethane-alkyd, but no differences in moisture content should be present because of the similar conditions to which the pure lacquer and lacquer on wood samples had been subjected. No difference in crosslink density is expected to occur between the pure lacquer and the lacquer on wood because curing is governed by the presence of atmospheric oxygen.

The reason for the significantly lower T_g for lacquer on wood is almost certainly due to the lacquer experiencing a higher free volume in the wood. This is argued to be due to tensile forces developing during curing because of good adhesion between the polyurethane-alkyd and the wood.

Loss Peak in the Tangential Direction

The motions in wood resulting in the loss peak between -1 and 8°C in Figure 2 have not been satisfactorily explained. It is possible that similar peaks are seen in refs. ^{15,19,20} but none of those measurements were done in the tangential direction. During measurements in DMTA for this article, it was found that the loss peak decreased in height, or totally disappeared when lumens were filled (see Fig. 16). All measurements were done in the tangential direction and, in the case of impregnating with PMMA, the peak totally disappeared. The peak at 40°C is most probably from a secondary transition in PMMA.²³ Specimens painted with polyurethane-alkyd showed a peak greatly reduced in height, but those specimens were not completely filled. We suggest the possibility that this loss peak is associated with the structure of wood in the tangential direction. In pure wood, small strains in the tangential direction result from bending of the cell walls.³² If wood is filled, the polymer inside the cell lumens will tend to prevent the cell wall bending and the loss peak disappears.

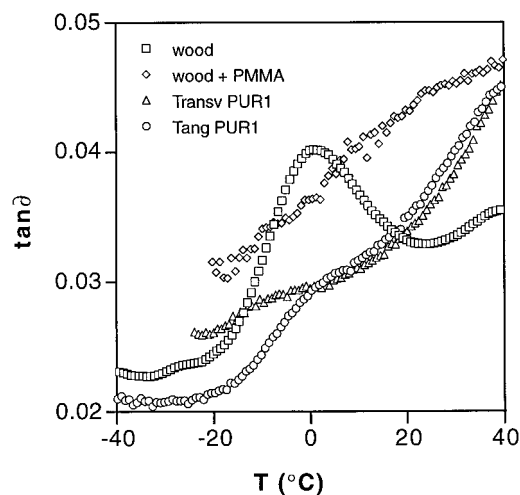


Figure 16 DMTA measurements in the tangential direction of wood, wood impregnated with PMMA, and wood painted transversely or tangentially with PUR1.

CONCLUSION

Good interaction between wood and a polyurethane-alkyd lacquer was demonstrated, with a decrease in T_g for the lacquer on wood compared to the pure lacquer. The lacquer adheres well to the wood at the microscale. The reason for the decrease in T_g is due to the lacquer having higher free volume when applied to the wood, most likely due to being subjected to tensile forces developed during drying. If the interaction is low, with poor adhesion between the wood and lacquer, no decrease in the T_g of the polymer is observed. Two different acrylate polymers which were cured in the same way with the same catalyst support the theory of a decrease in T_g if the polymer adheres well to the wood.

We propose the possibility of a loss peak at about 0°C, in the tangential direction, originating from the cellular structure of wood.

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