DOCTORAL THESIS

A study of wood adhesion and interactions using DMTA

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It is not possible for two things to be fairly united without a third for they need a bond between them which shall join them both, that as the first is to the middle, so is the middle to the last, then since the middle becomes the first and the last, and the last and the first become the middle, of necessity, all will come to be the same. And being the same with one another, all will be a unity.

Plato in Timaeus

For my son.

Never work in passivation or adhesion,
one is too simple, the other is too complex.

K.L. Mittal

Abstract

The aim of the work presented in this thesis was to investigate whether the adhesion of glues and lacquers to wood could be studied using dynamic mechanical thermal analysis (DMTA). This method has been widely used to study interactions in polymer blends, copolymers and in polymeric composites but very few investigations had been done on solid wood. DMTA has the ability to give basic information on polymeric structures, which is an advantage over other test methods for adhesion.

In this thesis pine wood (*Pinus sylvestris*) and several glues and lacquers have been studied using DMTA in the tensile mode. Both wood and pure polymers have been studied as well as polymers that have been polymerised in situ in wood, applied with a brush or as glue between wooden strips. The adhesion has then been studied and verified using fractography tests viewed with scanning electron microscopy (SEM). The adhesion has been characterised as "poor at the cell wall level" when there was a noticeable separation between the adhesive and the wood substrate as viewed in SEM. If the fracture occurred in the polymer or in wood cell walls, i.e. not at the interface, and no smooth polymer surfaces could be found, the adhesion was characterised as "good at the cell wall level".

The primary result was that the interaction as measured with DMTA between wood and polymers with high interaction and adhesion to wood showed a decrease in glass transition temperature (Tg) as compared to the Tg of the pure polymer material. Examples of high adhesion and interaction are the interaction between wood and a hydrophilic acrylate polymerised in situ from monomeric methacrylates. High interaction and adhesion was also found for two commercial polyurethane alkyd lacquers. No decrease in Tg was noted for polymers with low adhesion and interaction with wood. An example of low adhesion is polymethyl methacrylate (PMMA) polymerised in situ in wood. Low interaction and adhesion was also observed for a commercial polyvinyl acetate (PVAc) and wood. No change in interaction could be observed for the PMMA to wood when wood was made more unpolar (more lipophilic) by acetylation or silylation. The hydrophilic acrylate showed an increased interaction to silylated wood but unchanged interaction to acetylated wood.

The decrease in Tg for polymers showing high interaction and adhesion to wood is probably due to an increase of the free volume in the polymer. An increase in free volume can be due to tensile forces developing during polymerisation, drying or curing of the glues, lacquers and acrylate polymers.

This thesis shows that DMTA is an interesting method to obtain a basic understanding of adhesion phenomena and should be of interest for manufacturers of glues and paints and lacquers, and especially for thermoplastic adhesives. However, further experimental investigation is needed for the potential to test load-bearing glues.

Acknowledgement

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I would also like to thank my closest colleagues for all their help and discussions about my life and my work: Olov Karlsson, Eva-Stina Nordlund, Anna Pantze and Bror Sundqvist. During these years, many others have been friendly, fun and interesting to know, namely: Henrik Berglind, Jonny Grahn, Jan Nyström, Kristiina Oksman, Margot Sehlstedt-Persson, Magdalena Sterley, Lennart Wallström and many more. Thank you for your inspiration.

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Although I have chosen to first thank my professors, in my heart my greatest and warmest thanks goes to my husband Thomas. He has always believed in me and supported me; although I am sure that he really does not long for any more detailed declarations about the composite structure of wood. Our lovely little son Fabian is the reason the world exists, a thousand Ph.D. theses will not give the same satisfaction as one of his hugs.

With love to all,

Anna Backman Sandlund

Anna Backman Sandlund

Contents

Appended papers

Paper I A. C. Backman and K. A. H. Lindberg, "Differences in wood material responses for radial and tangential direction as measured by dynamic mechanical thermal analysis", *J. Mater. Sci.* **36** (2001) pp 3777-3783.

Paper II A. C. Backman and K. A. H. Lindberg, "Interaction between wood and polyurethane-alkyd lacquer resulting in a decrease in the glass transition temperature" *J. Appl. Polym. Sci.* **85** (2002) pp 595-605.

Paper III A. C. Backman and K. A. H. Lindberg, "Interaction between wood and polyvinyl acetate glue studied with dynamic mechanical analysis and scanning electron microscopy" *J. Appl. Polym. Sci.* **91** (2004) pp 3009-3015.

Paper IV A. Backman Sandlund, "Influence of surface structure on adhesion strength between wood and Melamine Urea Formaldehyde", to be submitted.

Included in this thesis are also unpublished results from DMTA studies on several commercially available glues and results concerning how the wood interaction is affected by hydrophobic treatment. The latter has been studied on silylated and acetylated the wood material.

The following publications have also been written as a result of the studies presented in this thesis:

- A. Backman, "SEM study of wood/paint interfaces", 17th Discussion Conference, "Surface and interfacial phenomena in macromolecular systems", Institute of Macromolecular Chemistry, Prague, 21-24 July, 1997.

- T. Olsson, A. Backman, J. Grahn, K. Oksman and H. Lindberg, "A method of measuring the fibril angle in softwood by using scanning electron microscopy", Tenth International Conference on Mechanics of Composite Materials, Riga Latvia, April 20-23, 1998.

- A. Backman, "Interaction and Adhesion at the Interface Between Wood and Paint, Glue, Lacquer Measured with DMTA and SEM", Licentiate thesis at Luleå University of Technology, 2000, ISSN 1402-1757 (51)

- K. A. H. Lindberg, A. C. Backman and M. Ericson, "Measurement of Polymer Interfacial Strength with an Instrumented Ultramicrotome", European Conference on Composites Materials, ECCM9, Composites - From Fundamentals to Exploitation, Brighton, Great Britain, June 4-7, 2000. ECCM9 CD-ROM, IOM Communications Ltd.

- A. Backman, "Interaction between wood and thermoset glues", in TRITA-BYMA 2002:3 "Limning av trä, Doktorandkurs läsåret 2001-2002", 2002, ISSN 0349-5752.

- A. Backman and H. Lindberg, "Ytinteraktioner i sammanbindningslinjen mellan trä och andra polymerer", 2002, Slutrapport till Formas för BFR-projekt nr 19970303.

Abbreviations

Symbols and abbreviations are explained in the text when they first occur. In addition, some of the most important ones are also listed below:

E^*	complex modulus (Pa)
E'	elastic or storage modulus (Pa)
E''	loss modulus (Pa)
$\tan\delta$	loss factor = E''/E'
ε	strain
σ	stress (Pa)
γ_S	surface free energy parameter (mJ/m^2)
γ_S^{LW}	surface free energy parameter for Lifshitz-van der Waals forces (mJ/m^2)
γ_S^{AB}	surface free energy parameter for Lewis acid-base forces (mJ/m^2)
γ_S^+	acidic surface free energy parameter (mJ/m^2)
γ_S^-	basic surface free energy parameter (mJ/m^2)
W_a	work of adhesion (mJ/m^2)
w_i	weight fractions
Tg	glass transition temperature (°C)
Tm	melting temperature (°C)
RH	relative humidity (%)

DMA	dynamic mechanical analysis
DMTA	dynamic mechanical thermal analysis
SEM	scanning electron microscopy
PVT	pressure-volume-temperature apparatus
WBL	weak boundary layers

EPI	emulsion polymer isocyanate glue, here a styrene-butadiene copolymer with isocyanate cross-linking agent
MUF	melamine urea formaldehyde glue
PEEK	polyetereterketon
PET	polyethylene tereftalate
PHEMA	polyhydroxyethyl methacrylate
PMMA	polymethyl methacrylate
PRF	phenol resorcinol formaldehyde glue
PS	polystyrene
PVAc	polyvinyl acetate glue
PVC	polyvinyl chloride
PTFE	polytetrafluor ethylene
HMDS	1,1,1,3,3,3-hexamethyldisilazan
TMSC	trimethylsilan chloride
TMSA	N-trimethyl-silylacetamid

1. Introduction

The adhesive forces between two solid materials are generally small because the intimate contact at the atomic scale that is needed between the surfaces is usually limited due to surface roughness. This prevents the utilisation of the available attractive forces since atomically smooth surfaces are impossible to produce. To decrease this limitation, a liquid adhesive which has the capability to mould itself and copy the topography of the solid surfaces can be introduced between the adherends. The same mechanism applies to a lacquered or painted surface, but here there is only one adherend surface, see Figure 1.

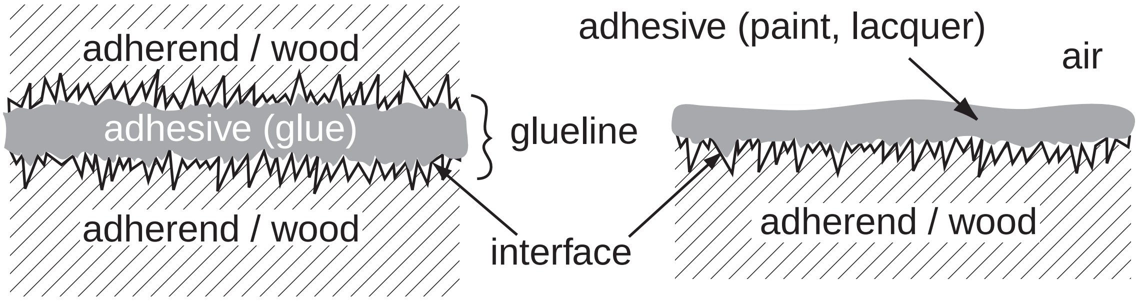

Figure 1: An adhesive can bond two adherends, a glued joint, or be applied on one adherend as is seen with a lacquer or paint.

Glued bonds are becoming more and more commonly used as a replacement for welds, riveted joints, joints with screws etc. In wood products, the joining of wood with glue has been used for thousands of years. One spectacular example is a glued wooden chest found in the grave of pharaoh Tutanchamon who reigned around 1350 BC. In the 1760's-1780's, when the well known carpenter Chippendale was making furniture, fish glue was very popular along with high quality animal glues. Later, bone glue became popular but since it is much more brittle than many other glues, it gave animal based glues a bad reputation. Although effective, animal glues have inferior water resistance and are not always suitable for modern applications such as load bearing structures. The need for better glues was obvious and in the 20th century the development of new types of polymer based adhesives started and is still continuing.

1.1. Objective of the research presented in this thesis

There are many methods that can be used to measure adhesion. They are usually designed for the type of loading that the adhesive will experience; peel off tests for paint or coat, bending tests for glulam, tensile tests for glued joints, etc. Most tests give results in the form of a fracture energy or fracture stress. However, such tests will not reveal information about why the adhesive adheres well, or not, to the adherend. Many adhesion theories exist but they are difficult to relate to practical adhesion tests.

A ‘perfect’ method for measuring adhesion, would give results that contained information that could be used to modify or change polymeric structures and additives used in paint, glue or lacquer to obtain stronger and longer lasting adhesion. Today no such method exists and there is an obvious need to obtain more explanatory information from adhesion tests to serve as a bridge between adhesion theories and practical adhesion tests, see Figure 2.

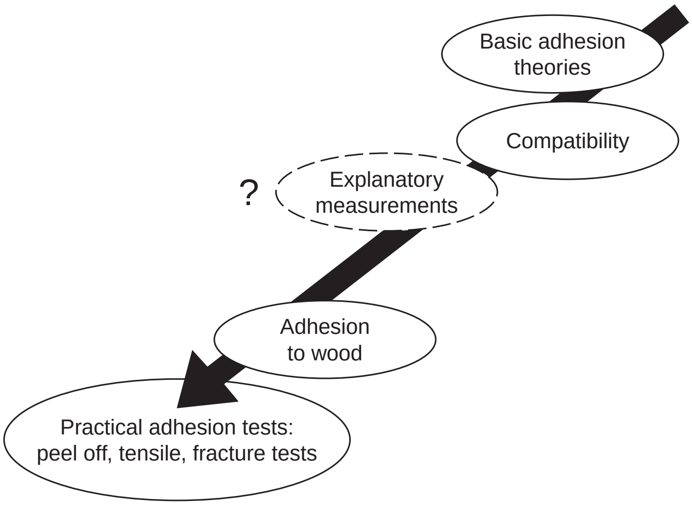

Figure 2: There is a significant information and knowledge gap between adhesion theories and practical adhesion measurements.

The work presented in this thesis has aimed to develop a method to fill this gap. Dynamic mechanical thermal analysis (DMTA) is widely used for investigations on polymeric structures and compatibility in blends. Only a few attempts [1, 2, 3, 4, 5, 6, 7, 8] have been made to use DMTA to study the interaction between wood and adhesives. If an interaction between the adhesive and the adherend can be observed, bonds exist between the polymers in adhesive and adherend. The degree of interaction between wood and paint, glue or lacquer revealed by DMTA measurements could be used as a diagnostic tool for predicting long-term stability. This thesis represents one of the many small steps that must be taken to reach this goal.

2. Background

2.1. Requirements on adhesives

Glues are widely used in joints or building materials; for example, glulam beams, windows, fibre- and particleboards. Mechanical properties, stability and long-term durability are key issues for glued and coated wood. The latter has been a concern for research and development for many years since the effective working life of many glue dependant products often is too short.

Understanding the properties and durability of adhesives exposed to different climates [9] is becoming more and more important. It is not only the quality of the adhesion between wood and adhesive that determines the long-term properties of coated panels and glued wood but also the stability and mechanical properties of the glue itself. Glues need to have a certain level of cohesive strength to be able to transfer stresses across the glue line during the entire product lifetime.

The requirements for paints and lacquers are in many ways the same as for glues. Resistance to weathering and ultraviolet light are obviously important parameters for paints used outdoors, but mechanical properties such as strength, modulus and resistance to fracture after cyclic stresses [1] imposed by moisture changes are equally important. Everyone who has painted their house would like increased durability so as to lengthen the time needed between repairs or repainting.

Normally we prefer to paint our houses, in spite of the fact that simply using untreated wood can in fact be a low cost maintenance option. Untreated wood erodes very slowly when subjected to weathering if it is protected from excessive moisture levels [10]. The purpose of a coating is therefore both aesthetic and to protect the wood surface, and needs to form a film without cracks and pores but that acts as a diffusion barrier for fluids and moisture. Similar requirements are placed on lacquered wood products such as furniture and wooden boats.

During the last decade, much attention has been paid to stress phenomena in organic coatings due to their important role in film cracking, degradation and delamination. Several factors cause organic coatings to experience stresses; the film formation process and variation in temperature and relative humidity. These factors are known to give internal, thermal and hygroscopic stresses. External mechanical forces are then superimposed on these stresses. In all cases, stresses arises when the expected motions provoked by these processes are prevented by coating adhesion to the substrate and/or by the stiffness of polymer segments [11].

Technical requirements are not the only ones to be considered; users of adhesives such as glue, paint and lacquers also have practical problems to cope with. For example adhesives should be environmentally friendly, have gap filling properties or a specific colour. Sometimes they should dry quickly sometimes slowly depending on the application. All these properties are important, but no one is interested in an adhesive if it does not have enough adhesion strength in a given environment and application.

2.2. The structure of the interface

The surface between the adherend and the adhesive is called the interface, see Figure 1. Interfaces exist in all paint/wood, lacquer/wood and glue/wood systems. The weakest part of the interfaces is often the bond between the adhesive and the wood.

Many demands must be satisfied to achieve a long lasting bond across an interface. Firstly, the contact area must be as large as possible and the adhesive should follow the surface roughness of the wood down to molecular dimensions. Secondly, there must be a certain level of compatibility between the molecules in the two phases in order for bonds to occur. It is seldom that these requirements are fulfilled. It has been shown that the glue in particle boards is very unevenly distributed and actually covers a very small part of the total surface [12]. Even with the relatively controlled gluing of polymer surfaces, which appear smooth, the interface strength varies considerably over small local areas [13].

The interface between wood and adhesives are much more complicated than the interface between glued, painted or lacquered metals or polymers due to the porosity of wood which gives a large, unavoidable roughness to the surface. Östman [14] showed that the surface roughness, Ra, for wood is about 10 μm. This surface roughness is around the same as the cell lumen size, or of a double cell wall thickness in the latewood of softwoods [15]. 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 monomer, oligomer or molecule in an adhesive has a cross section characteristic size of only parts of a nanometer. At that size the small cracks found in wood 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 even small cracks.

2.3. Influence of wood surface properties on adhesion

Many demands are put on adhesives, but it is evident that for a long lasting adhesion the surface structure of wood is just as important. Factors such as surface age, machining operations, structural features and weathering all affect the adhesion of glue, paint and lacquers to wooden substrates.

When using adhesives with metals, the cleaning of the mating surfaces is very important, but this is only rarely done to the surface of wood. Wooden panels are also often exposed to the outdoor climate for shorter or longer periods before finishing which can lead to severely decreased service life of the finishes [16, 17]. Occasionally, wooden panels can be left outside for months before painting. Should there be problems, customers will complain about paint quality and not the quality of the wood or any preparation. Despite the naturally rough surface of wood, the paint, glue or lacquer being used must be given the best possible surface to adhere to. The problem is that it is not always clear how to produce such surfaces and also to make it industrially and economically beneficial to spend time on surface preparation.

A lot of research has been done on surface preparation prior to gluing. For metals, the recommended time between the cleaning operation and coating or gluing can be very short. Newly created or cleaned surfaces have a high surface free energy and are thus more easily wetted. Chemicals in the air quickly migrate to these newly created surfaces resulting in deactivation. In wood, there is also a time aspect of days when extractives migrate from the interior of the wood structure onto freshly exposed surfaces [18]. Some glue manufacturers recommend a maximum time of three days between finishing a wooden surface, for example planing, and gluing in order to achieve optimal properties.

Structural wood features such as annual rings and knots affect joint strength. Adhesion to earlywood is normally higher due to deeper penetration of coatings [19]. The adhesion of paint to knots is also more difficult since these are often of denser wood and have high resin content. The surface often considered when painting is the tangential/radial surface but in glued finger joint the characteristics of the transverse surface are also important.

Achieving the optimal structure on machined wooden surfaces is the next problem. The main machining options are sawing, planing, sanding, abrasive planing, ablation with laser [20] or cutting with knives. The first three are the most commonly used and are thoroughly discussed in paper IV. The requirement is to create a sufficiently smooth surface so that only a thin layer of glue is needed to fill the gap between mating surfaces. It is also important to have produced a surface free from damaged wood fibres. Using dull blades when planing can smear out the wood cells and create damaged surfaces. Sanding with paper with a small grit size can produce cell debris that is sufficiently small to fill cracks and cell lumens [21]. It is important that the adhesive has an undamaged solid wood surface to penetrate and adhere to.

Weathered wood gives poor adhesion due to decreased cohesion in the outermost cell layers of the wood surface. The use of lacquered surfaces is normally avoided for outdoor use since most visible and ultraviolet light penetrates the lacquer and degrades the wood; mainly the lignin. In time this can cause delamination of the lacquer from the wood surface, or cohesion loss in the wood. However, a wood surface coated with an acrylic lacquer degrades more slowly than an uncoated surface [22].

3. Mechanisms of adhesion

Wetting is of great importance for achieving good interaction and adhesion between two phases. Wetting can be defined as the extent to which a liquid makes contact with a surface. When combining wood, which is a solid, with liquids such as paint, glue and lacquer, the liquids will penetrate the rough porous surface of the wood to different extents. These liquids subsequently become solids by different mechanisms, for example drying or cross-linking. Whilst the wetting behaviour of liquids is of great importance, it has not been studied in this thesis.

Adhesion is the joining of two surfaces so that stresses can be transmitted between the phases. Several different adhesion mechanisms have been proposed [23, 24, 25], today the adsorption theory seem to be the most predominant. The adsorption theory requires intimate contact and the development of physical forces at the interface, thus providing the basis for the formation of mechanical interlocking, interdiffusion and chemical bonding. The adsorption theory is explained below followed by the other mechanisms.

3.1. The adsorption theory

Good wetting to enable the adhesive to spread over the adherend is an essential fist step in establishing good adhesion. The adhesive will adhere to the substrate due to interatomic and intermolecular forces (interactions) at the interface. Binding forces such as Lewis acid-base and dispersion forces are those considered in adhesion science to describe the interaction mechanisms. The aim is to match these binding forces to achieve optimum adhesion.

The concept of dispersion forces also includes dipole interaction forces. This is because the contribution from the dipole component to work of adhesion is believed to be very low in the condensed phase (solid or liquid). The strong force existing between molecules with dipole moments is instead attributed to Lewis acid-base interactions. Hydrogen bonding is also included in Lewis acid-base interactions [23]. Several different methods can be used to calculate the theoretical work of adhesion; some using the wetting of different sets of liquids to calculate this property. The determination of the contribution from Lewis acid-base interactions to the work of adhesion is often done with the method developed in 1988 by vanOss, Chaudhury, and Good (vOCG) [26]. The work of adhesion (W_a) can be estimated by comparing surface free energy of the adhesive and the adherend (Dupré's equation):

$$W_a = \gamma_1 + \gamma_2 + \gamma_{12} \qquad [\ 1\ ]$$

Where γ_1 and γ_2 are the surface free energy of components 1 and 2 and γ_{12} is the interfacial free energy. The work of adhesion (W_a) is the sum of the dispersion (W_a^d) and Lewis acid-base (W_a^{AB}) work of adhesion, which in turn can be calculated from surface free energy parameters from reference liquids:

$$W_a = W_a^d + W_a^{AB} \qquad W_a = 2\left(\gamma_1^d\gamma_2^d\right)^{1/2} + 2\left(\gamma_1^+\gamma_2^-\right)^{1/2} + 2\left(\gamma_1^-\gamma_2^+\right)^{1/2} \qquad [\,2\,]$$

Where γ_1^+ and γ_2^+ represent the acidic parameter (electron-acceptor), γ_1^- and γ_2^- the basic parameter (electron-donor) and γ_1^d and γ_2^d the dispersion component of the surface free energy. Components 1 and 2 are a liquid and a solid respectively. The surface free energy parameter of solids can be determined with reference liquids of known γ_L^d, γ_L^+ and γ_L^-. Work on measuring Lewis acid-base parameters has been done on wood that has a predominantly basic surface character [18, 27].

3.2. More adhesion theories

Factors other than adsorption can play an important role in adhesion, for example mechanical interlocking, chemical bonding, weak boundary layers, polymer interdiffusion and electrostatic forces.

Mechanical interlocking theory: The adhesive adheres through keying or interlocking and by penetrating into pores and cavities. In this case, surface roughness is an important characteristic of the adherend. This mechanism is believed to contribute to the quality of adhesion to wooden surfaces but has also been showed to be important for many other materials [23]. However, although important for wood, mechanical interlocking is strictly speaking not an adhesion mechanism; at least not viewed from a molecular level. It is only a way to achieve adhesive bonding in a technological sense.

Theory of weak boundary layers: Close to the surface, a weak boundary layer (WBL) may be formed which determines the strength of adhesion; even when fracture appears to have occurred in the interface. The creation of thick interfacial layers has led to the concept of an interphase. In wood bonding two different WBLs have been proposed; a chemical WBL and a mechanical WBL[28]. The mechanical WBL often results from machining operations. Examples of the causes of chemical WBL include additives or low molecular weight fractions concentrated at the interface, a lower or higher degree of crystallinity at the interface than in the bulk polymer and orientation of chemical groups.

Chemical bonding theory: Chemical bonds formed across an interface increase the adhesion strength considerably. The bonds considered are primary bonds (covalent or ionic) rather than secondary bonds such as hydrogen or van der

Waal bonds which are more related to physical interactions between molecules. The use of silane coupling agents on glass fibers used in polymer composites and block copolymers stretching across interfaces are examples of chemical bonding.

Diffusion theory: Polymer chains can diffuse (move) across the interface between two different polymers or across a crack within a polymer. This diffusion is described as reptation; a snakelike movement in the direction of the chain. The polymer chain can thus form a bridge across the interface where it contributes greatly to the adhesion strength. An example is the diffusion of polymer molecules across an interface between polyvinyl chloride (PVC) and styrene acryl nitrile (SAN) resulting in high adhesion strength, see Figure 3. Diffusion is promoted in amorphous polymers at temperatures near the glass transition temperature (Tg) but becomes unlikely if both polymers are not sufficiently soluble, or are highly crystalline or cross-linked.

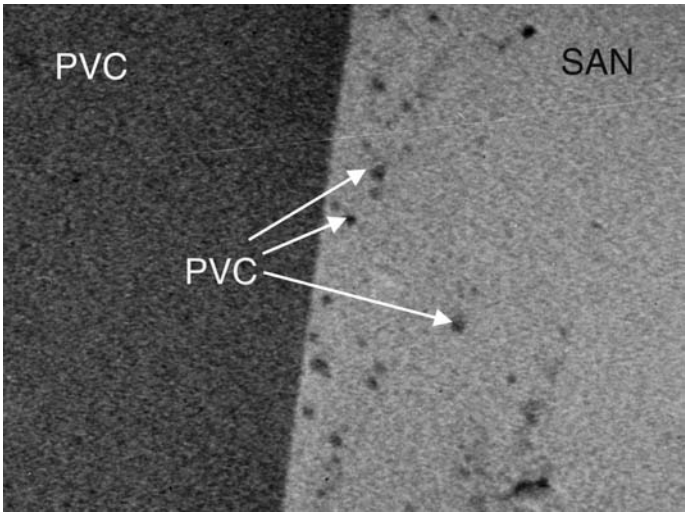

Figure 3: A scanning transmission electron microscope (STEM) picture of a thin ultramicrotomed section of a glue line between PVC and SAN. The solvent used for gluing was tetrahydrofurane. The width of picture is 3μm. Henrik Lindberg, unpublished results.

The interface can also be strengthened by diblock copolymers consisting of the two polymers where each polymer type can diffuse into the other. If the chain length is sufficiently long, the chain will be broken (i.e. chain scission) during failure, which is similar to the mechanism mentioned in the chemical bonding theory given above. One example of the use of diblockpolymers is the maleated styrene-ethylene/butylene-styrene (SEBS-MA) copolymer used as a compatibilizer in a low density polyethylene/wood flour (PE/WF) composite system to increase impact strength and elongation at break [7].

Electronic theory: Electrostatic forces exist because of the formation of a electrical double layer at the interface and contribute greatly to adhesion strength. This theory is not widely accepted, since it is believed that the electrical phenomena often observed during adhesion tests is a consequence of the test rather than being the cause of high bond strength. Some evidence of the electronic theory exists but the contribution to the total adhesion strength is often small [23].

3.3. Methods for measuring adhesion

When the results of experimental or practical adhesion strengths measurements made with, for example, a tensile test, peel test or wedge test are analysed, the contribution from the fundamental adhesion mechanism is difficult to estimate. The experimental values obtained using a method measuring the fracture energy G, will be dependent on G_0 and a term ψ. G_0 represents the surface energy and ψ involves other processes in the adhesion test that absorbs energy, for example plastic deformation [23] or crack generation [29]:

$$G = G_0 + \psi \qquad [3]$$

G_0 is then dependent on the surface energy of the materials and if the fracture occurs in the interface on W_A (work of adhesion) or if it occurs within the materials on W_C (work of cohesion). Practically measured fracture energies are almost always orders of magnitude greater than W_A or W_C due to the fact that ψ is usually much larger than G_0. Because of the difficulty of determining ψ, the practical adhesion achieved depends on the technique used and strengths obtained using different techniques may not be directly comparable.

3.4. Bonds

Bonds are a central issue in adhesion theory, and a short explanation of the bonds possibly present in wood adhesion are given below.

Primary bonds

A *covalent bond* involves the mutual sharing of one or more electron pairs between atoms. Two (or more) atoms joined by covalent bonds constitute a molecule. Elements that are neither strongly electronegative nor strongly electropositive, or that have similar electronegativities, tend to form bonds by sharing electron pairs. The bond energy [30] for single covalent bonds varies from about 150 to 570 kJ/mol. The carbon-carbon bond in a polymer chain has a bond energy of about 360 kJ/mol. For a covalent bond between different atoms the electron pair might not be shared equally due to differences in electronegativity and such bonds are sometimes called *polar covalent bonds*. One example is the chlorine atom bonded to a carbon atom seen in the polymer polyvinyl chloride (PVC), see Figure 4. The electron pair in this bond is displaced toward the more electronegative atom chlorine, which results in the chlorine having a partial negative charge, a dipole.

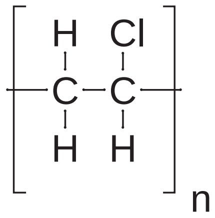

Figure 4: Structural unit of Polyvinyl chloride (PVC). The term ‘n’ indicates a number of repeated units.

The transfer of one or more valence electrons from one atom to another forms an *ionic bond*. Because electrons are negatively charged, the atom that gives up the electron(s) becomes positively charged, and vices verse. The ionic bond is a strong bond with bond energies [31] generally between 600 and 1500 kJ/mol. An example of an ionic bond is seen in salt, sodium chloride, where sodium becomes positive Na^+ and chlorine negative Cl^-. The ionic bond is found in materials that are composed of both metallic and nonmetallic elements. There are even ionic polymers that have ionic bonds between the molecules, but these are not normally used as wood adhesives. The zinc salt of polyacrylic acid copolymer which is expected to have ionic bonds has a glass transition temperature of over 400°C, if one exists at all. This material decomposes before softening. Even at 300°C this polymeric salt has a modulus about three times that of polystyrene at room temperature and behaves as it were highly cross-linked due to the strong attraction between ionic groups [41].

Secondary bonds

Covalent bonds, and also to some extent ionic and metallic bonds[*], are in materials science often called primary bonds. There are also other types of forces that occur between molecules, so called secondary bonds, which are discussed below.

The most common secondary bond is *van der Waals forces*, or London dispersion forces. The location of electrons in a molecule fluctuates and at some point in time the molecule will have an instantaneous dipole moment. This will induce a corresponding dipole moment in an adjacent molecule causing an attractive force between the two. The magnitude of the force depends strongly on the polarizability of the electrons in the molecules. A larger, more elongated molecule such as are seen in polymers is more easily polarized [32], which gives rise to a slightly stronger attractive force. The van der Waals force is often referred to as the weakest of the secondary forces, but is never the less important and sometimes the only possible secondary force.

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[*] Metallic bonds exist between metal atoms and are not discussed here.

If a molecule has polar covalent bonds the molecule will have a permanent dipole moment (unevenly distributed electrons) such as that seen in the bond described earlier between the chlorine atom and carbon atom in PVC. This creates the possibility of *dipole-dipole forces*, also called Keesom forces, which will result in a stronger attractive force than the van der Waals force. There is also the possibility for a dipole to induce a temporary dipole moment in another molecule, thus creating Debye or *dipole-molecule forces*.

A special case of the dipole-dipole force is called a *hydrogen bond*, which has a typical bond energy [30] of 20-40 kJ/mol. Very strong dipole-dipole interactions occur when hydrogen atoms are bonded to small, strongly electronegative atoms (O, N or F). Because of its small size and partial positive charge, the hydrogen atom can link electronegative atoms such as oxygen. The hydrogen bond is important in wood adhesion as there are a lot of hydroxyl groups (-OH) on the wood polymers and many polymers used in wood adhesives also contain hydroxyl groups.

As always in science there are different ways of grouping things. The usage of certain terminologies varies, which can be confusing. In a lot of the literature, van der Waals forces are defined as being intermolecular attractive forces not resulting from ionic charges. In this case, “van der Waals forces” is a collective term for London dispersion forces (ie the specific definition of van der Waals forces given above) as well as dipole-dipole and dipole-molecule forces. However, hydrogen forces are generally not included in this common broadening of van der Waals forces.

4. The structure of softwood

Softwoods consist primarily of tracheids, which are on average 2-4 mm long hollow cells with tapered ends, with radial and tangential dimensions of 20-40 µm. About 5% of the volume of softwood is taken up by ray cells; short cells oriented in rows from the pith towards the bark [33]. Figure 5 shows longitudinal, radial and tangential directions together with the three different surfaces. On the radial surface bordered pits are visible.

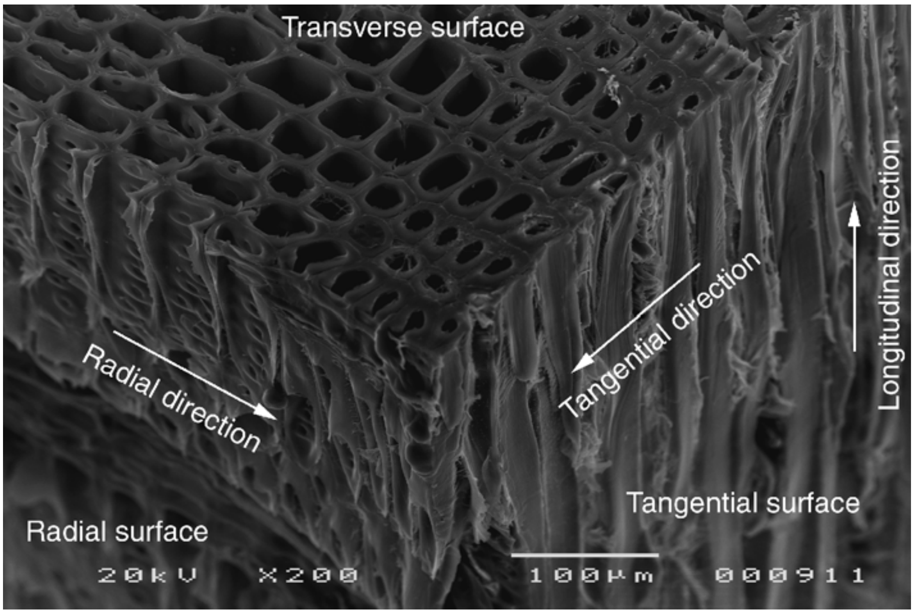


Figure 5: Scanning Electron Microscopy photograph of the cell structure of Scots Pine (*Pinus Sylvestris*) showing the three different surfaces and directions.

Wood from temperate zones is usually built by annual rings, first earlywood, and at the end of the growth season a transition to latewood. In earlywood the cell walls are thinner and the lumen, which is the void in the tracheid, is larger. Latewood is a lot denser since the density of the cell wall [15] is constant at about 1.5 g/cm^3. Figure 5 illustrates the transition between earlywood from the upper left corner to latewood down to the right.

Tracheids consist of a polymeric fibre composite containing the polymers cellulose, hemicellulose and lignin. Cellulose forms crystalline fibres which are surrounded by amorphous lignin and hemicellulose. Several different layers with different fibre directions form the cell wall, see Figure 6.

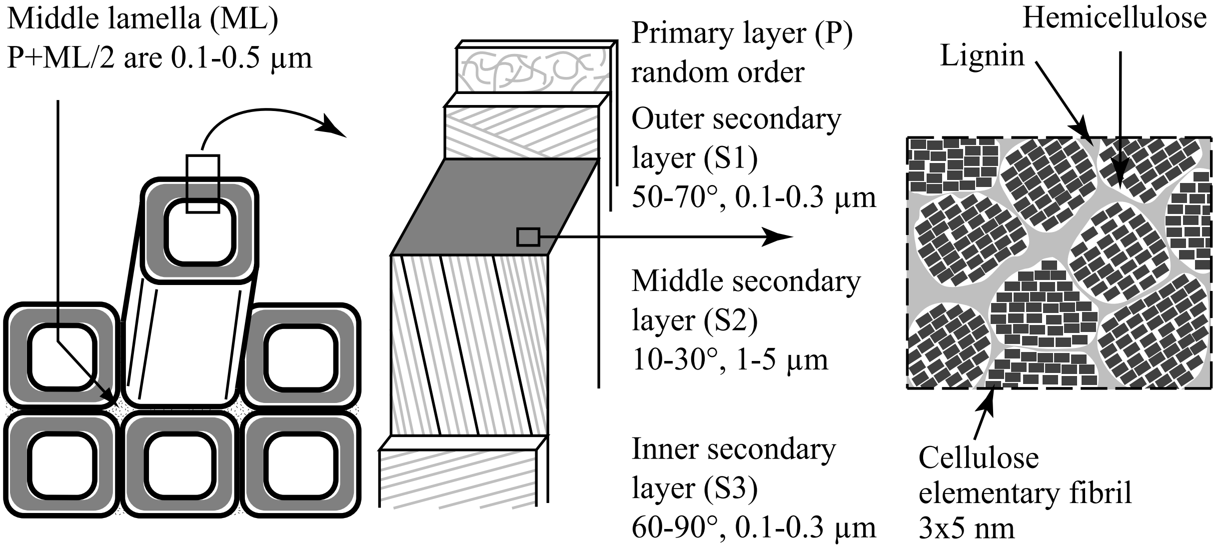


Figure 6: Schematic structure of the wood cell wall showing its different layers. Cellulose fibrils are oriented in different directions from the cell axis, as stated in the figure for the different layers.

Extractives are compounds that can be extracted from wood using various solvents. They are often of low molecular mass, less than 500 g/mol, and can be categorised into many groups, for example fatty acids and terpenes, according to their chemical composition. Extractive compounds are traditionally extracted with acetone but the nomenclature varies. Water soluble compounds, such as salts, pectins and starch also present in wood, are also sometimes included in extractives.Scots pine heartwood generally contains 12% extractives, while its sapwood contains about 4%. The strength of wood is not generally considered to be dependent on any extractives present. One of the functions of extractives is to defend against biological attacks. Extractives can migrate to newly machined surfaces causing the surface to have less than optimal properties for forming high strength joints (See section 2.3 above).

5. Polymer properties measured using DMTA

One way of characterising solid materials is to divide them into metals, ceramics and polymers. In this categorisation, wood would be considered a polymeric composite material made up of several different polymers. The glues, paints and lacquers applied to wood have, in most cases, polymeric binders. Polymeric materials have a special behaviour that metals and ceramics do not; they are viscoelastic materials. This means that they have both solid properties (elastic) and liquid properties (viscous). If a stress is applied to a polymer it will result in a certain strain, but in time, this strain will increase, this is known as creep. This phenomenon is due to the viscoelastic nature of polymeric materials. The amount of creep varies in different polymeric materials, and factors other than viscoelasticity can also contribute to creep deformation.

The viscoelastic properties of a polymer change considerably with temperature. Viscoelastic materials experience relaxation transitions associated with molecular mechanisms. These transitions mark a change in mechanical and other properties and are referred to as the glass transition temperature (Tg), which is normally associated with amorphous material, and the melting point (Tm) in crystalline polymers. Polymers also exhibit, so called secondary relaxations. Figure 7 shows examples of the change in shear modulus for different polymers over the temperature interval polymers are typically used in. Amorphous polymers such as PVC are used below their Tg, whilst semicrystalline polymers such as nylon can be used below or above their Tg but considerably below their Tm. Cross-linked rubber materials are used above their Tg.

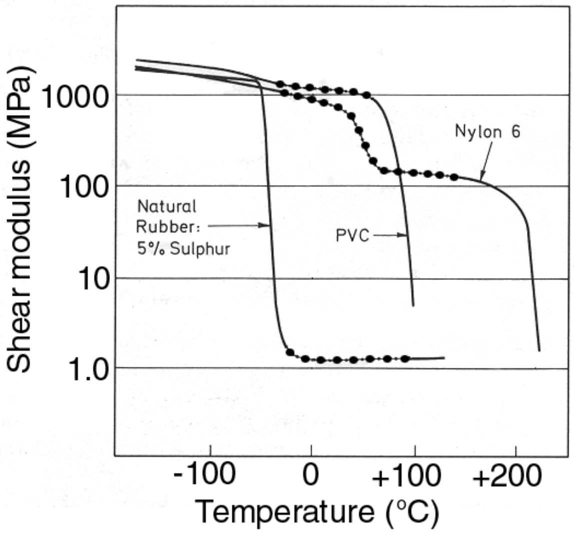


Figure 7: Shear modulus vs. temperature for three different types of polymers. The temperature interval at which these polymers are used is marked with (•-•-•-•-•). PVC is an amorphous polymer, Nylon 6 is semicrystalline and Natural rubber is lightly crosslinked. Based on Figure 4.21 in N. G. McCrum et al. [34].

The DMTA apparatus

One of the most powerful methods used to investigate the viscoelastic properties of polymeric materials is Dynamic Mechanical Thermal Analysis (DMTA). This technique applies a very small sinusoidally varying strain to a test piece at a constant frequency whilst the temperature is increased at a constant rate. The stress is measured and three different moduli are calculated; storage modulus E', loss modulus E", complex modulus E* and a loss factor (tanδ). These are explained below.

In this work, a DMTA MkIII from Rheometric Scientific has been used. Typical settings used were a dynamic average strain of 0.02-0.05%, frequency 1 Hz and a temperature increase of 2°C/min. Several different sample holders are available for this apparatus, see Figure 8. The tensile mode used in this work was chosen over the bending modes since the strain is approximately constant in the specimen.

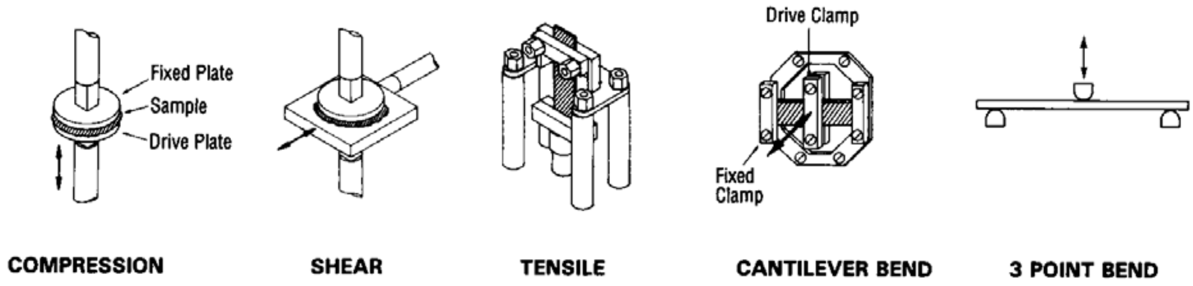


Figure 8: Sample holders that can be used with a DMTA MkIII from Rheometric Scientific, based on figure from Wetton et al. [35].

5.1. Theory of measurements with DMTA

A characteristic of DMTA analysis of viscoelastic materials is that the applied strain is not in phase with the stress but lags behind by a phase angle δ, see Figure 9. This results in the existence of a loss modulus (E"). Both viscoelastic and non-viscoelastic materials exhibit a so called storage modulus (E').

The sinusoidal stress curve shown in Figure 9 can be considered to consist of two components: one in phase with the strain and the other 90° out of phase. One way to explain this is to look at a purely elastic and a purely viscous material. Consider the response of elastic and viscous materials to an imposed sinusoidal strain, ε:

$$\varepsilon = \varepsilon_0 \sin(\omega t) \qquad [\,4\,]$$

Where ε_0 is the amplitude, t time and ω the angular frequency (rad/s). For a purely elastic body, Hooke's law is obeyed, and the stress is:

$$\sigma = G\varepsilon_0 \sin(\omega t) \qquad [5]$$

Where G is shear modulus. It is evident that stress and strain are in phase. Now, consider a purely viscous fluid. From Newton's law the shear stress is given by:

$$\sigma = \eta \cdot d\varepsilon/dt \qquad [6]$$

Which gives:

$$\sigma = \eta\varepsilon_0\omega \cos(\omega t) \qquad [7]$$

Where η is the viscosity. In this case the shear stress and the strain are 90° out of phase [36]. Viscoelastic materials can be considered as having a combination of elastic and viscous properties with the stress and strain out of phase by an angle δ which is less than 90°.

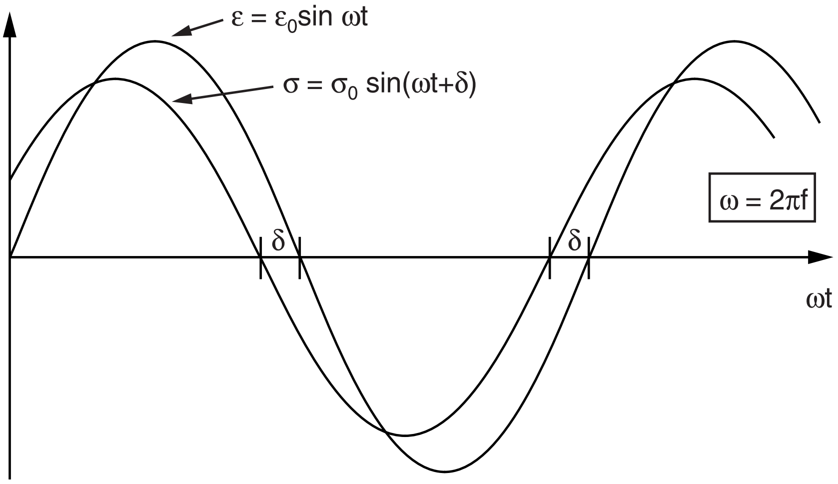


Figure 9: Phase angle difference between sinusoidally varying strain (ε) and stress (σ) at an applied frequency (f).

The angle δ varies considerably with temperature. The common polymer Polymethyl methacrylate (PMMA) (See paper II, figure 3) has a tanδ of 0.068 at room temperature which is equivalent to an angle of 3.9°. In the glass transition region (around 130°C) tanδ increases to 1.6 or 58°, indicating the increased influence of liquid properties but whilst maintaining a substantial proportion of elastic properties.

Two different moduli can be defined to describe the properties of viscoelastic materials: elastic modulus or storage modulus E' (with stress and strain in phase) and loss modulus E" (with stress and strain 90° out of phase). These moduli have the well-known relationship shown in Figure 10, where tanδ is termed the loss factor and E* the complex modulus. The loss modulus can be explained as an energy loss and is transformed into heat in the material. For bulky materials experiencing large deformations at high frequencies, such as rubber dampers, this heat increase from the energy loss can be substantial.

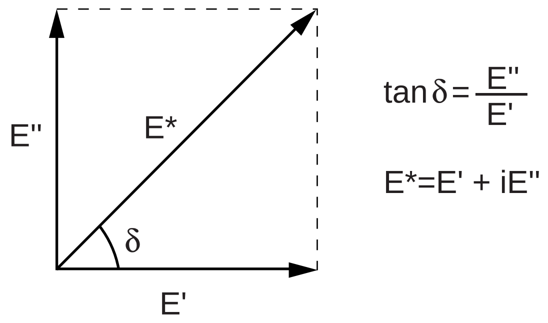


Figure 10: Dynamic mechanical relationship between: Storage modulus E', loss modulus E'', complex modulus E* and loss factor tanδ.

5.2. The use of DMTA in polymer research

DMTA gives information about molecular mobility and damping characteristics. It is widely used to determine, for example, the composition of copolymers and compatibility of blends, the degree and heterogeneity of cross-linking or the influence of crystallinity. Some examples of these are given below. DMTA has also been used to study factors not addressed here, such as molecular orientation, thermal history and Tg dependence on molecular weight. There are numerous references that provide an extensive view of dynamic mechanical measurement for the interested reader [35, 37, 38, 39, 40, 41].

Copolymers and blends

The mechanical properties of polymer blends, block copolymers or graft copolymers are determined primarily by the mutual solubility of the two homopolymers. The properties of a mixture are close to that of a random copolymer for complete solubility of the homopolymers. This can be studied with DMTA where a blend, block or graft copolymer with low solubility results in two Tg peaks close to those of the respective homopolymers. In a random copolymer which will show a single Tg peak, have the monomers through polymerisation been bonded and forced to interact.

Cross-linking

DMTA can be used to study the effect of cross-linking. When a polymer is cross-linked, covalent bonds are formed between the polymer chains which brings them closer together. This reduces the free volume and causes an increase in the glass transition temperature, see Figure 11. One of the ways of determining the glass transitions is to use the peak temperature of the loss factor (tanδ). An increase in cross-linking agent from 2% to 4% increases Tg. The storage (or elastic) modulus decreases when the temperature increases and shows a substantial drop at Tg for lightly cross-linked materials such as rubbers.

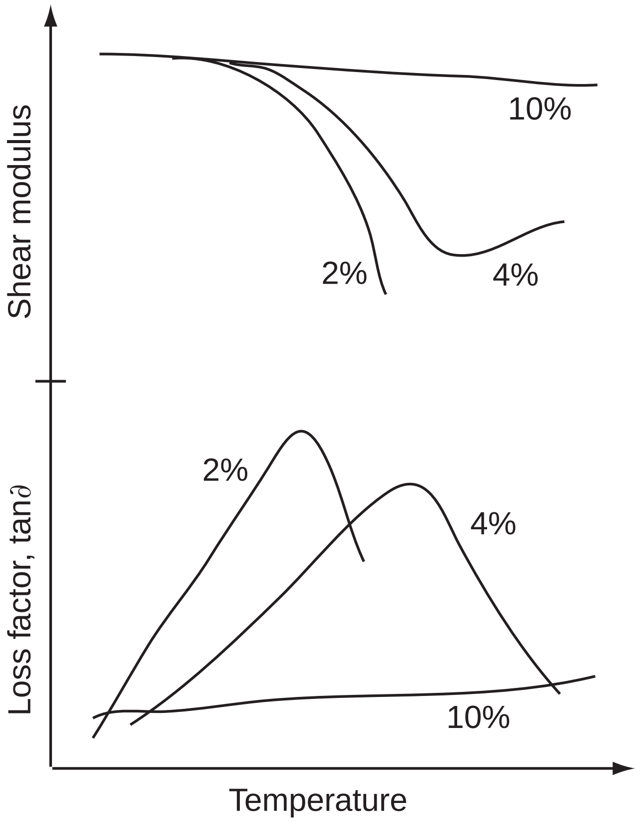


Figure 11: Storage shear modulus and loss factor, both on a logarithmic scale, vs. temperature for a phenol-formaldehyde resin crosslinked with hexamethylene tetramine at stated concentrations. Based on Figure 9.3 from Ward and Hadley [42].

Another effect of cross-linking is to cause a broadening of the loss factor peak, to the extent that very highly cross-linked materials have no glass transition at all since the motion of long segments of the main chain is not possible. This can also be seen as a decrease in the amount by which the storage modulus decreases at Tg [42].

Plasticization

Plasticizers, which are relatively low molecular mass organic materials, are added to rigid polymers to soften them. Plasticizers lower the glass transition temperature and also broaden the peak width (see paper II figure 15). Poorer plasticizers broaden the peak more than good ones [42].

Water can also act as a plasticizer in many polymer materials. An example is shown in Figure 12, where an increase in water content by about 4% in an aromatic poly(amide imide) decreases Tg from about 290°C to about 205°C.

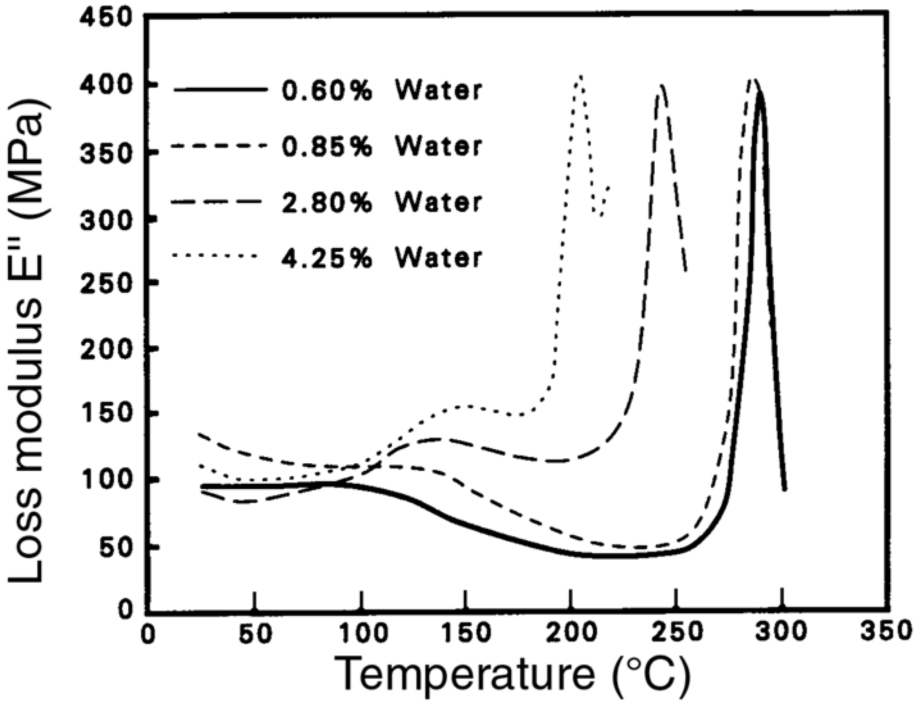


Figure 12: Loss modulus curve showing the effect of moisture content on glass transition of an aromatic poly(amide imide). Figure from Chartoff [43].

Crystallinity

The influence of the degree of crystallinity can also be studied using DMTA. Figure 13 shows the storage modulus and loss modulus for PET, Polyethylene terephthalate. The lowest degree of crystallinity (5%) shows a severe drop in storage modulus at about 80°C, which is associated with the glass transition temperature. This is also called the α-relaxation. When the crystallinity increases the α-relaxation broadens and the glass transition temperature increases. This is due to the remaining amorphous components experiencing restriction of motions in the long-range polymer segments.

Secondary relaxations

The glass transition temperature is the major transition for amorphous polymers. Below Tg some amorphous polymers may have so called secondary transitions which are localised molecular movement often coupled to side group motions. Semicrystalline polymers often have several relaxation peaks originating from Tm, Tg and short segmental motions. Secondary transitions can also be a result of plasticizers and moisture coupled to polymers. The secondary transition in PET, see Figure 13 (β-relaxation), is interpreted as movement in the COO main chain segments [37].

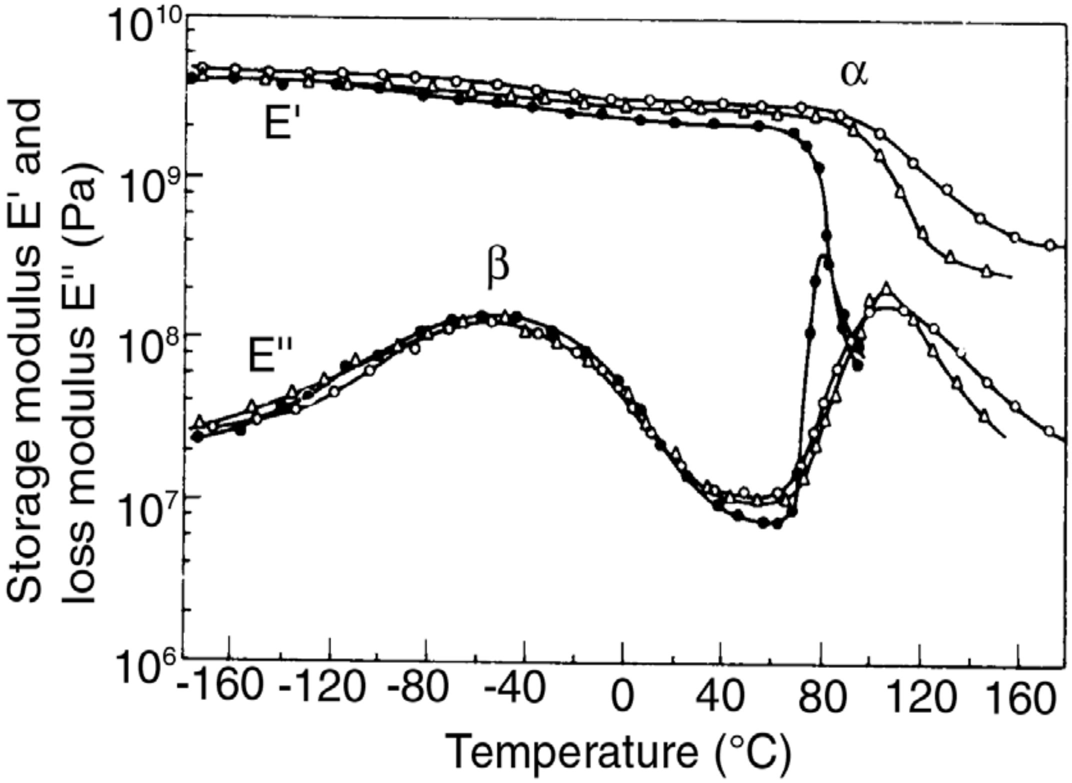


Figure 13: Storage modulus E' and loss modulus E'' as a function of temperature at 138 Hz for PET at different degrees of crystallinity (● 5%; Δ 34%; O 50%), the melting temperature of crystalline PET is 260°C [37]. Based on Figure 9.8 from Ward and Hadley [42].

5.3. The use of DMTA in wood research

Viscoelastic investigations on wood using DMTA and similar techniques have mainly concentrated on understanding the structure of cellulose, hemicellulose, lignin and the different extractives found in wood and/or the effect of moisture on key properties. Whilst there are some similarities between different wood species, few articles cover more than a few species. Birkinshaw et al. investigated the difference between ten different softwoods and hardwoods [44] and measured how the dynamic mechanical properties change with γ irridation and with brown- and white rot fungus [45]. In the case of fungal attack, the dynamic modulus falls more quickly than the modulus measured using static three point bending, showing the dynamic measurements higher sensitivity to molecular changes. Obataya and Norimoto [46] showed the dependence of the storage modulus and loss factor on water extractable molecules in cane. A loss factor peak associated with sugars disappeared after water extraction and reappeared after impregnation with sugars.

The great variation in glass transition temperatures for the principle components of wood under varying levels of moisture is showed in a review article [47]. Data was obtained for isolated cellulose, hemicellulose and lignin, however, the extraction process most probably change the structure of the components.

Salmén[48] showed that the transition in the vicinity of 100°C in water saturated Norway spruce was most probably due to the Tg of in situ lignin. A lower Tg for lignin was found by Kelley et al.[49], who measured the viscoelastic properties of Sitka spruce and sugar maple and showed two distinct relaxation peaks (α_1 and α_2 in Figure 14), which were attributed to lignin and hemicellulose. The existence of two different Tg peaks associated with in situ polymers in wood show the immiscibility of lignin and hemicellulose.

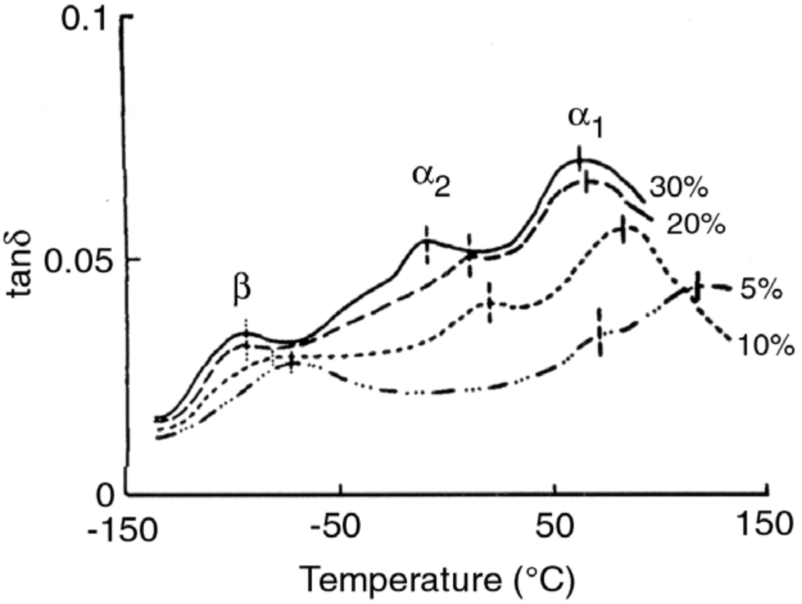


Figure 14: DMTA measurement on solid spruce wood at moisture contents rising from 5% to 30% showing the loss factor (tanδ). Peak α_1 was thought to be the Tg of lignin, peak α_2 the Tg of hemicelluose and peak β the site exchange of water. From Kelley et al.[49].

Many researchers have also made dielectric experiments on wood. Dielectric measurements give similar information and some of the relaxation peaks can be compared. Dielectric measurements, like DMTA, can be used to study the molecular structures of wood and wood-water interactions. For example, Maeda and Fukada[50] compared piezoelectric, dielectric and mechanical measurements and observed good correlation between the relaxation peaks observed. Kabir et. al[51] presented a study on how the grain direction and moisture content affect dielectric properties. The difference between the behaviours of moisture adsorbed on wood and WPC was investigated by Handa et al.[3].

5.4. Glass transition temperature

The most important relaxation process in amorphous polymers is seen at the glass transition temperature, Tg. Several examples have been given above. At this temperature the polymer changes from a relatively hard and glass-like material to a soft and rubber-like material. For a typical amorphous polymer the storage modulus decreases by three orders of magnitude at Tg. If the polymer is cross-linked, semicrystalline or reinforced, the decrease of storage modulus at Tg is generally lower.

The chemical structure of the polymer affects Tg. Stiffness of the main chain, large rigid side groups and molecular polarity increases Tg whilst long aliphatic side chains lower Tg. Backbone symmetry and tacticity can also affect Tg [41].

The glass transition temperature can be defined on the basis of dilatometric measurements, which provide stress and frequency independent information about Tg (See Figure 15). When the specific volume of the polymer is measured against temperature, a change in slope is observed at a temperature which is characteristic for each polymer, by extrapolating the straight lines Tg can be determined. When dilatometric measurements are carried out with a very slow rate of temperature increase, Tg approaches a constant value [42]. Since Tg is a time independent property, dynamic mechanical measurement techniques are not suitable for determining Tg but are an appropriate and powerful method to determine changes in Tg.

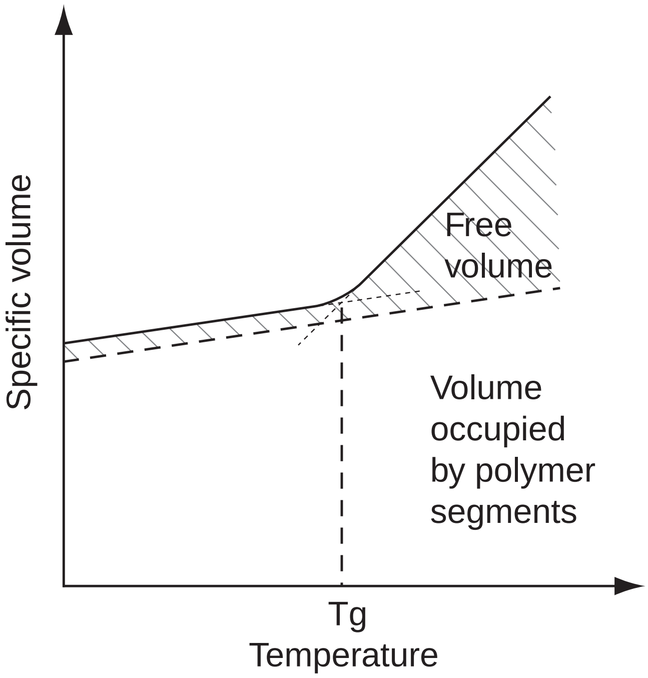


Figure 15: The volume-temperature relationship for a typical amorphous polymer. The specific volume is the same as the inversion of density.

Figure 15 shows schematically the difference between the total volume divided into volume actually occupied by polymer molecules and the free volume. Free volume for wood materials is related to the solid wood polymers and extractives, it is not related to the void volume due to lumens and pores. The free volume can be said to describe how tightly the polymer chains are packed together. A large free volume indicates a more loosely packed structure. Free volume is thus used for polymers the segment-size voids that exist between polymer chains [37, 42]. Mechanical relaxation times depend on temperature largely through their dependence on free volume.

The temperature at which the glass transition occurs depends on the free volume. At Tg the mobility of the polymer chain is greatly increased when the free volume is increased and movement in the long main-chain molecules become possible, See Figure 15. The frequency used when making the measurement is important; a higher frequency moves relaxations to higher temperatures. There is a relaxation time for molecular movement at a certain temperature. When that time is the same as the applied frequency of the measurement, high losses in the material are observed, i.e. a peak in loss modulus (E") and loss factor (tanδ).

The glass transition temperature (at a constant frequency) for a given polymer can be changed using copolymers, blends or plasticizers. The effect of these on the glass transition temperature can be calculated with the well-known equation:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \qquad [\ 8\ ]$$

Where T_g is the glass transition of the “mix”, w_1 and w_2 are the weight fractions of the two constituents having glass transition temperatures T_{g1} and T_{g2}. This is a generalised equation [43] but give sufficiently accurate results for many polymers. The presence of a plasticizer or moisture will approximately decrease Tg in the same way.

5.5. Stress related changes in Tg

As already mentioned, a change in the free volume will cause a change in the glass transition temperature. Decreasing the free volume will increase Tg and vice versa. There are several ways of changing the free volume, one is to use copolymerization or blending with plasticizers, to chemically bond polymer chains through cross-linking or the application of stresses. The mechanism by which tensile stresses decrease Tg is central in this thesis. Very few experimental results have been published concerning the effect on Tg of applied stresses or pressures. These are discussed below.

McKinney and Belcher [52] found an increase in the glass transition temperature of polyvinyl acetate by about 20°C when the applied pressure increased from 0 bar to 981 bars (98MPa) at a frequency of 100 Hz, see Figure 16. Data was obtained using a dynamic compressibility chamber which measured the compressibility, or compliance (B*), and its real (B') and imaginary (B") parts. The explanation given for the increase in Tg was a decrease in free volume.

McCrum et al. [37] gave the following explanation to the phenomena seen in Figure 16:
"… This effect is opposite to that observed by the addition of plasticizer and must be attributed to the increased hinderance to molecular motions caused by a decrease in fractional free volume."
For all three pressures shown in Figure 16, it can also be seen that the relaxation region shifts to higher temperatures at increased frequency, as it should.

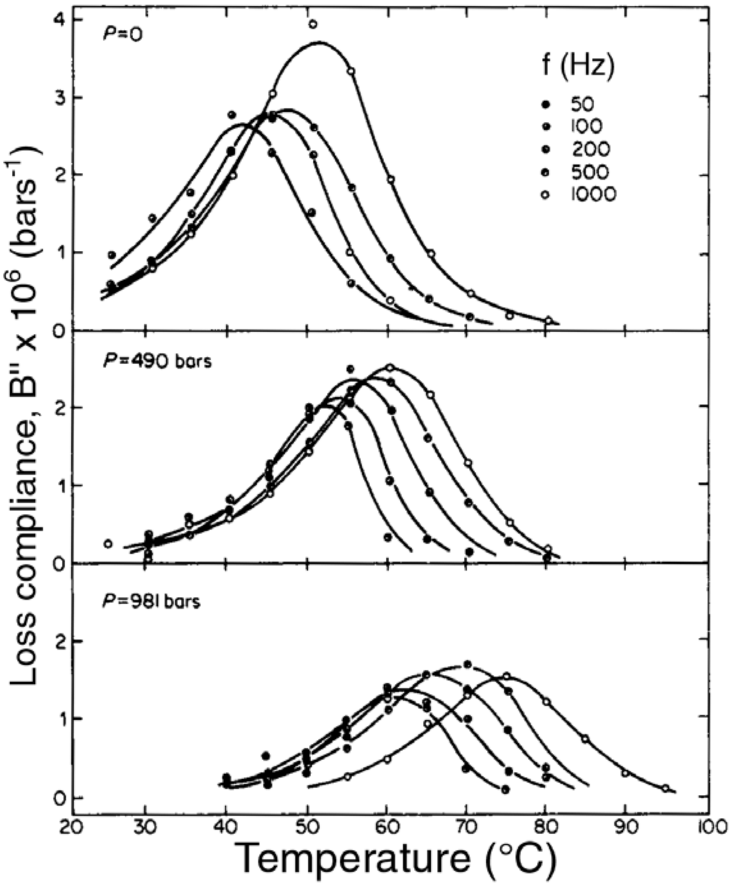


Figure 16: Plots of loss compliance vs. temperature for PVAc (Polyvinyl acetate) at several frequencies (f) and static pressures (P). From McKinney and Belcher [52].

Chartoff investigated the effect of pressure on the Tg of Polystyrene (PS). The results shown in Figure 17 were obtained isobarically using a pressure-volume-temperature (PVT) apparatus [43]. Tg can be seen to increase from a value of about 100°C at an applied pressure of 0 MPa to Tg at 160°C at 200 MPa. For the polymer Polyetereterketon (PEEK) similar data measured with the PVT apparatus indicated an increase in Tg from 152°C at atmospheric pressure (P= 0 MPa) to a Tg of about 270°C for an applied pressure of 200 MPa [53]. No specific explanation was given by the authors, but the likely explanation is, as above, a decrease in free volume causing an increase in Tg.

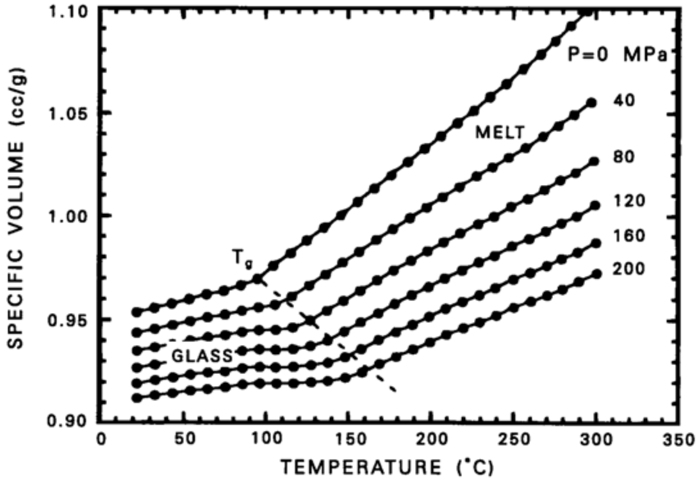


Figure 17: Pressure-volume-temperature data for polystyrene showing the pressure dependence of Tg, in R. P. Chartoff[43].

One example of a decrease in Tg being attributed to increased adhesion has been found (Chartoff[43, 54]). The investigation concerned the adhesion of graphite particles to polyisobutylene polymer. The two curves shown in Figure 18 are for untreated graphite platelet particles and for particles treated with silane coupling agents to create strong adhesion. Normally there is poor adhesion between graphite and the matrix polymer. The silane treatment creates strong adhesion and the Tg damping peak temperature decreases. The stronger adhesion between the matrix and silane treated filler was shown with SEM fractography. The curve for the material with the silane treated filler have a relatively narrow loss dispersion peak compared to that for the untreated filler[43, 54]. This is the same phenomena that is interpreted in this thesis as an increase in free volume due to isostatic tensile stresses developing during curing.

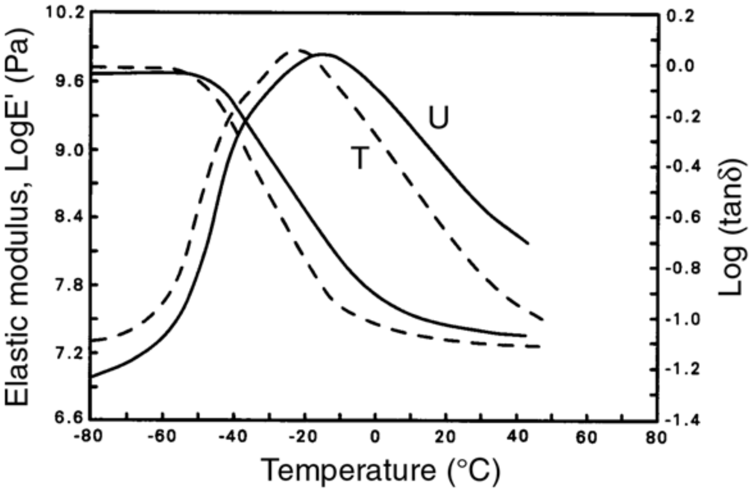


Figure 18: Dynamic mechanical analysis data for the glass transition region in polyisobutylene compounded with platelet graphite particles; silane treated (T) and untreated (U). From R. P. Chartoff[43, 54].

6. Material and methods

Material

The wood species used in all DMTA measurements presented in this thesis is conventionally dried Scots Pine (*Pinus sylvestris*). The samples used were taken from sapwood with a dry density of about 0.5 g/cm^3 (See Paper I). The acetylated pinewood had acetyl content of 21% and was kindly provided by Pia Larsson Brelid at Chalmers University in Gothenburg, Sweden.

The glues, lacquers and acrylate monomers were used as according to the description by the manufacturers. The acrylates, PVAc glue without hardener (also called white glue) and the two polyurethane-alkyd lacquers are described in papers II-III.

The EPI (emulsion polymer isocyanate) glue used was Cascolit 1984 with 10% hardener 1993 obtained from Casco Products AB, Box 11538, 100 61 Stockholm, Sweden. This is a waterbased dispersion of styrene-butadiene copolymer with a MDI type isocyanate hardener (methylene diphenyl diisocyanate). It is approved to EN 204 D4 and Watt 91. The PVAc glue used was Cascol 3335 with 6% hardener 3387. Again, sourced from Casco Products. This is a water based dispersion of polyvinylacetate polymer with an aluminium nitrate hardener. It is approved to EN 204 D4. During curing carbon dioxide was formed as a by-product, causing some foaming of EPI and PVAc glue.

When gluing wood using EPI and PVAc with hardener, a clamping pressure of 1MPa was applied for 40 min in room temperature. The wooden samples had been planed on the tangential surface to a thickness in the radial direction of 1.2-1.3 mm. The wood was conditioned before gluing in 65% RH at 21°C. Three wood pieces were glued together with two glue joints of approximately 150 g/m^2 glue applied per joint. Specimens of the pure glue were obtained by spreading a single layer of glue on a plate of polytetrafluorethylene (PTFE) and drying in room temperature.

The melamine urea formaldehyde (MUF) resin used was prepared in the laboratory according to the formulation reported in Pizzi [55] with a ratio (M+U):F of 1:1.9. The resin was prepared to a degree of advancement defined by a water tolerance of 130%. It was used as manufactured with a solid content of 59% and a viscosity of 0.5 Pas at 20 rpm measured in RT. The hardener used was 5% by weight of 98% formic acid, giving a pH of 5-6 and a pot life at room temperature of 3.5 hours. The resin was prepared by Milena Properzi at ENSTIB, Epinal, France. Pure glue specimens for DMTA were obtained by mixing the glue in an aluminium cup, allowing it to harden and then sanding down slightly to a thickness of 1mm.

The phenol resorcinol formaldehyde (PRF) glue was obtained from Casco Products. Wood samples were conditioned at 20°C and 65%RH. A single layer of ca. 250g/m^2 of 100 weight parts of Cascosinol 1711 mixed with 15 parts of Hardener 2520 were spread on the tangential surfaces. After an open time of 14 minutes, the samples were joined and pressed at 30°C at 1MPa for 2.5 hours (The minimum time required for the glue to cure at 30°C was 2 hours.) Pure glue samples were obtained by spreading a layer of glue on a PTFE plate and curing it for 3 days at 30°C. The specimen was then sanded down slightly to a thickness of 0.8 mm.

Silylation of wood

Silylation was performed in a 30 ml E-glass bottle. HMDS (1,1,1,3,3,3-hexamethyldisilazan) 0.6ml and TMSC (trimethylsilan chloride) 0.3 ml were mixed in dry pyridine (12ml). Nine ovendry (103°C for 6h) pinewood specimens (30x3x3 mm in length x radial x tangential direction) were silylated. The warm wood pieces were added to the silylation solution and put in a desiccator under reduced pressure for 3h to submerge the wood pieces and enable penetration into wood. After 3 hours the bottle was sealed with glass cork and silylated for further 21 hours. The samples were rinsed repeatedly in dry 99.5% acetone, left in acetone for 5 days and finally dried at 50°C in reduced pressure. The weight of the wood specimens was 1.0493g before and 1.1289g after silylation giving a weight increase of 8%. Wood pieces were left in laboratory for a day, then impregnated in PMMA or hydrophilic acrylate using reduced pressure in a desiccator and cured in 60°C for 63 h. The curing was made in small glass tubes of length 30 mm and diameter 5 mm with plastic corks having teflon sealing (polytetrafluor ethylene) and thin teflon film separating the wood pieces.

Several unsuccessful experiments with silylation were made showing no weight increase. The conditions for these are given below to give further guidance on silylation of wood. Pine wood specimens, 3g (size as above) were dried in 103°C and put in a solution of 18g of TMSA (N-trimethyl-silylacetamid) in 180 ml of 99.7% tetrahydrofuran (THF) degassed in a desiccator with reduced pressure. Reduced pressure was applied for 1h and sealed bottle then left in room temperature for 24h. Wood pieces were then transferred to a degassed solution of 9g TMSA in 90 ml of THF in reduced pressure for 30min and left sealed for 24h. The wood pieces were then washed repeatedly in 99.7% ethanol, for 4 hours and dried in room temperature. The PMMA specimens measured in DMTA showed double loss factor peaks. The same silylation procedure where washing in ethanol for 6 hours was followed by washing in water for 24 hours gave no double peaks in PMMA with DMTA analysis but also no apparent change in viscoelastic properties as compared with polymer impregnated unsilylated wood. The latter silylation gave a decrease in oven dry weight of 4-4.5% for silylated wood. Similar silylation as above with HMDS in etylacetat followed by washing in acetone gave an oven dry weight loss of 6.9%.

Dynamic mechanical thermal analysis

The viscoelastic properties in this thesis have been investigated using dynamic mechanical thermal analysis (DMTA); a DMTA MkIII from Rheometric Scientific. Typical settings used were a dynamic average strain of 0.02-0.05%, a frequency of 1 Hz and a temperature increase of 2°C/min.

The force was applied in tensile mode (See Figure 19). This mode was originally chosen so that the whole specimen would experience approximately the same strain. If bending had been used instead (See Figure 8) the strains would differ within the specimen. For example, if a wood specimen coated on the top and bottom surfaces with lacquer is tested in bending, the lacquer would experience higher bending strains than the core of wood. This would be an obstacle when estimating the contribution to the viscoelastic response of the two materials (wood and lacquer).

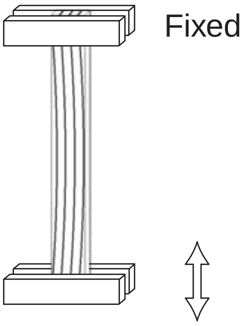


Figure 19: Set-up in the DMTA used for testing in tensile mode. The upper clamps are fixed while the lower ones are moved up and down with a sinusoidally varying strain amplitude.

The dimensions of the specimens that can be tested are limited by the force that can be exerted by the DMTA apparatus. The length of the specimens and the applied deformation amplitude give the dynamic strain which has been held at 0.02-0.05% in this work. In Table 1 a summary of the sample dimensions used is presented. For the measurements presented in Paper I, the strain was applied in the radial or tangential direction of the wood. For all other measurements the strain was applied in the tangential direction with the clamps applied at the transverse surface.

Table 1: Specimen dimensions (mm) used for the DMTA tests.

	Length	Width	Thickness
Wood (Paper I)	12-24 (R, T)	3 (R, T)	1.5 (L)
Wood with polyurethane alkyd lacquer (Paper II)	12-20 (T)	2-3 (R)	1-2 (L)
Polyurethane alkyd lacquer (Paper II)	15	5	0.3
Wood with acrylate polymers (Paper II)	18-20 (T)	2-3 (R)	1-2 (L)
Acrylate polymers (Paper II)	18-20	2-3	1-2
Wood with white glue (Paper III)	23 (T)	4 (R)	3 (L)
White glue (PVAc) (Paper III)	12	8	0.3-0.4
Wood with cross-linked PVAc	16 (T)	3.5-3.7 (R)	3.0-3.6 (L)
Cross-linked PVAc glue	22	4.1-5.1	0.6-0.8
Wood with EPI glue	16 (T)	3.2-3.3 (R)	3.0-3.7 (L)
EPI glue	22	5.1-5.5	0.30-0.41
Wood with PRF glue	22 (T)	4 (R)	3 (L)
PRF glue	22	5	0.8
MUF glue	22	4	1

The direction of wood, L- longitudinal, R- radial and T- tangential is shown in parenthesis. The data for acrylate polymers also apply for silylated and acetylated wood impregnated with acrylates.

Mechanical testing in single and double overlap

The single- and double overlap tensile tests described in paper IV were performed using an Instron 4467 with a speed of 4 mm/min some 7-10 days after gluing. The specimens used were clear wood of Scots Pine (*Pinus sylvestris*) and Beech (*Fagus sylvatica*). Specimens were circular sawn, sanded by hand and rotary planed to 115 x 25 x 3 mm (length · width · thickness). Two pieces were used for the single overlap tests and three pieces for the double overlap tests. The glued surfaces were not purely tangential and an angle of at least 30° between the surface and the tangential direction was maintained. The glue used was MUF produced in the laboratory. Surfaces for gluing were 46-96 hours old, being conditioned at 20°C and 65% relative humidity (RH). An excess of glue was spread on both surfaces of the glue joint, then assembled to give a bonded overlap of 25 x 25 mm. The joint was then clamped with a pressure of 0.5-0.7 MPa for 22-38 hours followed by storing at 20°C and 65% RH.

7. Results and discussion

The results of this thesis work are summarised below. Most of the results have been published in articles but some additional, inconclusive, results concerning glues have been included for the benefit of researchers who wish to use this methodology for further studies on adhesion.

The work showed that:

- Wood shows different viscoelastic behaviour in radial and tangential directions. (Paper I)

- A loss factor peak for the tangential direction in wood was found at around zero degrees Celsius. This may originate from the cellular structure of wood. (Paper I-II)

- A decrease in glass transition temperature was noted for polymers with high interaction and adhesion to wood. (Paper II-III)

    - Examples of high adhesion and interaction were seen between wood and a hydrophilic acrylate polymerised in situ from monomeric acrylate esters. (Paper II)

    - High interaction and adhesion were seen for two similar commercial polyurethane alkyd lacquers applied to wood. The Tg of the lacquers decreased when combined with wood, i.e. when applied to the tangential or transverse surfaces. (Paper II)

- No decrease in glass transition temperature was noted for polymers with low interaction and adhesion to wood.

    - An example of a low adhesion polymer is polymethyl methacrylate (PMMA) polymerized in situ from monomeric methyl methacrylate. (Paper II)

    - Low interaction and adhesion was observed for a commercial polyvinyl acetate (PVAc) glue (white glue) to wood. No change in Tg was observed when the glue was combined with wood. (Paper III)

- No change in interaction could be observed for PMMA to wood when the wood was made more unpolar (more lipophilic) by acetylation or silylation. The hydrophilic acrylate showed an increased interaction with silylated wood but unchanged interaction with acetylated wood.

- It was difficult to obtain conclusive results concerning the viscoelastic properties of commercial chemically cross-linked glues. The materials tested were PVAc with a cross-linking agent, emulsion polymer isocyanate (EPI), phenol resorcinol formaldehyde (PRF) and melamine urea formaldehyde (MUF).

- The influence of the physical wood surface on joint strength was also studied using a standard tensile test on beech and pine glued with MUF (melamine urea formaldehyde) and measured with single and double overlap tensile tests. Highest strength was found for sawn surfaces, decreasing strength was found in the following order: sawn, sanded, planed. (Paper IV).

The use of DMTA for measurement of the interaction and adhesion between polymers and wood is primarily of interest for manufacturers of glue, paints and lacquers to enable them to develop more durable adhesives. The commercial materials investigated so far indicated that this method is primarily suitable for thermoplastic or slightly cross-linked adhesives. Strongly cross-linked materials, such as many glues used for structural bearing purposes, do not have the glass transition peaks this method requires.

Adhesion has also been studied on fractograhy specimens using scanning electron microscopy (SEM). In these studies adhesion was characterised as "poor at a cell wall level" when there was a noticeable separation between the adhesive and the bulk wood. The penetration of adhesive from the wood surface into voids in the wood, so called mechanical interlocking, also contribute to the joint strength in an adhesion test but is not in itself a sufficiently strong adhesion mechanism to ensure long term stability. If the adhesion observed using SEM was primarily through mechanical interlocking, the adhesion was characterised as “poor at a cell wall level.” If the fracture occurred in the polymer or in wood cell walls, i.e. not at the interface, and no smooth polymer surfaces could be found, the adhesion was characterised as "good at a cell wall level".

The interaction measured using DMTA requires an intimate contact between the wood and adhesive through primary or secondary bonds. If no contact is present, the polymers will show the same loss factor peaks as the pure material. With only mechanical interlocking, the kind of intimate contact necessary for interaction to occur and for the adhesive to experience tensile stresses is not present.

Paints have not been investigated in this work; primarily due to the presence of high amount of pigments. However, there is no reason why paints could not be successfully studied using this technique.

Successful investigations were made on one thermoplastic glue (polyvinyl acetate, PVAc) and two polyurethane alkyde lacquers (slightly cross-linked). PVAc is a very common glue for indoor use and the lacquers tested are intended mainly for outdoor use, for example in boats. However, analysis of phenol resorcinol formaldehyde (PRF) glue or melamine urea formaldehyde (MUF) glue were less successful probably due to high degree of cross-linking that these materials exhibit. An EPI-glue, which is based on a styrene-butadiene copolymer with isocyanate cross-linking agent, and a cross-linked PVAc-glue gave inconclusive results. It must be pointed out that reference to pure polymers in these investigation is to specimens made from commercial glues. These glues contain more components than stated in the information sheets and these additional chemicals and pigments may influence the results.

7.1. DMTA on wood, Paper I

An initial study (Paper I) of DMTA measurements on wood was made to characterise the viscoelastic properties of Scots pine (*Pinus sylvestris*). This was necessary to obtain background knowledge about how to differentiate the response of the wood from that of the applied glue or lacquer and to see if there was a special response for composite (i.e. wood:glue, wood:laquer) material originating in the interface. One of the results was an increased understanding that variation in biological material gives rise to significant scattering of the measurement results. There was also a problem with the noise level of the loss factor, which was only slightly above background noise, and measurements had to be repeated several times on the same specimen to achieve good results. It was evident at this stage that the research would concentrate on the behaviour of the glue or lacquer and their behaviour when combined with wood.

Wood is a complex porous hygroscopic semi-crystalline material, its modulus of elasticity, like other viscoelastic materials, also decreases with increasing temperature, see Figure 20. During measurement from 0° to 80°C the storage modulus (E') was seen to decrease in the radial direction by 20% and in the tangential direction by 28%. Several small decreases in E' with corresponding loss factor peaks (α, β, γ) can be seen in the interval presented in Figure 20. The storage modulus E' differs between the radial and tangential direction in pinewood, but has approximately the same levels as in static measurements of Young's modulus in pine [15]. Several different explanations for the difference between radial and tangential directions have been proposed. In the tangential direction, early and late wood are parallel, but in the radial direction they are serial. This would imply a lower modulus in the radial direction governed principally by the modulus of early wood. However, this is not the case and the difference observed has instead been largely explained by the stiffening effect of ray cells in the radial direction [56]; primarily their effect on modulus in early wood in the radial direction [57]. An alternative explanation is that the different modulus in the early wood seen in the two directions [58], explained by Watanabe at al [59], is due to the cell shapes in coniferous wood which result in different bending deflection in the two directions. In the radial direction, due to a strong degree of cell alignment, the macroscopic strain is primarily achieved by local strain in the cell walls, whereas in the tangential direction the macroscopic strain is mainly by cell wall bending.

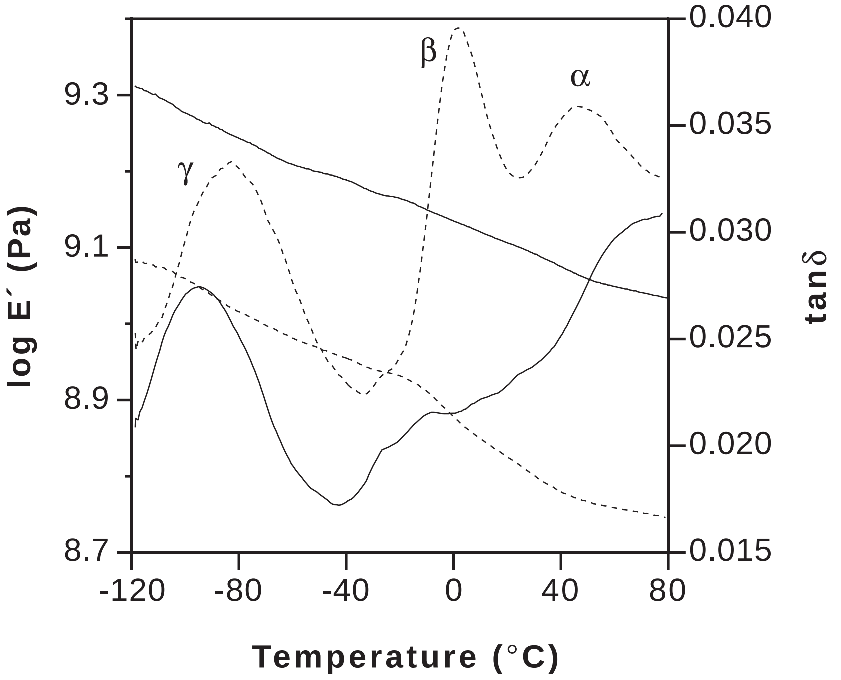


Figure 20: DMTA measurement of Scots Pine (*Pinus sylvestris*) with a moisture content of approximately 7%. Tensile force was applied in the radial (—) or tangential (·····) direction of the wood. The storage modulus and loss factor are displayed as function of temperature. The measurements are those presented in Paper I [60].

The loss factor γ-peak at -70 to -90°C in Figure 20 is a secondary transition from methylol side groups (-CH_2OH) with coupled water molecules [3, 50]. It was found (Paper I) that the loss factor peaks in radial and tangential direction also appear at slightly different temperatures. For wood with 3% moisture content the stiffer radial direction has a 5 to 17°C lower γ-peak temperature than the tangential direction (see Table 1 in Paper I). However, Salmén [61] showed a loss modulus peak E" at 5-10°C lower temperature for the transverse direction compared to longitudinal direction in water saturated Norway spruce. Hoffmann et. al [62] showed a dielectric loss peak in wood at about -80°C for the tangential direction and at about -60°C for the longitudinal direction. Theocaris et. al [63] showed a loss modulus peak in a unidirectional glass fibre/epoxy composite at 160°C in the tangential direction and at 180°C in the longitudinal direction. The results obtained in the present work are contradictory to the results of other researchers mentioned above for wood and composites where the stiffer longitudinal direction has a higher transition temperature. This discrepancy remains unexplained and needs to be studied further.

A new loss factor peak was found, the β-peak, at around 0-10°C in the tangential direction. This peak has not, to the authors knowledge, been noticed before. The peak was distinct in all tangential specimens but as can be seen from Figure 20, is almost absent in the radial direction. Some radial specimens, however, display a tendency towards a peak at this temperature. The origin of this peak is not clear. In Paper II it is suggested that the origin of the peak is from bending of the wood cell walls since it decreases in height when the structure is filled with polymers, see Figure 21. The cellular structure of coniferous wood is different in the two transverse directions where the macroscopic strain is more likely to give cell wall bending in the tangential direction.

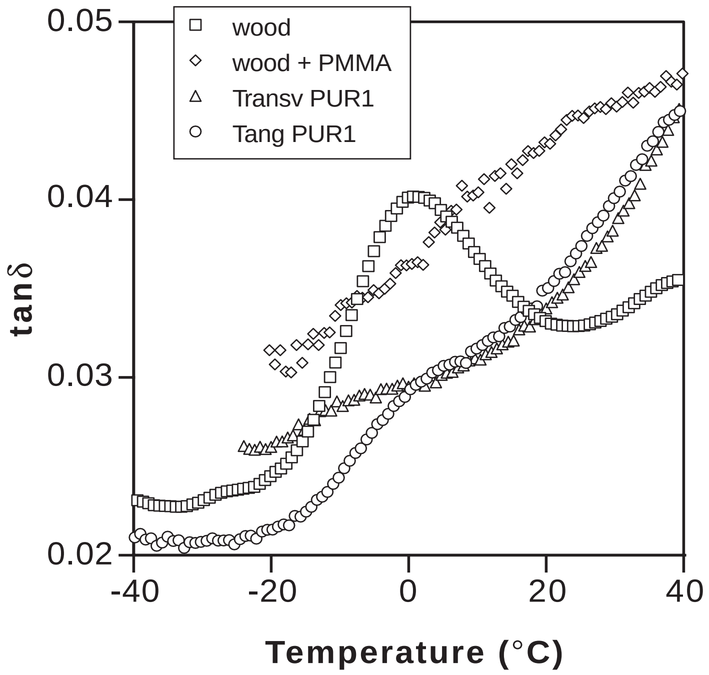


Figure 21: A DMTA measurement showing a loss factor peak in wood at around 0°C. The peak is just visible in wood painted with a polyurethane alkyd lacquer (PUR1) on the tangential or transverse wood surface but the peak cannot be distinguished when wood is impregnated with PMMA. Results from Paper II.

The loss factor α-peak at 40-60°C is most likely due to the glass transition for moist hemicellulose [49]. The assignment of the α-peak in this work is difficult since the wood specimens were subjected to a decrease in moisture content as the temperature increased above 0°C. The glass transition for lignin and cellulose at higher temperatures is thoroughly reviewed by Klason and Kubát [64].

7.2. Interaction and adhesion methodology, Paper II

The methodology is based on finding a loss factor peak (of a glass transition) that does not appear at the same temperature for the pure polymer compared to the polymer applied to wood. Studies of pure polymers and polymers in wood which reveal changes in Tg due to high levels of adhesion have not, to the authors knowledge, been reported before. These results indicate that DMTA can be used to evaluate bonding between wood and wood adhesives at a macro molecular level. For measurements where the transition temperature for the polymer applied to wood were lower, it was argued that the high level of interaction and high adhesion at a cell wall level were the cause. This is most likely the result of the shrinkage of the polymer system being hindered during drying and/or polymerisation of polymers in contact with the wood. The basic idea is that polymers adhering to cell walls were prevented from shrinking whilst polymers not adhering were free to shrink. Where shrinkage was limited, i.e. in the case of high levels of adhesion, the polymer is subjected to tensile stresses resulting in a decreased glass transition temperature. No change in the glass transition between pure polymer and polymers on wood indicated low interaction and adhesion. The results and conclusions concerning interaction obtained from the DMTA measurements have then been complemented and strengthened by fractography investigations of adhesion at a cell wall level using SEM.

In the DMTA studies, two acrylate polymers were used as model polymers to study interaction. The polymers chosen were selected for their assumed low and high adhesion to wood. The high adhesion polymer was a commercial grade developed for impregnation of electron microscopy specimens, and having high adhesion to biological materials. This material is called Unicryl and is a hydrophilic acrylate consisting of four different types of methacrylate monomers. The low adhesion polymer (here excluding mechanical interlocking) was PMMA which is also an acrylate, known to exhibit poor adhesion to wood at the cell wall level.

Both polymers were impregnated into the wood as monomers with a benzoyl peroxide catalyst and polymerised in situ. A micrograph of a fractured wood sample impregnated with PMMA is presented in Figure 22, and shows a rod of PMMA filling the cell lumen. The arrows indicate a cast of a bordered pit and the clear gap between the PMMA rod and the wood cell wall substance, which indicate low levels of adhesion at a cell wall level.

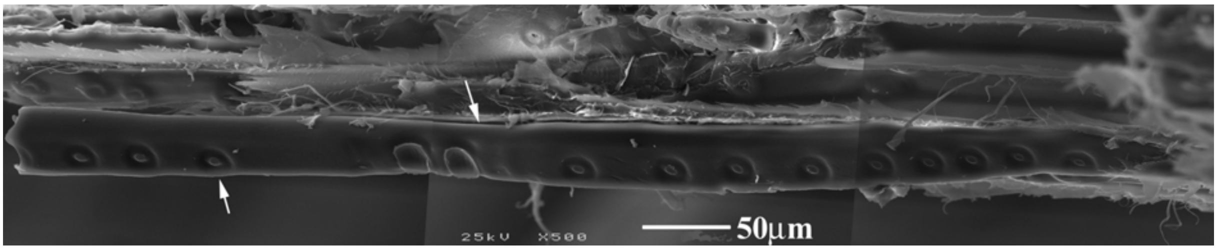


Figure 22: SEM micrograph of a fractured sample of PMMA impregnated wood, showing a rod of PMMA with a cast of bordered pits and a clear gap between PMMA and wood. The micrograph is a composite of three pictures, the middle one from Paper II.

DMTA measurements of the two polymers impregnated in wood or as pure polymers are presented in Figure 23-24. The hydrophilic acrylate has a 10°C lower Tg when impregnated in wood compared to the pure polymer. The result for PMMA was a 0 to 4°C lower Tg for PMMA in wood. No change in Tg was observed over repeated measurements of the same specimens. A DMTA measurement can be considered as a type of heat treatment of the material and if the wood samples had lower Tg due to the presence of low molecular compounds plasticizing the system this would have been seen.

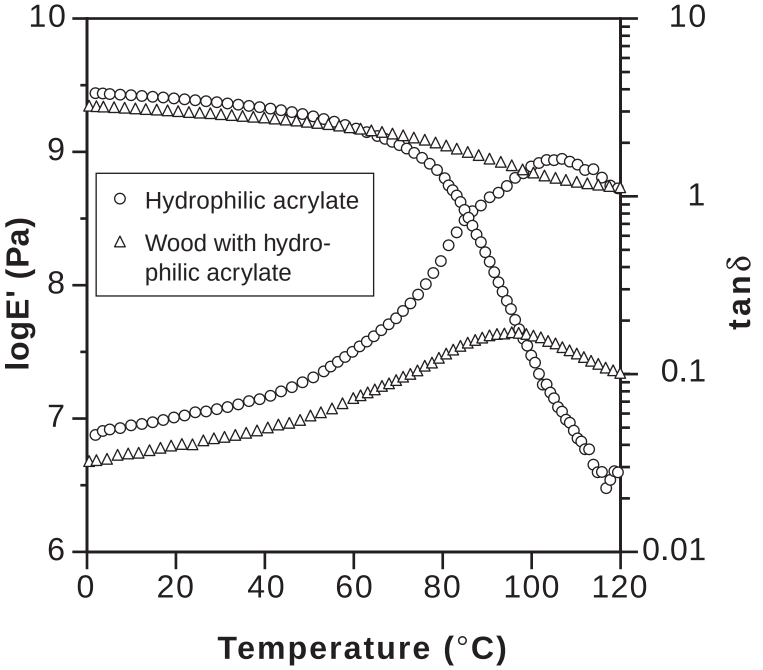


Figure 23: Storage modulus and loss factor of hydrophilic acrylate, on its own and impregnated in wood. The results are from Paper II. The polymer impregnated in wood has a Tg of 96°C and alone a Tg of 106°C.

The decrease in Tg observed for the hydrophilic acrylate polymerised in situ in wood is due to a higher free volume. It is suggested that this higher free volume is the result of tensile forces and not due to plasticizion (Paper II and III). In Paper II micrographs of fracture surfaces are presented that show a high level of adhesion between wood and hydrophilic acrylate but very low adhesion between PMMA and the wood cell wall. The adhesion for PMMA and an acrylate ester called PHEMA (polyhydroxyethyl methacrylate) to wood were studied using SEM by Kawakami et al. [65]. They too found low adhesion for PMMA and higher adhesion for PHEMA to wood cell walls. PHEMA is of the same hydrophilic acrylate type used in the present work.

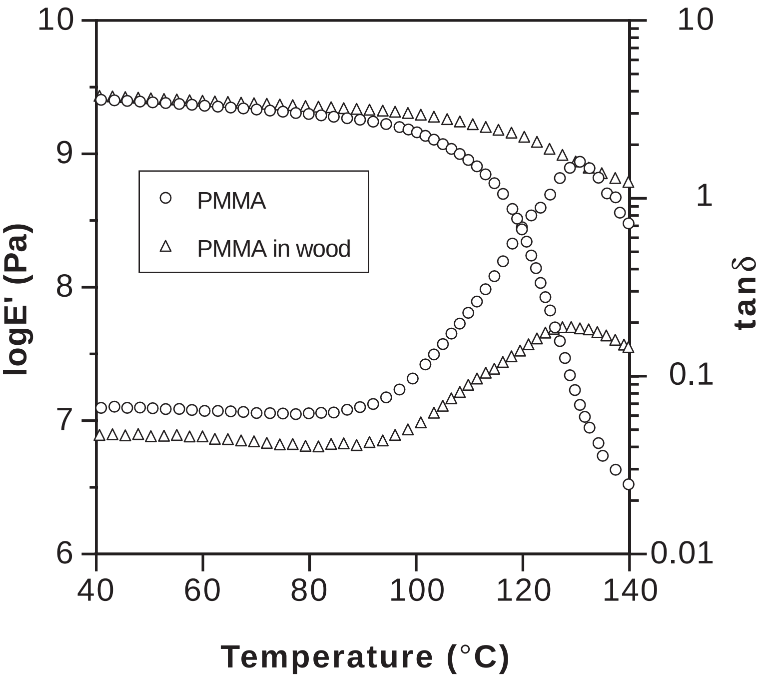


Figure 24: Storage modulus and loss factor of PMMA, on its own and impregnated in wood. The results are from Paper II. PMMA in wood has a Tg of 127-129°C and pure PMMA a Tg of 129-131°C.

Polymers, glues and lacquers solidify in different ways. They can be polymerized from monomers or oligomers such as PMMA and the hydrophilic acrylate. Drying can also be a physical process due to solvent evaporation, for example water evaporation from PVAc glue. In the polyurethane alkyd lacquer solvent evaporates and the chain length of the polymer in the lacquer increases and/or possibly cross-linked by auto-oxidation. All of these processes result in shrinkage, due either to evaporation of solvents or to chemical reactions bonding molecules closer together.

The acrylates used in this work shrink during the solidification process. If the polymer is adhering to the cell wall structure of the wood during solidification it must be somewhat restrained from shrinking. This behaviour probably occurs during the later stages of polymerisation when the chain length becomes sufficiently long. The restrained shrinking will then result in tensile stresses occuring in the polymers. In the DMTA measurements this will be observed as a decrease in Tg due to the higher free volume induced by the tensile stresses.

Surface free energy parameters as an explanation of the adhesion to wood for acrylates.

The more hydrophilic acrylate is, according to the manufacturer, largely hydrophilic and contains four monomeric methacrylates. These are probably similar in structure to the polyhydroxyethyl methacrylate (PHEMA) shown in Figure 25, which is a more hydrophilic structure than PMMA.

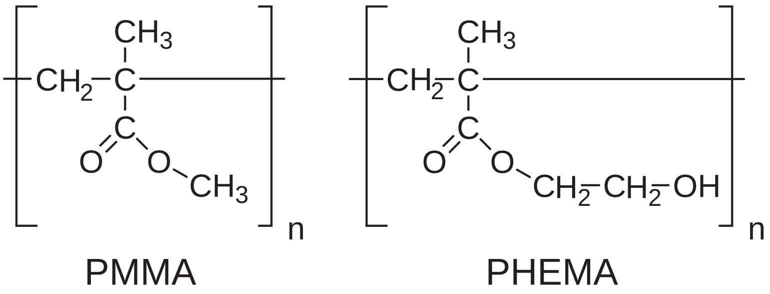


Figure 25: Structural units of two acrylate polymers: Polymethyl methacrylate (PMMA) and polyhydroxyethyl methacrylate (PHEMA).

These types of acrylates polymerized in situ in wood have also been studied by Kawakami et al. [65]. When they investigated PMMA using SEM, they found that a certain amount of void space existed between the wood and the PMMA indicating low adhesion. When studying samples of wood impregnated with PHEMA they found that the void appeared instead within the polymer and that no voids between polymer and wood could be observed. This suggests better adhesion of the polymer PHEMA to the inner surface of wood cell wall.

The current leading theory in adhesion science with Lewis acid-base interactions point to a high joint strength between wood and PHEMA. As a polymer PHEMA has an unusually high acid-base surface free energy parameter (γ_S^{AB}=10.4), see Table 2. More importantly, PHEMA also has a high acidic surface free energy parameter (γ_S^{+}=2.1) which by interacting with the basic surface free energy parameter (γ_S^{-}) of wood, could result in high work of adhesion (Wa, see adsorption theory). The Lewis acid-base theory of fundamental adhesion can therefore explain why the PHEMA bond to wood is much stronger than that of PMMA. (PMMA has γ_S^{AB} and γ_S^{+} equal to zero.)

The school of hydrophilic/ hydrophobic interactions also suggests that there is a good possibility of a strong interaction between the acrylate polymer PHEMA and wood since PHEMA is a rather hydrophilic polymer. It may thus be compatible to wood since cellulose and hemicellulose are also hydrophilic polymers.

Table 2: Surface free energy parameters γ_S (mJ/m^2) of different solid (s) polymers.

	γ_S	γ_S^{LW}	γ_S^{AB}	γ_S^{+}	γ_S^{-}
Pine heartwood	44.3	37.5	6.7	0.5	21.8
Pine sapwood	38.2	32.4	5.8	0.2	38.5
PMMA	39-43	39-43	0	0	9.5-22.4
PHEMA	50.6	40.2	10.4	2.07	13.1
PS	44.9	44.9	0	≈0	1.33
PE	33	33	0	0	0.1

The data on freshly cut Scots pinewood is from Wålinder [18] and the remaining polymer data from Pizzi [23] (p.108). The surface free energy parameters are γ_S^{LW} for Lifshitz-van der Waals forces, i.e. dispersion forces and γ_S^{AB} for Lewis acid-base parameters with an acidic (γ_S^+) and a basic (γ_S^-) parameter calculated as: $\gamma_S^{AB} = 2\sqrt{\gamma_S^+\gamma_S^-}$ and $\gamma_S = \gamma_S^{LW} + \gamma_S^{AB}$

The fundamental adhesion to wood for PMMA should be lower than for PHEMA based on the Lewis acid-base (AB) parameters, since the dispersion parameter (γ_S^{LW}) is similar for these two acrylates. By comparing the surface free energy parameters shown in Table 2, it can be seen that γ_S^{AB} equals zero or, more importantly, γ_S^+ equals zero which would give a low acid-base interaction between PMMA and wood.

7.3. DMTA measurements on silylated and acetylated wood

Experiments with silylation of wood

The interaction and adhesion methodology presented would benefit from more experimental studies of its validity. It is of interest to study whether a change in the chemical properties of wood would move the glass transition peaks for PMMA and the hydrophilic acrylate. Silylation chemicals can be used to react with hydrophilic hydroxyl groups in wood and replace them with hydrophobic silyl groups, see Figure 26.

Zollfrank investigated silylation of wood (beech and fir) with several types of silylation chemicals. He showed that N-(trimethylsilyl) acetamide (TMSA) [66] penetrates solid wood and FTIR (fourier transformation infrared spectroscopy) spectra showed that the basic wood parameters were not changed. Penetration into the inner surface of wood as viewed by FTIR and SEM-EDX (SEM-energy dispersive x-ray spectroscopy) was also found for silylation with TMSC (trimethylsilyl chloride) in pyridine and THF (tetrahydrofuran) [67].

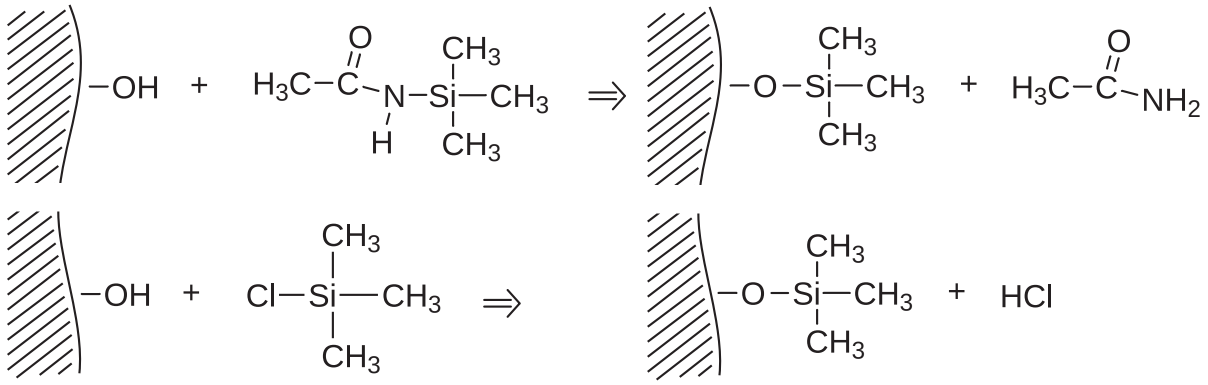


Figure 26: Top: Reaction of wood hydroxyl group with N-(trimethylsilyl) acetamide (TMSA) resulting in a silyl group and the by-product acetamide. Bottom: Trimethylsilyl chloride (TMSC) reacts with hydroxyl groups giving hydrochloric acid as a by-product.

In this work (unpublished) two types of silylation chemicals have been used, penetrating the wood according to Zollfrank. However, in the present work, silylation with TMSA gave no weight increase in the wood. Furthermore appeared double loss factor peaks in the PMMA impregnated specimens. The double peaks appeared when the silylated wood specimens were washed with only ethanol, the same washing procedure as used in the method from Zollfrank. If the specimens were thoroughly washed with both ethanol and water, the double peaks disappeared. No change in loss factor peaks could be observed compared with untreated wood.

Silylation of wood with HMDS (hexametyl disilazan) and TMSC in pyridin followed by washing in acetone gave an apparent weight increase of 8%. It was difficult to know the homogenity of the wood silylation but it is reasonable to assume the highest degree of silylation would be at lumen and outer surfaces. The wood samples were then impregnated with methyl methacrylate and the hydrophilic acrylate and polymerized in situ in wood. The elastic modulus and loss factor for pure polymer (specimen 1&2) polymerized in the same glass bottle as silylated wood had loss factor peaks at 138-139°C, see Figure 27. A reference specimen had a loss factor peak at 130°C. The specimens had been manufactured in exactly the same way at the same time from the same monomer mix, only the presence of silylated wood differed. The temperature difference was significant and not readily explainable.

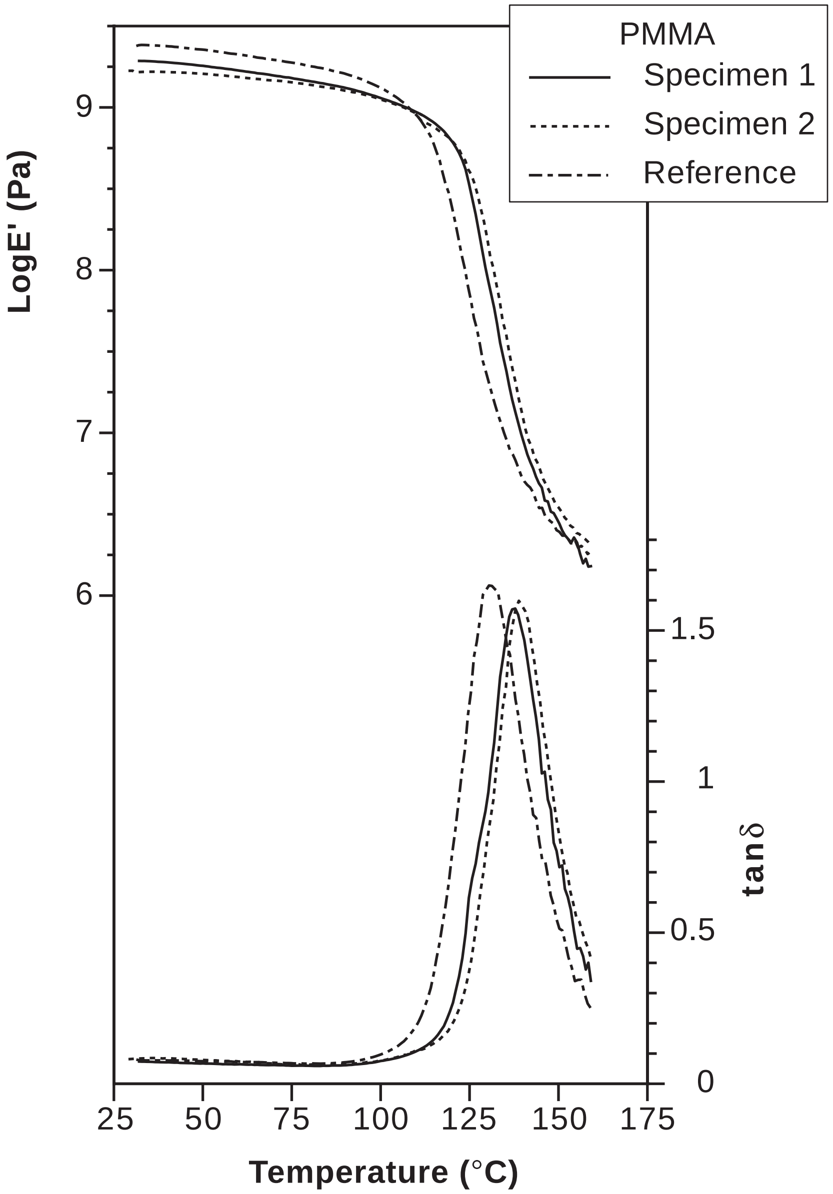


Figure 27: Storage modulus and loss factor for PMMA polymerised near silylated wood, specimen 1 with Tg=138°C and specimen 2 with Tg=139°C, . Reference specimen of PMMA not in contact with the wood has a Tg of 130°C. DMTA measurements were made 12-14 days after polymerisation.

Wood specimens impregnated with PMMA had loss factor peaks at 134-136°C, (see Figure 28) with a corresponding decrease in storage modulus. This was slightly lower than for pure PMMA polymerized in the presence of silylated wood which had a Tg of 138-139°C. However the latter result are uncertain as several other experiments (unpublished) with different solvents and silylation chemicals show a great scattering of Tg for PMMA. The loss factor peak temperature for the polymer specimens of PMMA ranged from 131°C to 142°C (6 specimens) and for PMMA in wood from 129°C to 135°C (10 specimens). None of these other experiments had shown any weight increase in the wood after silylation. This scattering in loss factor peak temperature makes it difficult to draw conclusions from the silylation experiments on PMMA.

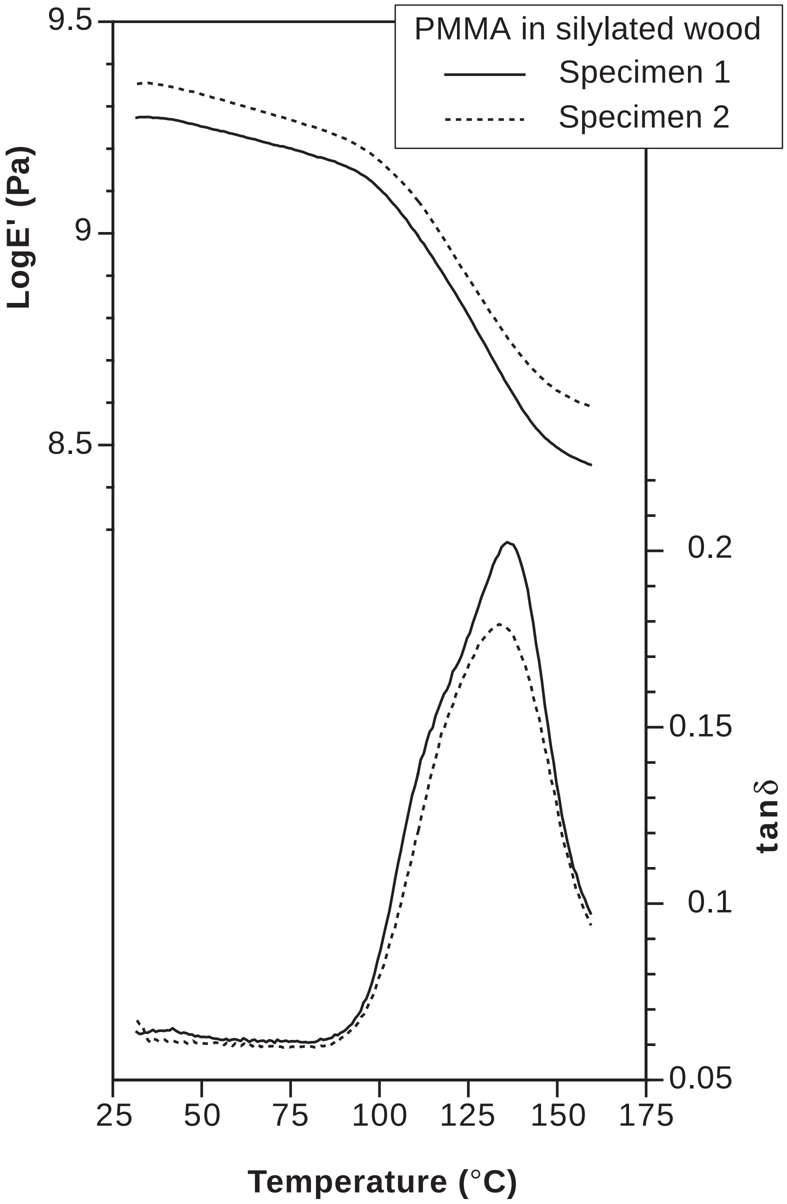


Figure 28: Storage modulus and loss factor for PMMA polymerised in situ in silylated wood, specimen 1 with Tg= 136°C and specimen 2 with Tg=134°C. DMTA measurements were made 12-14 days after polymerisation.

DMTA measurements were made on wood silylated with TMSC and HMDS in pyridin and then impregnated with the more hydrophilic acrylate. The loss factor peak for the pure polymer (specimen 1 and 2) was at 105-111°C, see Figure 29. The modulus and loss factor curve for specimen 1 was very similar to those for hydrophilic acrylate polymerised together with untreated wood (Figure 23).

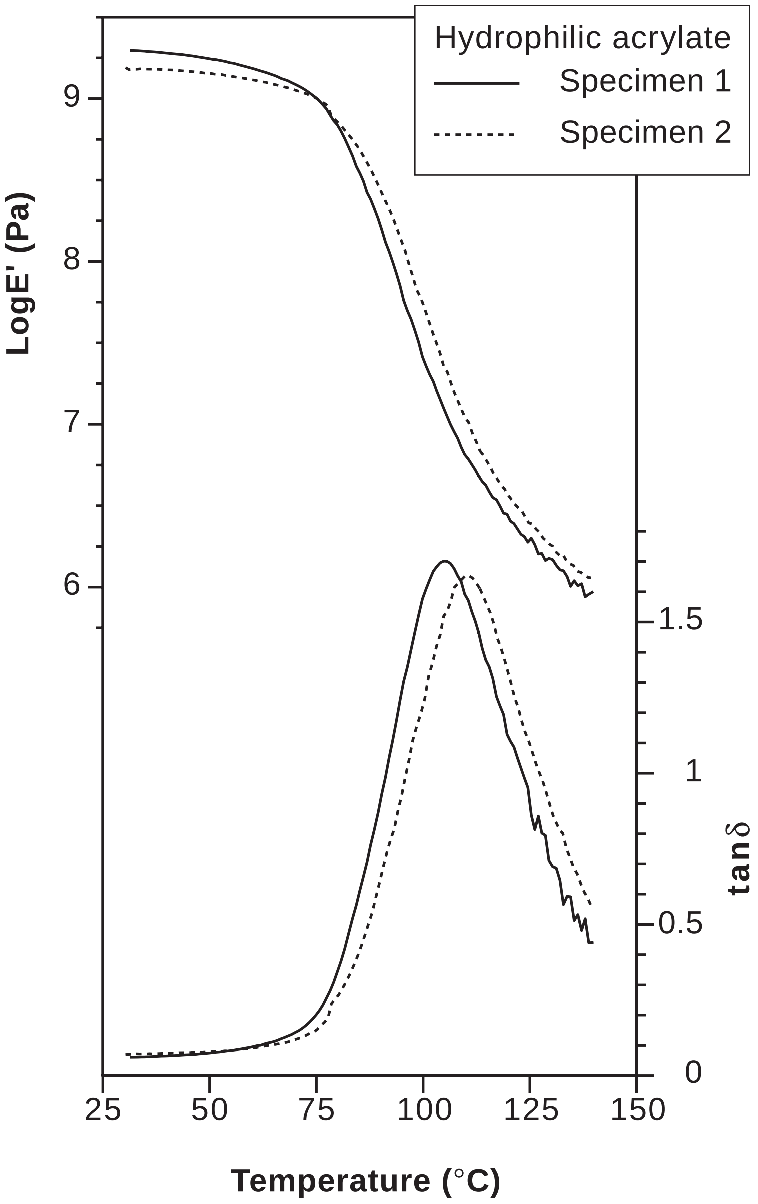


Figure 29: Storage modulus and loss factor for hydrophilic acrylate polymerised in presence of silylated wood. Loss factor peak temperatures for specimen 1 at 105°C and at 111°C for specimen 2. DMTA measurements were made 14-17 days after polymerisation.

Hydrophilic acrylate impregnated in wood had a peak at 84-87°C (see Figure 30) which was about 20°C lower than pure polymer but also about 10°C lower than previous results concerning interaction with unsilylated wood (Paper II). The results point to a strong interaction between the hydrophilic acrylate and the less hydrophilic silylated wood. Silylation of wood most probably gives the wood cell wall even better properties to enable it to interact with the hydrophilic acrylate.

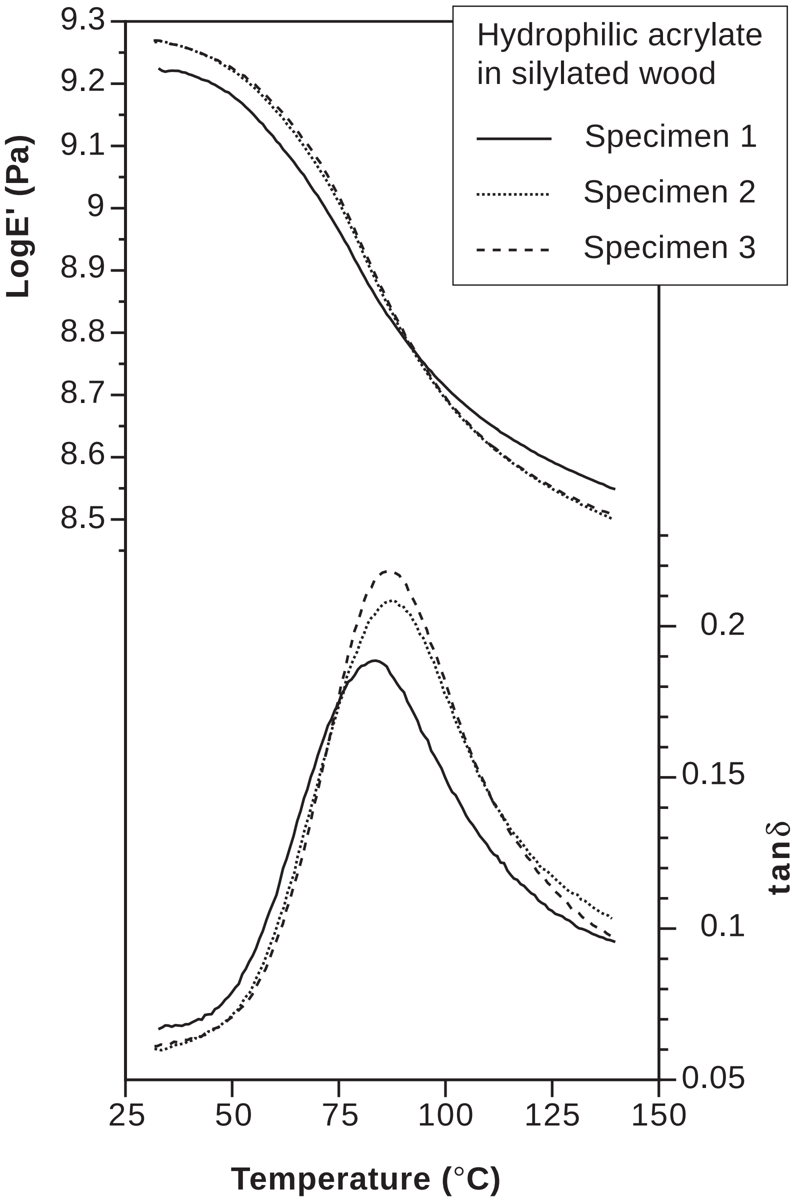
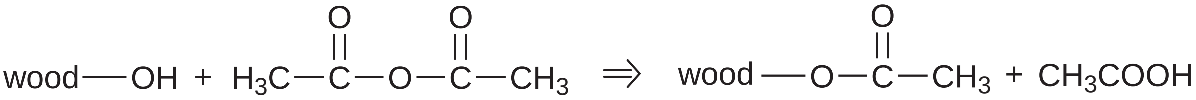


Figure 30: Storage modulus and loss factor for hydrophilic acrylate polymerised in situ in silylated wood. Loss factor peak temperatures for specimen 1 was at 84°C and at 87°C for specimen 2-3. The DMTA measurements were made 14-17 days after polymerisation.

Experiments with acetylated wood

The hydrophilic properties of wood can also be changed with a process called acetylation. With this process, the hydroxyl group is replaced with a more hydrophobic acetyl group, see Figure 31. The acetyl group is less hydrophobic than the silyl groups described above.



$$\text{wood}-\text{OH} + H_3C-\overset{\overset{\displaystyle O}{||}}{C}-O-\overset{\overset{\displaystyle O}{||}}{C}-CH_3 \Rightarrow \text{wood}-O-\overset{\overset{\displaystyle O}{||}}{C}-CH_3 + CH_3COOH$$

Figure 31: During acetylation wood hydroxyl groups reacts with acetic anhydride to form acetyl groups on the wood with acetic acid as a by-product.

Tests were made with acetylated wood impregnated with PMMA and hydrophilic acrylate to study whether acetylation gives rise to a change in loss factor peaks. No change in Tg could be observed between pure PMMA and PMMA polymerised in situ in acetylated wood. The loss factor peak temperature was at 131°C, the same level as observed for PMMA in untreated pinewood but, as for silylated wood, the pure PMMA polymerised in the presence of acetylated wood showed an unexplained and rather high loss factor peak temperature of 137°C. The uncertainty of the peak temperature makes it impossible to draw any conclusions about the interactions between PMMA and acetylated wood.

Acetylated wood was also impregnated with the hydrophilic acrylate. The loss factor peak temperature of 94°C observed for the polymer impregnated wood is comparable with other measurements on hydrophilic acrylate impregnated in situ in untreated wood namely at 96°C (Paper II) and in wood silylated in different ways between 91-96°C (5 specimens). The loss factor peak temperature for pure hydrophilic acrylate was 108°C which can be compared, as above, with values of 101° to 111°C observed in other experiments. The loss factor peak temperature suggests no change in the level of interaction between the hydrophilic acrylate and wood when wood is acetylated.

The height of tanδ at the peak temperature for both PMMA and hydrophilic acrylate in wood was considerably lower than for impregnated specimens of silylated or untreated wood, see Figure 32. The height of the loss factor peak was about 0.15 for the former, but for other measurements the level was closer to 0.2. There was also an indication of the beginning of a second loss factor peak since the loss factor levels increased after the peak shown in Figure 32. This increase in tanδ level was not observed for the acetylated wood which showed an increase in tanδ level, see Figure 32, but not to a degree that could explain the increase of the impregnated specimens. Complementary analysis might show an interaction between acetylated wood and the acrylates (PMMA and hydrophilic acrylate).

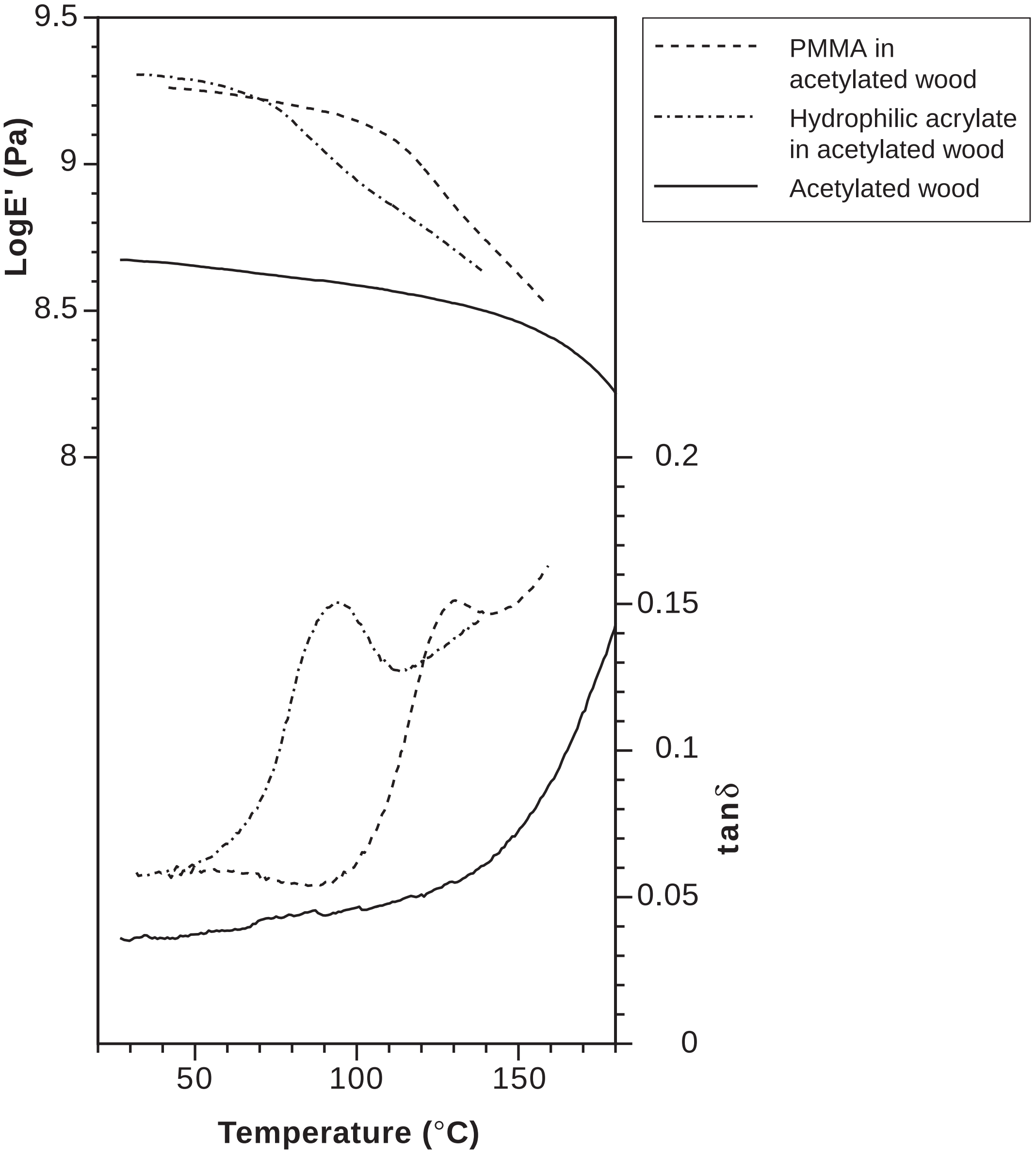


Figure 32: Storage modulus and loss factor for acetylated wood, alone or impregnated, and in situ polymerised with PMMA or hydrophilic acrylate. Specimens were conditioned at 33%RH. DMTA measurements were made 22-23 days after polymerisation.

7.4. DMTA measurements on polyurethane alkyd lacquer, Paper II

The results from DMTA measurements point to a high level of interaction and adhesion between wood and polyurethane alkyd lacquer. These results were based on two similar commercial lacquers (PUR1, PUR2) from different manufacturers (Paper II) normally intended for use on wooden boats. They dry by solvent evaporation and are cross-linked by auto-oxidation.

Specimens of pure lacquer and wood applied with lacquer were studied using DMTA. The storage modulus of the two lacquers, PUR1 and PUR2, was seen to decrease by almost three orders of magnitude around the glass transition temperature of 57°C and 60°C. The glass transition temperature was lower for lacquer on wood compared to pure lacquer, Table 3, indicating interaction between the wood and lacquers. After a heat treatment, see Table 3, the difference in Tg was even more significant with a ca. 10°C lower Tg for lacquer on wood. Both lacquers showed the same behaviour and had similar DMTA curves. When studying fractography specimens using SEM, good adhesion at the cell wall level could be observed. This points to a high interaction and adhesion between the wood and the investigated polyurethane alkyd lacquers. This again supports the use of DMTA as a tool for adhesion studies.

Table 3: Glass transition temperature as measured using DMTA at 1Hz for two polyurethane alkyd lacquers (PUR1 and PUR2) as pure lacquers and with wood.

	Pure lacquer, Tg (°C)	Lacquer with wood, Tg (°C)
PUR1, untreated *	57	50-54
PUR1, heat treated $^{\Delta}$	76	66
PUR2, untreated *	60	52-54
PUR2, heat treated $^{\Delta}$	74	62

* Dried at room temperature or at 35°C. $^{\Delta}$ Dried at 80°C for 48h.

7.5. DMTA measurements on white glue (PVAc), Paper III

Low interaction and adhesion were found between wood and polyvinyl acetate (PVAc) glue, also called white glue, studied in Paper III. PVAc is common wood glue for indoor applications and is based on a dispersion of PVAc in water.

Pure glue and glued wood were tested using DMTA. Measurements of four specimens of pure glue gave a Tg of 37.6±0.6°C. One specimen stored one year and dried at 103°C for 48 hours had a Tg of 38.5°C. Wood glued with PVAc had a loss factor peak, originating from the PVAc, at 39-40°C. The temperature interval used in these experiments was from room temperature to 80°C. Repeated measurement showed no increase of Tg. No significant difference between the Tg of glue and of glued wood were observed, indicating a low level of interaction between the wood and PVAc glue.

SEM fractography of the glued wood confirmed the low adhesion at a cell wall level. Figure 33, shows two rods of glue that have been drawn out of the cell lumen of the transverse surface of wood on the opposite side. The double cell wall is no longer present between the rods. The rods show a smooth surface and in a similar photo presented in Paper III, a cast of bordered pits can be seen on a rod, indicating close contact between the wood cell wall and the glue but with very low adhesion at a cell wall level. The low interaction observed using DMTA was verified by low adhesion at a cell wall level viewed using SEM.

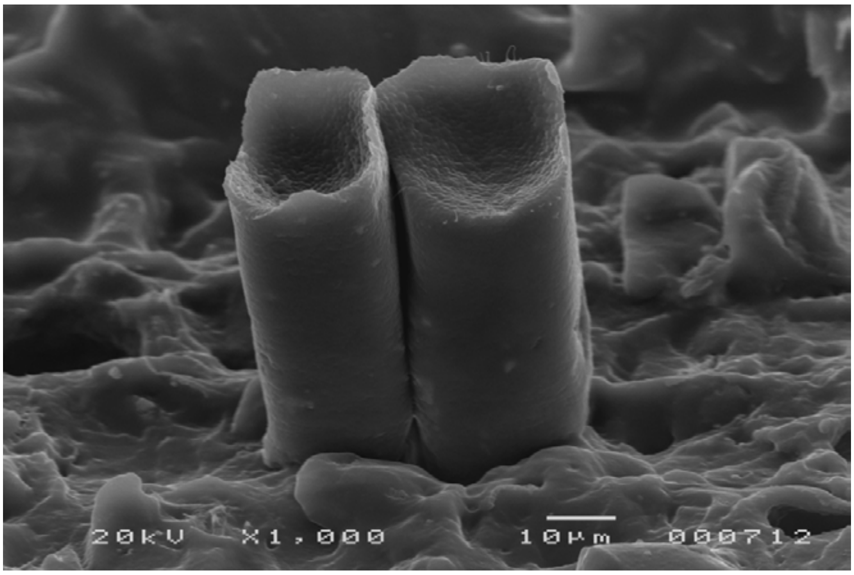


Figure 33: SEM micrograph of the fracture surface of two transverse wood surfaces glued with PVAc, showing two protruding rods of glue. The picture was taken at the same time as similar micrographs presented in Paper III.

7.6. DMTA measurements of cross-linked PVAc glue

A DMTA study was made of cross-linked polyvinyl acetate glue (unpublished). A graph of the loss factor and storage modulus for the glue is presented in Figure 34. The storage modulus decreased one order of magnitude and two loss factor peaks (α and β), corresponding to the modulus decrease, can be seen. Specimen 1 was probably not fully dried since a large increase in storage modulus was also seen above 80°C where the specimen might be dried or postcured. Measurements with two weeks longer drying times (specimen 2) showed a peak at the same temperature and a clear α-peak. In samples stored for three years, the peaks remained at the same temperatures but the β- peak increased in height. The decrease in modulus was smaller for the cross-linked PVAc than for thermoplastic PVAc (Paper III) which showed a decrease of two orders of magnitude at the glass transition. This is the normal behaviour of a cross-linked system.

The β-peak in Figure 34 was most probably the glass transition for PVAc, having a Tg of 30-32°C and an activation energy of 234kJ/mol (as calculated from measurements at frequencies of 1, 10 and 50 Hz). The data was similar to literature data on the polymer polyvinyl acetate [37], which has a Tg of 28°C, and activation energy of 251kJ/mol. The increase in height of the β- peak for longer storage times for these two PVAc glues were also similar with a starting height of 0.6 increasing to 1 for the thermoplastic PVAc and to 0.8 for the cross-linked PVAc.

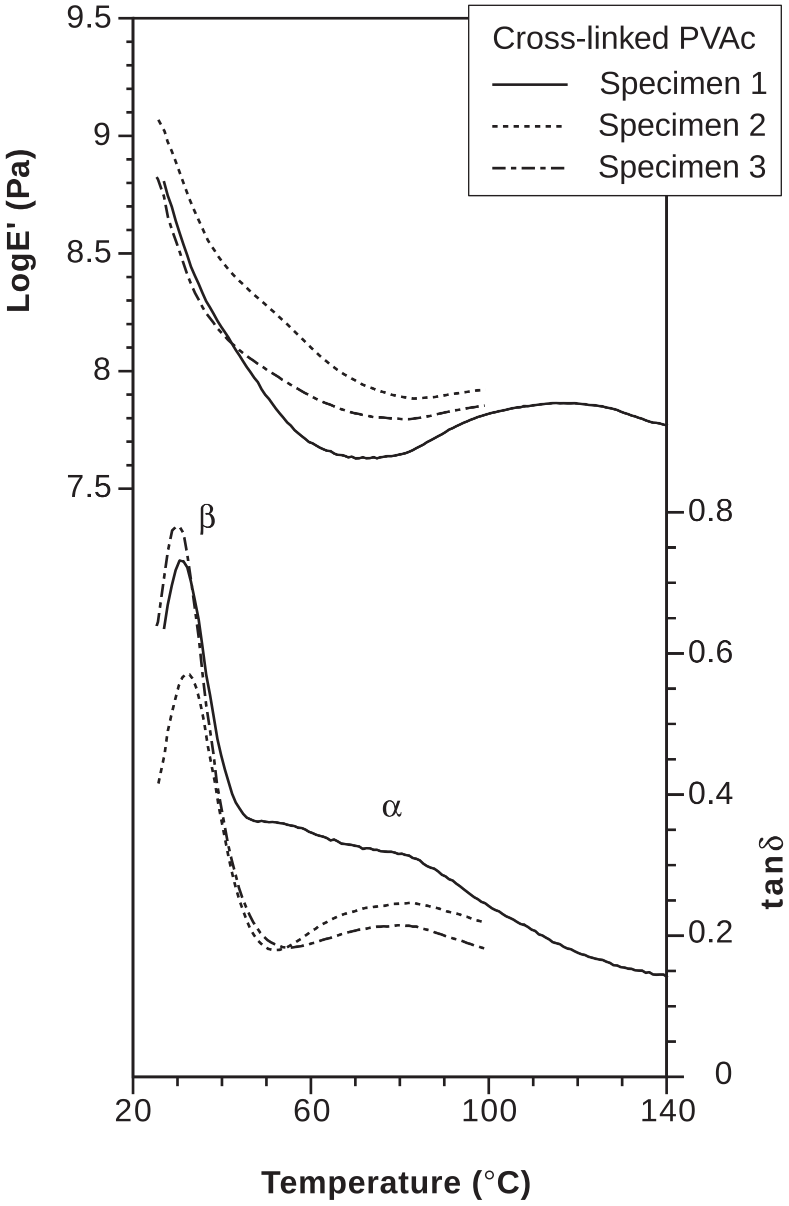


Figure 34: Storage modulus and loss factor for a cross-linked PVAc glue (polyvinyl acetate). Specimen 1 stored for 24 days before testing, specimen 2: 36 days and specimen 3: 3 years.

The origin of the α-peak appearing at about 80°C for the pure glue sample is unknown, see Figure 34. This peak was barely visible in measurements of glued wood. A similar α-peak could be seen at 70°C for the thermoplastic PVAc glue (Paper III) but the peak disappeared after drying times exceeding eight days. The origin of the α-peak is not clear, but would be interesting to investigate further.

DMTA measurements of glued wood showed a clear loss factor peak at 40-43°C coinciding with a drop in storage modulus, see Figure 35. No significant difference could be observed between measurements made on glued wood specimens with drying times of a few days to a specimen stored for three years.

The glass transition temperature increased from 30-32°C for the pure glue to 40-43°C for glue in wood. This increase in Tg was unexpected and has no obvious explanation. It is possible that the water soluble cross-linking agent might promote cross-links not only between PVAc chains but also between PVAc chains and wood. If the PVAc was cross-linked to the wood cell wall, it would experience decreased mobility which should increase Tg. This mode of increase in Tg for adhesives interacting with wood was originally expected when this research was started since an interaction with wood polymers having high Tg's would increase the Tg of the glue polymers.

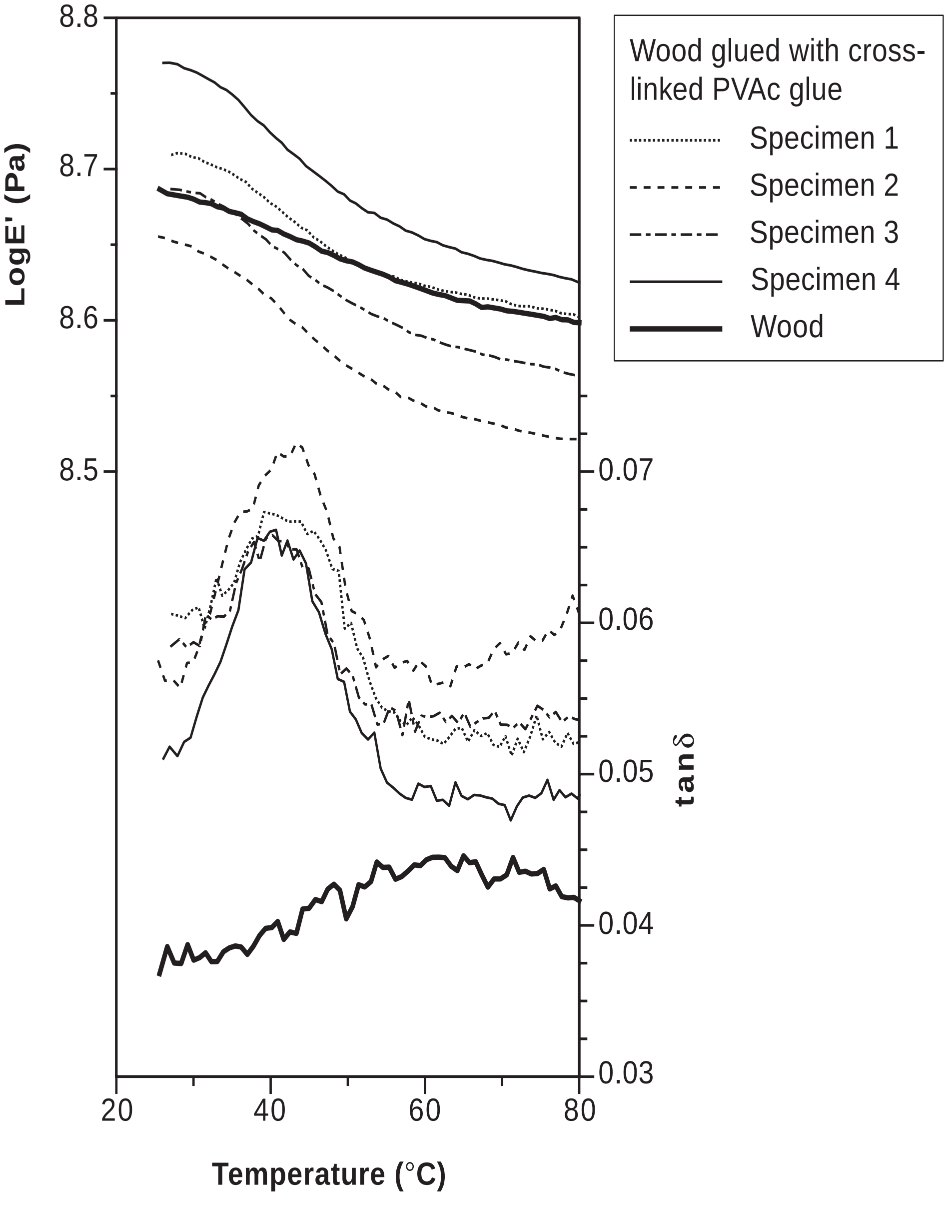


Figure 35: Storage modulus and loss factor of wood glued with a cross-linked PVAc glue (polyvinyl acetate). Glued wood specimen 1 stored for 4 days before testing, specimen 2 and 3 stored for 5 days and specimen 4 stored for 3 years. All specimens were conditioned at 33% RH before measurement.

Other possible explanations for an increase in Tg, which is due to a decrease in free volume, could be a higher degree of cross-linking in the glue or compressive stresses acting on the glue. A higher degree of cross-linking between the PVAc chains in glue in wood compared to pure glue implies a higher degree of cross-link agent for glue in wood, which is most improbable. It is known that glue shrinks during drying and curing and this should rather lead to tensile stresses and not compressive stresses.

The great difference in interaction with wood for the two PVAc glues was remarkable. For the thermoplastic PVAc glue no increase (or only a few degrees) of Tg was observed for glued wood but for the cross-linked PVAc glue Tg was increased by about 10°C. Unfortunately no SEM investigations have been made on wood glued with cross-linked PVAc to study whether it shows a visibly improved adhesion to wood at a cell wall level.

7.7. DMTA measurements on EPI glue

A DMTA study was made on EPI glue (unpublished), it was not possible to draw any conclusions regarding the interaction between the wood and glue. The EPI glue is an emulsion polymer isocyanate, in this case a styrene-butadiene copolymer with an isocyanate cross-linking agent.

The storage modulus of pure glue specimens decreased by slightly more than one order of magnitude from 30 to 180°C, see Figure 36. The loss factor shows a series of peaks and it is possible to distinguish peaks at 60°C, 80°C and 140-160°C. There was considerable scattering between measurements, even though the specimens were from the same glue mix and cut side by side. If the results had been repeatable, some information could probably have been extracted through deconvulation of the peaks into individual peaks. No such effort was made because of the scattering in the results. No easy explanation has been found as to why the specimens showed so much scattering in their viscoelastic properties.

The presence of several loss factor peaks for the EPI glue was probably from the styrene-butadiene copolymer. The EPI glue is a copolymer consisting of two different polymers with different glass transition temperatures; a polybutadiene with a Tg below zero and polystyrene with a Tg of 100°C. A random copolymer could be designed to give a Tg somewhere between the two homopolymers glass transition temperatures. The three peaks appearing in the DMTA measurements probably result from a mix of different styrene-butadiene copolymers.

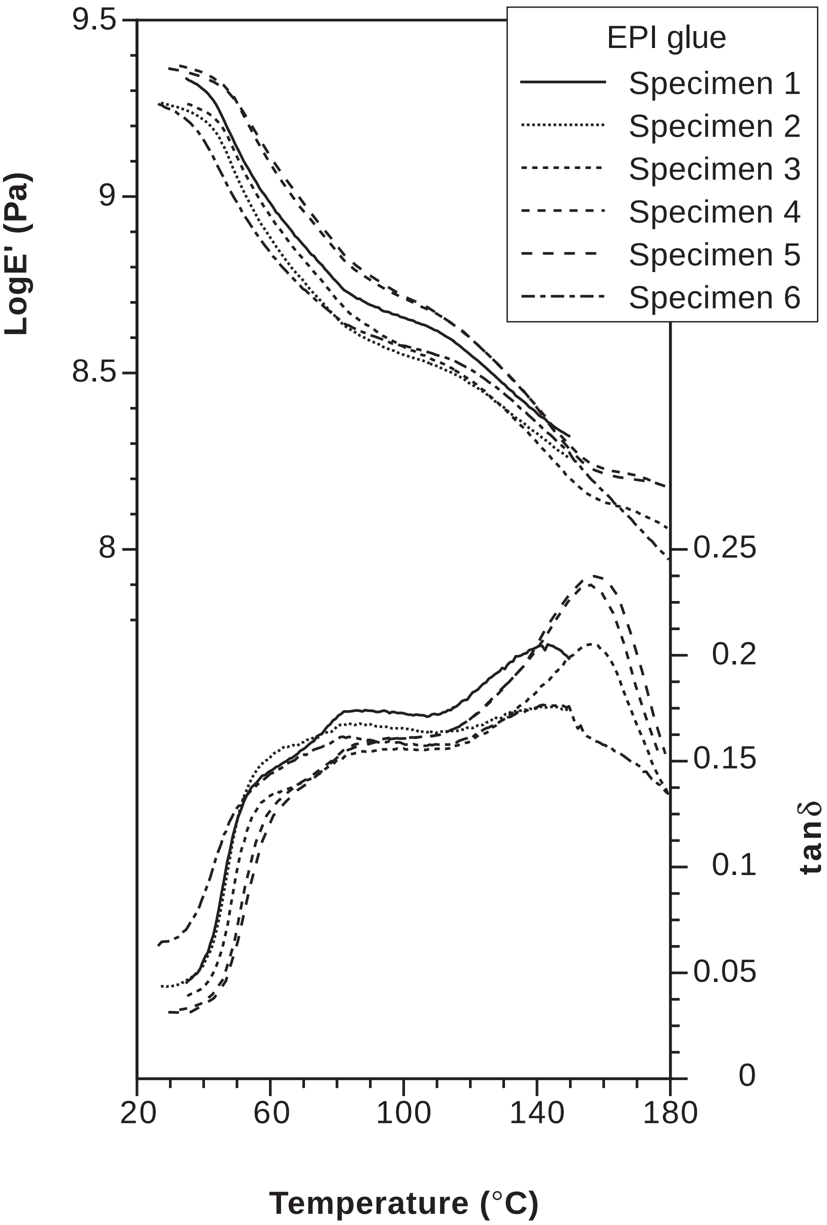


Figure 36: Storage modulus and loss factor for EPI glue. The time between curing and measurement using DMTA was 28, 32, 35, 38, 39 days and 3 years for specimens 1 through 6 respectively.

Wood glued with EPI was also measured using DMTA and showed a loss factor peak at about 80°C, see Figure 37. This peak most probably was not from the wood, see Figure 37. Even though wood shows a peak at around 60-70°C the measured glued wood had a significantly higher loss factor level. It is interesting to note the appearance of only one loss factor peak in the glued wood specimens, originating from EPI glue, which differs from the three peaks observed for the pure glue. No explanation for this can here be presented. There was no possibility to draw any conclusions concerning the interaction and adhesion between wood and EPI glue from this DMTA study, mainly due to the large scattering of the results, but also because of the uncertainty related to the peaks in the pure glue with which to make comparisons.

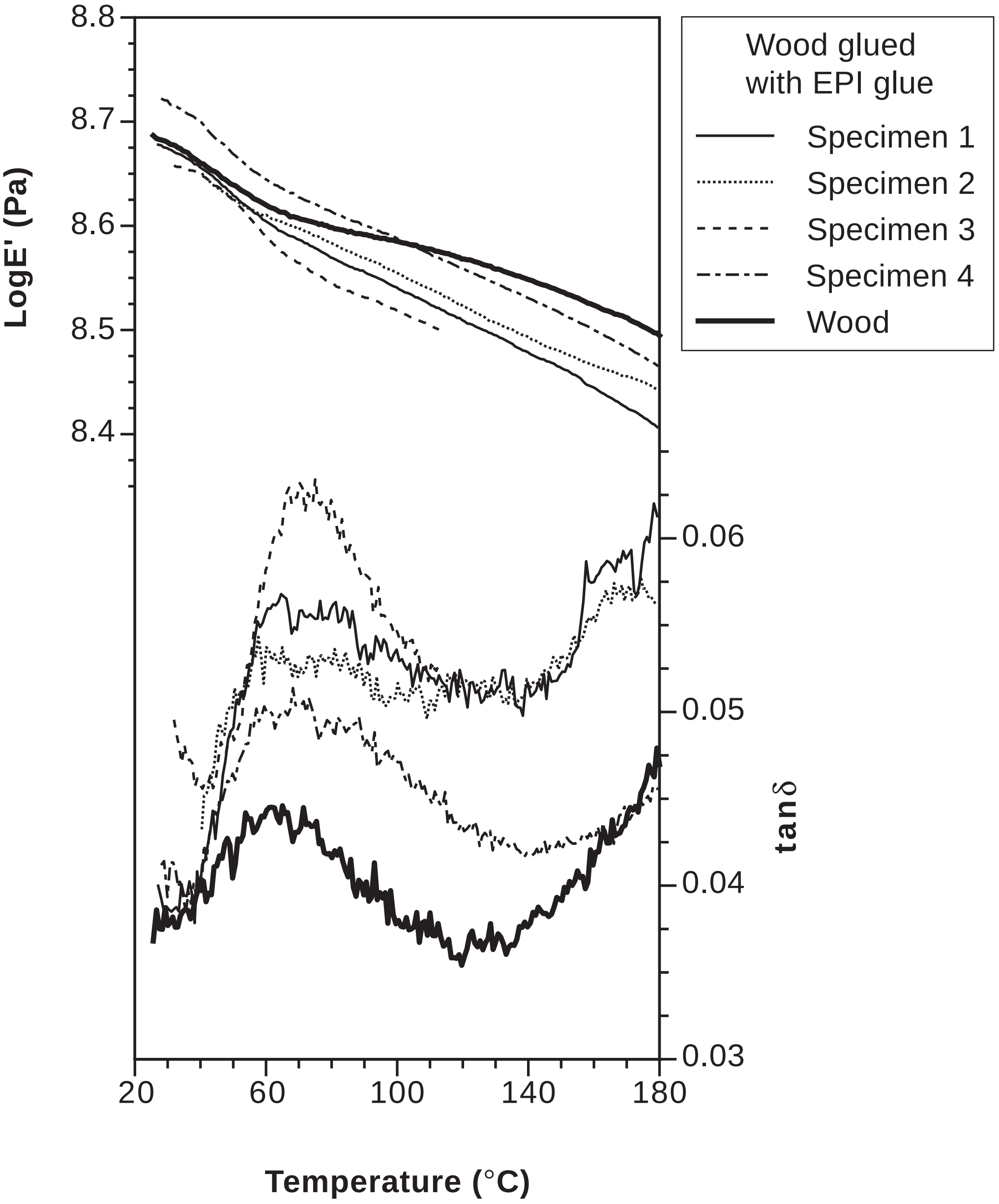


Figure 37: Storage modulus and loss factor for four specimens of wood glued with EPI (WEPI1 to 4). The time between curing and measurement using DMTA was four days for specimens WEPI1 and 2. For specimen WEPI3 and 4 the time was 3 years. Wood and glued wood were conditioned at 33% relative humidity before measurement.

7.8. DMTA measurements on PRF and MUF glue

Phenol resorcinol formaldehyde (PRF) glue and melamine urea formaldehyde (MUF) glue are two types of glues approved for load-bearing timber structures such as Glulam. Whilst there is a possibility that these glues could be studied using the present DMTA technique, they revealed themselves to be unsuitable for this test method and no interaction behaviour could be estimated from some limited preliminary studies (unpublished results).

The PRF glue is a cross-linked polymer giving characteristic brown gluelines. Pure glue and wood glued with PRF were studied using DMTA, see Figure 38. The storage modulus was observed to decrease by about one order of magnitude up to 150°C where there was a small increase in modulus. Such an increase can often be due to post curing reactions which results in higher modulus but degradation probably also occurred during measurement to 190°C since the specimen lost 4% in weight and shrank by 2% in length. There was a corresponding loss factor peak at 152°C which might have been a glass transition peak. In highly cross-linked polymers the Tg peak is not always especially clear, but here it was easily observed. In a second measurement of the same specimen, the peak had moved to above 200°C, see Figure 38, due to the heat treatment a specimen is exposed to during a DMTA measurement.

When studying wood glued with PRF, see Figure 38, no loss factor peak corresponding to PRF glue could be observed within the measured temperature range. The loss factor had increased from 0.045 at its lowest (at 130°C) up to 0.06 at the end of measurement at 190°C which indicates the beginning of a loss factor peak most probably originating in the wood. The PRF glue should be observable in these glued wood specimens when compared with levels seen in cross-linked PVAc having two gluelines of $150 g/m^2$ and a loss factor peak up to 0.6. A peak from PRF should be seen since the specimen had similar dimensions with one glueline of $250 g/m^2$ and a loss factor peak of up to 0.3. The thickness of the glueline has not been studied.

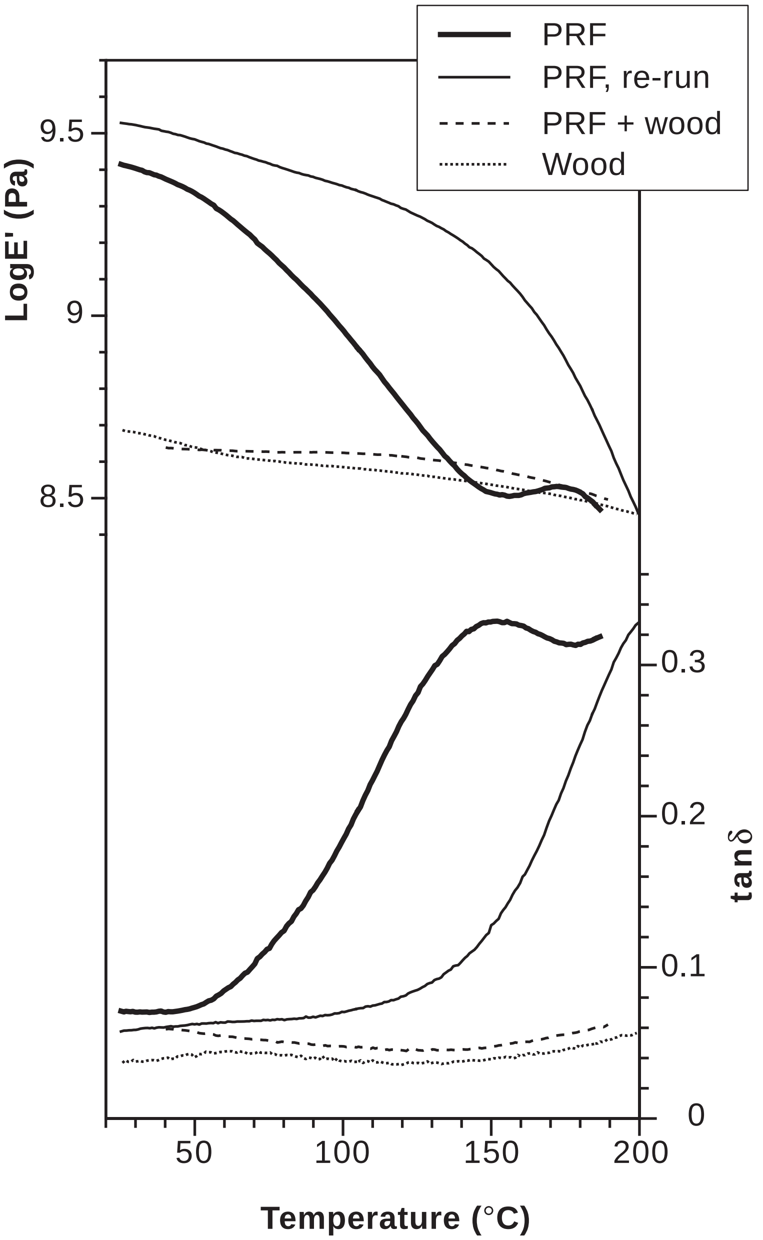


Figure 38: Storage modulus and loss factor of PRF (phenol resorcinol formaldehyde) glue and pine wood glued with PRF. Glue and glued wood were stored for one month before testing, the re-run was made on the same specimen after one day. The wood specimen as well as the glued wood were conditioned at 33% relative humidity before measurement.

MUF glue gives light gluelines. A laboratory made MUF glue was tested using DMTA. The storage modulus decreased by two orders of magnitude and the loss factor showed a promising loss factor peak, see Figure 39. Unfortunately, specimens fractured during analysis and bubbles were formed within the specimens during measurement. The weight loss was more than 25% in this measurement to 160°C and the specimen became very brittle. The MUF glue used here could not be analysed but measurement may be possible on commercial MUF glue.

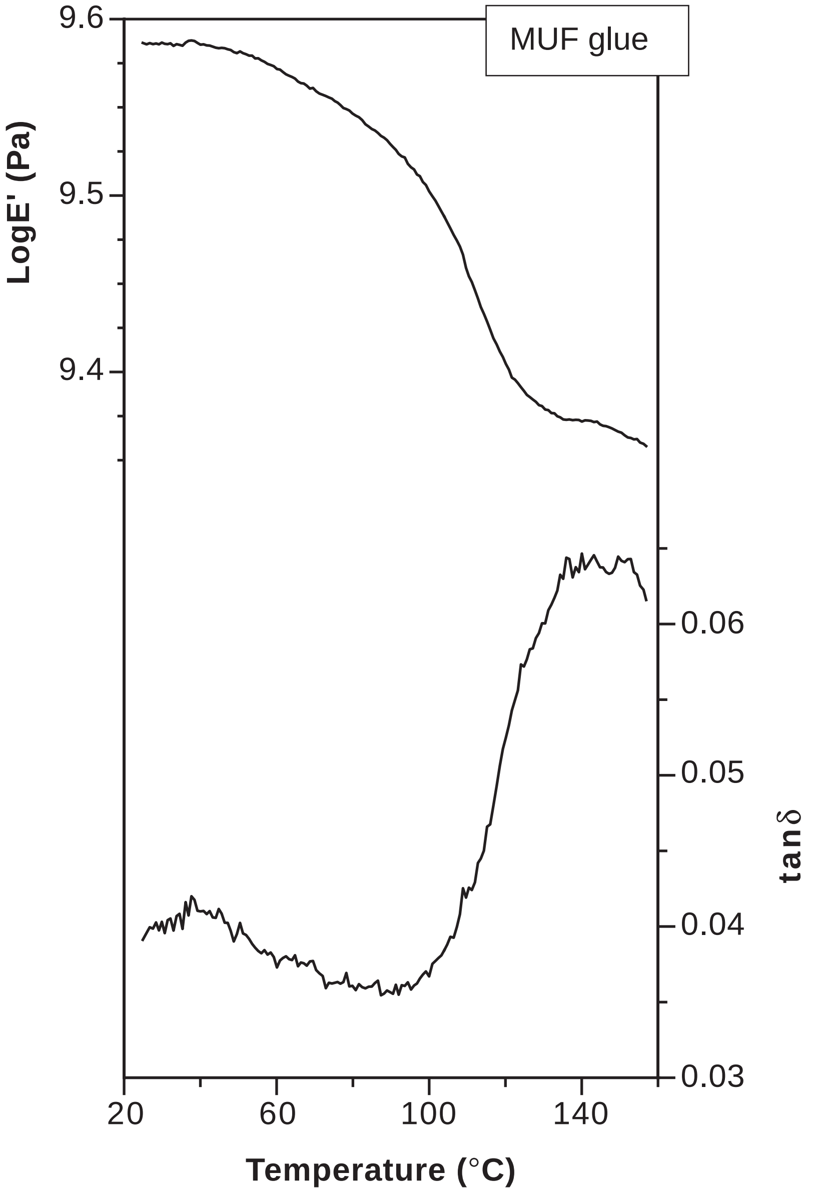


Figure 39: Storage modulus and loss factor of melamine urea formaldehyde (MUF) glue. The glue had been stored at room temperature for eight months before testing.

7.9. Influence of surface structure on adhesion, Paper IV

The chemical structure and properties of the adhesive and adherend are important, as has been discussed earlier in this thesis, but the physical structure of the adherend also influence the practical joint strength. Researchers of adhesion have long discussed the importance of mechanical interlocking on bond strength, especially with porous materials as wood is interlocking considered an important factor. A recent study of adhesion of glue to steel showed that surface structure of non-porus materials also affects joint strength [68].

Many studies have been made on the structure of machined wood [69, 70, 71, 72, 73, 74, 75] but no article has been found which compares the comparative effects of the three most common wood surfaces, sawn, sanded or planed, on joint strength.

Such a comparative test was carried out on beech and pinewood (Paper IV) where the testing of joint strength was done using fracture tests on single and double overlap joints (SJ and DJ) in tension. The wood pieces were glued with laboratory made melamine urea formaldehyde (MUF) glue. For the beech samples, no apparent difference could be observed in the failure stress for the two types of joints but for pinewood the failure stress was significantly higher for the DJ test. The SJ test gives higher peeling stresses than the DJ and it is clear that pinewood was the most susceptible to the effects of this.

For the beech samples, the sawn surfaces gave the highest failure stress and percent wood failure, followed in order of decreasing strength by the sanded and planed surfaces respectively. Scanning electron microscopy of the as-machined beech surfaces showed that the planed surface had a smeared appearance whilst much debris from torn wood cell walls was found on the sawn and sanded surfaces but not on the planed surface. Microscopic investigation of gluelines showed no apparent difference between the sawn and planed surfaces as far as penetration depth into fibres and vessels was concerned. However, the sanded surfaces had much smaller glue penetration depth into vessels. The differences found were difference in depth of penetration and presence, or otherwise, of debris on the machined surfaces, see Table 4. The sawn surface had both debris and high penetration, the sanded surface had debris and low penetration and the planed surface small amounts of debris and high penetration. Further studies are required to investigate whether the presence of debris serves a useful purpose, such as acting as a reinforcement to the glue.

The pinewood showed the same trends as were noted for the beech wood with highest failure stress for the sawn sapwood, followed in decreasing order by the sanded and planed surfaces. Unfortunately, very few planed sapwood specimens were tested but, supported by the findings for beech, it was clear that the planed pinewood gave the lowest failure stresses. No microscopy study was made on the pinewood.

Table 4: Schematic representation of results of fracture tests and microscopy investigation of glued beech wood and machined beech wood surfaces.

	Joint strength	Percent wood failure	Debris	Penetration depth
Sawn	+ + +	+ + +	+ +	+ +
Sanded	+ +	+ +	+ +	+
Planed	+	+	+	+ +

+ A high score indicates higher joint strength, high percent of wood failure, an abundance of debris and/or large penetration depth of glue into wood vessels respectively.

8. Future work

The use of DMTA for measurements of adhesion of polymers to wood is at present at a research level and there is a long way to go before it can be used as a standard technique for the control and evaluation of adhesion. The results, however, indicate that the technique is worth further exploration.

It would be very interesting to work more closely with a paint or glue manufacturer so that the details of commercial formulations could be obtained and to use DMTA measurements to help investigate the possibility to improve adhesion through formulation changes.

Another interesting research area would be to work with thermosetting glues with sufficiently distinct glass transition peaks to perform measurements.

The DMTA measurements in this thesis were made on softwoods and it would be interesting to test the technique on hardwoods as well. The cellular structure of hardwoods is quite different with the dimension of vessels being much larger than in softwood tracheids whilst the hardwood fibres are much smaller. This dimension divergence might well produce different results for hardwood than for softwood when using the DMTA adhesion methodology.

9. References

1. K. Horiuchi and K. Sato, "Viscoelastic and adhesion properties of air-drying coating films", *Journal of Coatings Technology* **63** (1991) pp 55-61.
2. T. Handa, S. Yoshizawa and I. Seo, "Polymer-performance on the dimensional stability and the mechanical properties of wood-polymer composites evaluated by polymer-wood interaction mode" *Org. Coat. Plast. Chem.* **45** (1981) pp 375-381.
3. T. Handa, M. Fukuoka, S. Yoshizawa, Y. Hashizume and M. Suzuki, ”The dielectric properties of wood and wood-polymer composite (WPC) containing moisture at low temperature regions”, The 23rd Japan Congress on Materials Research-Non-Metallic Materials, March 1980, pp 338-342.
4. T. Handa, S. Yoshizawa, Y. Ikeda and M. Saito, "Dynamic Mechanical Properties of Wood-Polymer Composite (WPC) and Polymerization of Methyl Methacrylate (MMA) in wood", *Reports on Progress in Polymer Physics in Japan* **XIX** (1976) pp 293-296.
5. G. A. Bernier and D. E. Kline, "Dynamic Mechanical Behaviour of Birch Compared with Methyl Methacrylate Impregnated Birch from 90 to 475K*", Forest Products Journal* **18** (1968) pp 79-82.
6. K. Oksman and H. Lindberg, "The influence of a SBS compatibilizer in polyethylene-wood flour composites", *Holzforschung* **52** (1998) pp 661-666.
7. K. Oksman and H. Lindberg, "Influence of thermoplastic elastomers on adhesion in polyethylene-wood flour composites", *J. Appl. Pol. Sci.* **68** (1998) pp 1845-1855.
8. K. Oksman and H. Lindberg, "Interaction between wood and synthetic polymers", *Holzforschung* **49** (1995) pp 249-254.
9. E. Raknes, "Durability of structural wood adhesives after 30 years ageing*", Holz als Roh- und Werkstoff* **55** (1997) pp 83-90.
10. W. C. Feist and D. N.-S. Hon, "Chemistry of Weathering and Protection" in The Chemistry of Solid Wood, R. Rowell (Ed.), American Chemical Society, Washington D.C., 1984, ISBN 0-8412-0796-8.
11. D. Y. Perera, "On adhesion and stress in organic coatings*", Prog. Org. Coat.* **28** (1996) pp 21-23.
12. S. A. Grundberg and P. O. G. Hagman, "Measuring active wood fracture surfaces. An indirect method for evaluating gluing techniques in particle board " *Holz als Roh- und Werkstoff* **51** (1993) pp 49-54.
13. K. A. H. Lindberg, M. L. Ericson and A. C. Backman, "Measurement of polymer interfacial strength with an instrumented Ultramicrotome" in Proceedings of ECCM 9, ECCM 9 CD-ROM 2000: Composites from Fundamentals to Exploataition, 4-7 June 2000, Brighton, United Kingdom.
14. B. A-L. Östman, "Surface roughness of wood-based panels after aging", *Forest Products Journal* **33** (1983) pp 35-42.
15. F. F. P. Kollmann and W. A. Côté, "Principles of Wood Science and Technology, Volume I: Solid Wood", Springer-Verlag, Berlin, 1984. ISBN ???
16. R. S. Williams and W. C. Feist, “Duration of wood pre-weathering: Effect of the service life of subsequently applied paint”, *JCT* **73** (2001) pp 65-72.
17. R. S. Williams and W. C. Feist, “Effect of preweathering, surface roughness, and wood species on the performance of paint and stains”, *JCT* **66** (1994) pp 109-121.
18. M. E. P. Wålinder, “Study of Lewis acid-base properties of wood by contact angle analysis”, *Holzforschung* **56** (2002) pp 363-371.
19. M. de Meijer, H. Militz, "Wet adhesion of low-VOC coatings on wood. A quantative analysis", *Prog. Org. Coat.* **38** (2000) pp 223-240.

20. M. Stehr, "Adhesion to machined and laser ablated wood surfaces", Ph.D. thesis, Royal Institute of Technology, Sweden, 1999, ISSN 1104-2117.
21. J. Belfas, K. W. Groves and P. E. Evans, Bonding surface-modified Karri and Jarrah with resorcinol formaldehyde, *Holz als Roh- und Werkstoff* **51** (1993) pp 253-259.
22. I. T. MacLeod et al., "Photodegradation at the wood-clearcoat interface*", Wood Science and Technology* **29** (1995) pp 183-189.
23. A. Pizzi and K. L. Mittal, "Handbook of Adhesive Technology, second edition", Marcel Dekker Inc, New York, 2003, Chapter 3-5, ISBN 0-8247-0986-1.
24. D. E. Packham (Ed.), "Handbook of Adhesion", Longman Scientific & Technical, Avon, Great Britain, 1992, ISBN 0-582-04423-5.
25. L-H. Lee, "Recent studies in polymer adhesion mechanisms" in Adhesive Bonding, L-H. Lee (Ed.), Plenum Press, New York, 1991, ISBN 0-306-43471-7.
26. C. J. van Oss, R. J. Good and M. K. Chaudhury, "Additive and nonadditive surface tension components and the interpretation of contact angles" *Langmuir* **4** (1988) pp 884-891.
27. M. Gindl, S. Tschegg, "Significance of the acidity of wood to the surface free energy components of different wood species", *Langmuir* **18** (2002) pp 3209-3212.
28. M. Stehr, I. Johansson, "Weak boundary layers on wood surfaces*", J. Adhesion Sci. Technol.* **14** (2000) pp 1211-1224.
29. M. L. Ericson and H. Lindberg, "A method of measuring energy dissipation during crack propagation in polymers with an instrumented ultramicrotome", *J. Materials Sci.* **31** (1996) pp 655-662.
30. H. Hart, L. E. Craine and D. J. Hart, "Organic Chemistry, Tenth Edition", Houghton Miffin Company, Boston, 1999, ISBN 0-395-90225-8.
31. W. D. Callister, Jr., "Materials Science and engineering, an introduction, Third edition, John Wiley & Sons, New York, 1994, Chapter 2, ISBN 0-471-30568-5.
32. T. W. G. Solomons, "Fundamentals of organic chemistry", John Wiley & Sons, Inc., New York, 1994, Chapter 2, ISBN 0-471-30562-6.
33. M. Ilvessalo-Pfäffli, "Fiber Atlas", Springer Verlag, Berlin, 1995, ISBN 3-540-55392-4.
34. N. G. McCrum, C. P. Buckley and C. B. Bucknall, "Principles of polymer engineering", Oxford University Press, Oxford, 1992, Chapter 4, ISBN 0-19-856152-0.
35. R. E. Wetton, et. al., "Third generation DMTA instrumentation", *American Laboratory* (Fairfield, Conn.) **25** (1993) pp 15-20, ISSN 0044-7749.
36. R. O. Ebwele, "Polymer Science and Technology", CRC Press, London, 2000, ISBN 0-8493-8939-9.
37. N.G. McCrum, B.E. Read and G. Williams, "Anelastic and dielectric effects in polymeric solids", Dover Publications Inc, New York, 1991, Chapter 9, ISBN 0-486-66752-9.
38. E. A. Turi (Ed.), Thermal Characterization of polymeric materials, Second edition, Volume 1&2, Academic Press, London, 1997. ISBN 0-12-703783-7.
39. J. A. Manson and L. H. Sperling, "Polymer Blends and Composites", Plenum Press, New York, 1976, pp 90-93. ISBN 0-306-30831-2.
40. R. Hagen, "Influence of crosslinks and molecular mobility restraints on viscoelastic properties of polymers as studied by mechanical spectroscopy", Ph.D. thesis, Royal Institute of Technology, Sweden, 1995, ISBN 917170723-9.
41. L. E. Nielsen and R. F. Landel, "Mechanical properties of polymers and composites, second edition", Marcel Dekker Inc., New York, 1984, Chapter 1&4, ISBN 082478964-4.
42. I. M. Ward and D. W. Hadley, "An Introduction to the mechanical properties of solid polymers", Chapters 6 & 9, John Wiley & Sons, New York, 1993, ISBN 0471938874.

43. R. P. Chartoff, "Thermoplastic polymers" in Thermal Characterization of polymeric materials, E. A. Turi (Ed.), Academic Press, London, 1997, ISBN 0-12-703781-0.
44. C. Birkinshaw, M. Buggy, G. G. Henn, "Dynamic mechanical analysis of wood", *Journal of material science letters* **5** (1986) pp 898-900.
45. C. Birkinshaw, C.J. McCarthy, N. Reagan, M.D.C. Hale, D. Cahill, and M. McCourt, "The thermomechanical behaviour of wood subject to fungal decay", *Holzforschung* **53** (1999) pp 459-464.
46. E. Obataya and M. Norimoto, "Mechanical relaxation processes due to sugars in cane (*Arundo donax* L.)", *J Wood Sci* **45** (1999) pp 378-383.
47. E. L. Back and N. L. Salmén, "Glass transitions of wood components hold implications for molding and pulping processes", *Tappi* **65** (1982) pp 107-110.
48. L. Salmén, "Viscoelastic properties of in situ lignin under water-saturated conditions*", J. Mater. Sci* **19** (1984) pp 3090-3096.
49. S. S. Kelley, T. G. Rials and W. G. Glasser, "Relaxation behaviour of the amorphous components of wood", *Journal of Materials Science* **22** (1987) pp 617-624.
50. H. Maeda and E. Fukada, "Effect of Bound Water on Piezoelectric, Dielectric, and Elastic Properties of Wood", *Journal of Applied Polymer Science* **33** (1987), pp 1187-1198.
51. M. F. Kabir, W.M. Daud, K.B. Khalid and H.A.A. Sidek, "Dielectric and ultrasonic properties of rubber wood. Effect of moisture content, grain direction and frequency", *Holz als Roh- und Werkstoff* **56** (1998) pp 223-227.
52. J. E. McKinney and H. V. Belcher, "Dynamic compressibility of Poly(vinyl acetate) and its relation to free volume", *Journal of Research of the National Bureau of Standards-A. Physics and chemistry* **67A** (1963) pp 43-53.
53. P. Zoller et. al., "The Equation of State and Heat of Fusion of Poly(ether ether ketone)", *J. Polym. Sci. Part B: Polym. Phys*. **27** (1989) pp 993-1007.
54. R. P. Chartoff, "Using Amorphous Polymers Containing Platelet Graphite Fillers for Vibration Damping", Society of Plastic Engineers. In Proceedings of Technical Conference Atlanta: Antec 88, 1988, pp 1143-1145.
55. A. Pizzi, "Advanced Wood Adhesives Technology", Marcel Dekker Inc., New York, 1994, pp 78-87, ISBN 0-8247-9266-1.
56. L. J. Gibson and M. F. Ashby, "Cellular Solids, Structure & Properties", Pergamon Press, Oxford, 1988, ISBN 0-08-036607-4.
57. A. Bergander and L. Salmén, "Variations in transverse fibre wall properties: Relations between elastic properties and structure", *Holzforschung* **54** (2000) pp 654-660.
58. J. B. Boutelje, "The relationship of structure to transverse anisotropy in wood with reference to shrinkage and elasticity", *Holzforschung* **16** (1962) pp 33-46.
59. U. Watanabe, M. Fujita and M. Norimoto, "Transverse Young´s moduli and cell shapes in coniferous early wood", *Holzforschung* **56** (2002) pp 1-6.
60. Paper I. A. C. Backman and K. A. H. Lindberg, "Differences in wood material responses for radial and tangential direction as measured by dynamic mechanical thermal analysis", *J. Mater. Sci.* **36** (2001) pp 3777-3783.
61. L. Salmén, "Directional viscoelastic properties of wood*", Progress and Trends in Rheology II* (1988) pp 234-235.
62. G. Hoffmann, S. Poliszko, "Model Approach to Dielectric-Thermal Analysis of Wood Modified with Polymer", *Journal of Applied Polymer Science*, **39** (1990) pp 153-167.
63. P. S. Theocaris, G. Spathis, E. Sideridis, "Elastic and viscoelastic properties of fibre-reinforced composite materials", *Fibre Science and Technology* **17** (1982) pp 169-181.

64. C. Klason and J. Kubát, ”Thermal Transitions in Cellulose”, *Svensk Papperstidning* **15-1976** (1976) pp 494-500.
65. H. Kawakami, K. Taneda, S. Ishida, J. Ohtani, "Observation of the polymer in wood-polymer composute II. On the polymer location in WPC prepared with methacrylic esters and the relationship between the polymer location and the properties of the composite", *Mokuzai Gakkaishi* **27** (1981) pp 197-204. In Japanese.
66. C. Zollfrank and G. Wegener, “FTIR microscopy and ultrastructural investigation of silylated solid wood”, *Holzforschung* **56** (2002) pp 39-42.
67. C. Zollfrank, “Silylation of solid beech wood”, *Wood Science and Technology* **35** (2001) pp 183-189.
68. M. R. Groth, , Structural adhesive bonding of metals - surface and fracture mechanics aspects, Doctoral thesis, Luleå University of Technology (2001) ISSN 1402-1544.
69. R. W. Jokerst and H. A. Stewart, “Knife- versus abrasive-planed wood: quality of adhesive bonds”, *Wood and Fiber* **8** (1976) pp 107-113.
70. H. A. Stewart and J. B. Crist, “SEM examination of subsurface damage of wood after abrasive and knife planing”, *Wood Sci.* **14** (1982) pp 106-109.
71. L. Murmanis, B. H. River and H. A. Stewart, “Microscopy of abrasive-planed and knife-planed surfaces in wood-adhesive bonds”, *Wood and Fiber Sci.* **15** (1983) pp 102-115.
72. L. Murmanis, B. H. River and H. A. Stewart, “Surface and subsurface characteristics related to abrasive-planing conditions”, *Wood and Fiber Sci.* **18** (1986) pp 107-117.
73. J. Belfas, K. W. Groves and P. E. Evans, “Bonding surface-modified Karri and Jarrah with resorcinol formaldehyde”, *Holz als Roh- und Werkstoff* **51** (1993) pp 253-259.
74. R. O. Ebwele, B. H. River and J. A. Koutsky, “Tapered double cantilever beam fracture tests of phenolic-wood adhesive joints”, *Wood and Fiber* **12** (1980) pp 40-65.
75. R. E. Hernandez, “Effect of two wood surfacing methods on the gluing properties of sugar maple and white spruce”, *Forest Prod. J.* **44** (1994) pp 63-66.

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Errata: The densities of wood on page 3782 is in g/cm^3, not in kg/m^3.

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Differences in wood material responses for radial and tangential direction as measured by dynamic mechanical thermal analysis

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Wood is a complex cellular structure with different properties in the radial and tangential direction. Many researchers have measured dynamic properties in the longitudinal direction and a few in the radial direction but very little data can be found in the literature on dynamic mechanical properties in the tangential direction. The purpose of the work presented in this paper was to investigate the dynamic mechanical behaviour in the radial and tangential directions of wood (Pinus sylvestris). Testing was done in tension at 1 Hz with a Dynamic Mechanical Thermal Analyser. Properties in radial and tangential direction were different. The radial direction showed a higher elastic modulus and lower loss factor levels at temperatures between −120°C and 80°C. The tangential direction had on average a higher peak temperature than the radial direction for a loss factor peak around −80°C. It is the opposite of synthetic composites where the stiffer direction has a higher peak temperature. A loss factor peak at around 0°C was seen, most significantly in the tangential direction. This peak has scarcely been reported in the literature before. The distance between annual rings did not significantly affect the dynamic behaviour in the tangential direction.

1. Introduction

The interactions between polymers in polymer blends and in copolymers have been widely investigated using various dynamic measurement techniques. However, wood, which consists of a natural polymer blend of the three principal polymers cellulose, hemicellulose and lignin, has not been investigated to the same degree.

Dynamic mechanical analysis can give important information about the compatibility of wood and other polymers, information needed when considering the application of glue and paint to wood. The dynamic mechanical and dielectric properties of wood and wood products have mainly been investigated using dielectric measurement and torsional pendulum.

Wood is an anisotropic material with three principal axes; longitudinal, radial and tangential, the latter two sometimes being called transverse directions. Only a few references to the difference between the radial and tangential direction measured with dielectric methods have been found [1–5]. The longitudinal direction was found to exhibit higher dielectric constant (ε') and dielectric loss factor (ε'') than the radial and tangential directions for oven-dried wood. The radial direction often has slightly higher ε' than the tangential direction. The anisotropy of the dielectric constant in the transverse directions is mostly influenced by latewood fraction and cell arrangement [5].

Only one reference was found for differences in radial and tangential direction measured with dynamic mechanical measurements [6]. It was on water-swollen softwood (Japanese cypress) with temperature varied between 10°C and 95°C. A loss factor ($\tan\partial$) peak in transverse direction at 80°C was attributed to micro-Brownian motions of matrix substances. The peak was above 95°C for the longitudinal direction.

Handa [7] measured the dielectric properties of beech in the longitudinal direction and the dynamic mechanical properties in tangential direction at different moisture contents (m.c.) below 0°C. Dry wood was shown to have a dielectric loss peak at about −105°C (30 Hz). This peak decreases in height but does not move when the m.c. is increased, and is not visible above 1.7% m.c. At low m.c. a new peak appears at −40°C (0.7%) and then moves to lower temperatures with increasing m.c. At 5.6% the peak is at −92°C and at 8.7% at −108°C. Peak height increases with increasing m.c. Maeda [8] measured the dynamic mechanical properties of bamboo at 10 Hz and obtained a loss modulus (E'') peak at −87°C for 3% m.c. and at −97°C for 6%. The same experiments with Japanese cedar gave a loss modulus peak at −93°C for 7% m.c. The loss modulus peak is normally a few degrees lower than the $\tan\partial$ peak. Kelley [9] measured the longitudinal properties of spruce in dual cantilever and at 1 Hz at different m.c. with a Dynamic Mechanical Thermal Analyser (DMTA). At a m.c. of 10% a tan ∂ peak at about -85°C with a tan∂ height of about 0.025 was observed. For the same m.c. a peak at about 20°C was also seen which was thought to be associated with the T_g of hemicellulose and at another peak at about 80°C, the T_g of lignin. At a m.c. of 5% these peaks move to approximately -75°C, 70°C and 120°C. Salmén [10] measured dynamic mechanical properties of water-saturated Norway spruce and determined the T_g for lignin to be about 100°C, measured both longitudinally and transversely at 10 Hz.

When measuring dynamic mechanical properties in tension the results are presented as elastic modulus (E'), loss modulus (E'') and loss factor (tan $\partial = E''/E'$). A sinusoidally varying strain is applied to the specimen with the measurement being made at constant frequency with varying temperature, or the opposite. In a temperature scan, a peak of tan ∂ or E'' in the graph indicates a certain molecular movement having the same relaxation time as the applied frequency. In this paper a frequency of 1 Hz was used and the temperature was increased from -120°C to 80°C by 2°C/min. The tan ∂ peak measured in a DMTA at 1 Hz can be 15–20°C higher than the true glass transition temperature [11], but for simplicity tan ∂ peaks are often taken as being representative of T_g peaks. Other transition peaks than T_g are also dependent on the frequency. When analysing dynamic mechanical properties, it is the changes in peaks observed in one analyser that should be studied. Comparison with absolute values of peak temperatures obtained with other machines should be treated with caution since the same material measured in several different machines, even those from the same manufacturer, will give different responses [12]. This is due to temperature measurement errors from the thermocouples, differences in heat transfer to the specimen and the way the machines carry out measurements. Variation due to the way in which the operator handles the specimens and equipment also has a contributory effect on the results.

Wood is also a highly complex cellular composite. Softwood (earlywood) consists mainly of tracheids, which are closed tubes with tapered ends with approximately $40 \times 40\,\mu$m cross section and 2–4 mm length. The tracheids are oriented in the direction of the stem, the longitudinal direction, Fig. 1. Latewood tracheids have thicker cell walls than earlywood tracheids. Radially oriented cells are known as ray cells, and are much shorter than tracheids and have thin cell walls. In the wood cell walls, cellulose molecules are arranged in the form of microfibrils with the polymers hemicellulose and lignin which act as matrix material. Dry hemicellulose and dry lignin have glass transition temperatures (T_g) of 150–220°C and 130–205°C respectively, while cellulose glass transition varies between 200°C and 250°C [13].

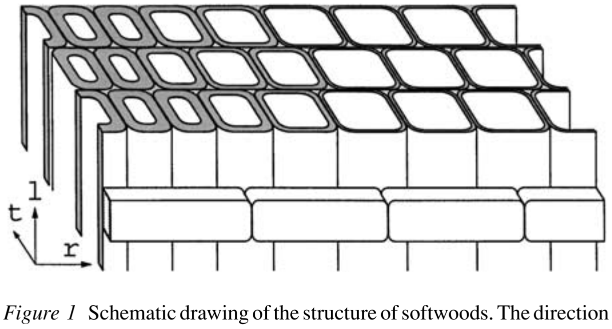

Figure 1 Schematic drawing of the structure of softwoods. The direction of growth is to the left. On the right can cross-sections of earlywood tracheids be seen, and to the left latewood tracheids. On the side of the tracheids a single row of ray cells has been drawn.

Many researchers have measured dynamic properties in the longitudinal direction or in the longitudinal and one of the transverse directions. Very little data can be found in the literature on dynamic mechanical properties in the tangential direction. Unfortunately, the directions in which measurements were made are poorly defined in some papers on dynamic mechanical measurements [10, 14–17]. This indicates a lack of understanding in regard to the important differences in wood anisotropic behaviour due to its complex cellular structure. The purpose of the work presented in this paper was to investigate the dynamic mechanical behaviour in the radial and tangential directions of wood. The effect of different levels of moisture content was also considered. The reason for this work was the need for understanding of the properties of wood for future studies of interaction with synthetic polymers such as glue and lacquer. The dynamic mechanical properties of wood were tested in tension using a DMTA.

2. Method and material

The wood used was clear sapwood from Scots pine (Pinus sylvestris). Slices 1.5 mm thick were sawn perpendicular to the longitudinal direction. From these slices, smaller specimens ($3 \times 1.3 \times$ length (mm)) were cut using a razor blade and finally smoothed using 80-grade sandpaper. The wood had been dried without external heating and was stored in a laboratory climate. Only one radial specimen (R1) had been exposed to temperatures exceeding 80°C. Tangential (T) and radial (R) specimens were paired from two adjacent slices. Before testing the specimens they were conditioned at room temperature in a sealed container over a saturated solution of Magnesium Chloride ($MgCl_2$) or Lithium Chloride (LiCl) which gave 33% or 11% relative humidity (RH) respectively at 20–30°C [18]. This corresponds to a moisture content of 6–7% for 33% RH and 3–3.5% for 11% RH [19].

After removing a specimen from the conditioning container, each specimen was then mounted in a Dynamic Mechanical Thermal Analyser MkIII (DMTA) from Rheometric Scientific at room temperature. Clamps were attached at both ends at room temperature with a torque force of 0.1 Nm. The DMTA chamber closed two minutes after the specimen was removed from the conditioning container. Cooling down to the starting temperature of -120°C took 20 minutes. Two types of specimen were used, radial and tangential, Fig. 2. In both cases the clamps were applied against the transverse plane (RT-plane). A Sartorius scale with an accuracy of 0.1 mg was used to check the weight of the specimens, which were in the range 40–60 mg. The

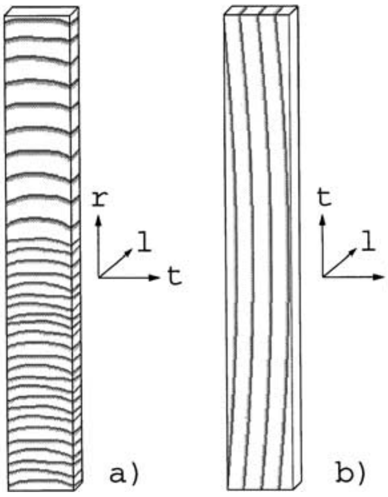

Figure 2 DMTA samples for tensile testing: (a) for the radial and (b) for the tangential direction.

DMTA chamber had no climate control, but the weight loss during measurement up to 0°C was deemed negligible. It was measured by weighing specimens before measurement and after measurement to 0°C.

The DMTA was used in tension mode at a frequency of 1 Hz. Runs were made from −120°C to 80°C at 2°C/min and data was collected at intervals of about 1°C. The length and dynamic strain varied between different specimens; however, all strains were considered to be within the linear viscoelastic range. Specimens varied in length between 12 mm and 24 mm, and the dynamic average strain varied between 0.02% and 0.05%. When measuring in tension, a static force equivalent to about twice the force necessary for the dynamic amplitude was applied to prevent buckling.

The $\tan \partial$ values obtained during measurements were low and only slightly above background noise. The data was smoothed using an average of seven consecutive values of $\tan \partial$. To further reduce the effects of noise, the curves were an average of two or more DMTA measurements on the same specimen. The temperature of the $\tan \partial$ peak was taken as the location of the maximum value.

Specimen density was measured at RT by immersion in mercury. The specimens had been conditioned in 33% RH. Specimen weight was between 40 and 60 mg and was measured on a scale with 0.1-mg resolution. The specimen was then pushed down by the use of two needles into a tared jar filled with mercury placed on a scale with 1-mg resolution. The measured mass is the volume of the mercury and the mass of the specimen. Specimen volume was then calculated as the mercury mass subtracted by specimen mass and then divided by the density of mercury (13.55 kg/dm^3).

3. Results and discussion

There was a clear difference in the elastic modulus (E') in the radial and tangential directions, the elastic modulus being much lower in the tangential than in the radial direction, Fig. 3. At 25°C the radial value averaged 1.26 GPa and the tangential value 0.66 GPa, the radial being some 90% higher. This is consistent with the difference in static Young's modulus for Pinus sylvestris [20], which at room temperature is 93% higher in the radial direction (1.14 GPa) than in the tangential direction (0.59 GPa). The elastic modulus was only a few percent higher than the static Young's modulus. The measurement of elastic modulus with DMTA was very reproducible. No significant difference in E' between 3% and 6% moisture content was observed.

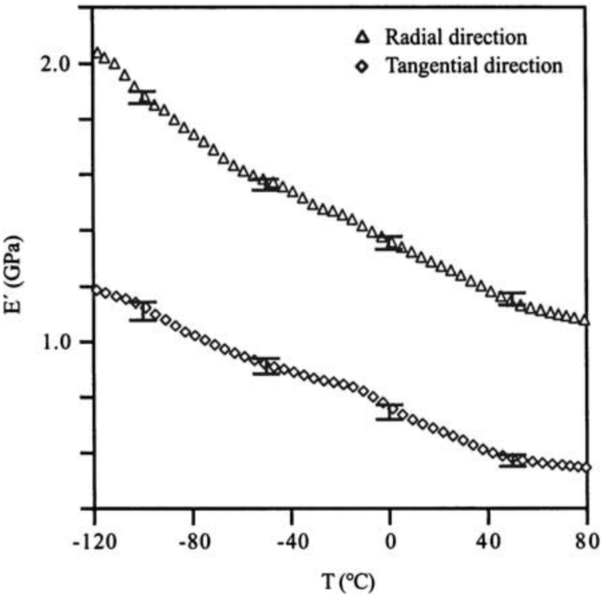

Figure 3 Elastic modulus (E') for radial and tangential directions. Error bars indicate 95% significance in a one-sample t-test.

The reason for the large difference in modulus in the radial and tangential directions remains unclear. Since latewood has much higher density and therefore a higher modulus than earlywood, it was surprising to find that the radial direction, with its serial early- and latewood cells, had a higher modulus. Several explanations for this behaviour have been proposed. One theory is that ray cells oriented in the radial direction act as stiffening ribs. However, the ray cells in Scots pine have thin cell walls so their stiffening effect cannot be significant [21].

The radial cell walls have pits, and therefore the cellulose microfibrils are distorted from the longitudinal direction, giving the radial cell wall higher transverse stiffness, although this is not sufficient to cause the large differences observed.

The irregular hexagonal cell structure in Scots pine and many other softwoods gives a higher stiffness in the radial direction. According to [22] the stiffness for wood is about 50% higher in the radial than in the tangential direction. The Young's modulus for regular hexagonal cellular structures in the transverse direction is proportional to the square root of the density [22].

If the latewood is assumed to have a density of 1.2 g/cm^3 and the earlywood 0.25 g/cm^3, the Young's modulus would be 23 times higher for the latewood. Compression experiments have shown that earlywood has a much lower stiffness in the tangential than the radial direction whilst latewood was observed to have comparable stiffness in the two directions [21].

When using the rule of mixtures and the inverse rule of mixtures, reasonable data of the modulus in radial

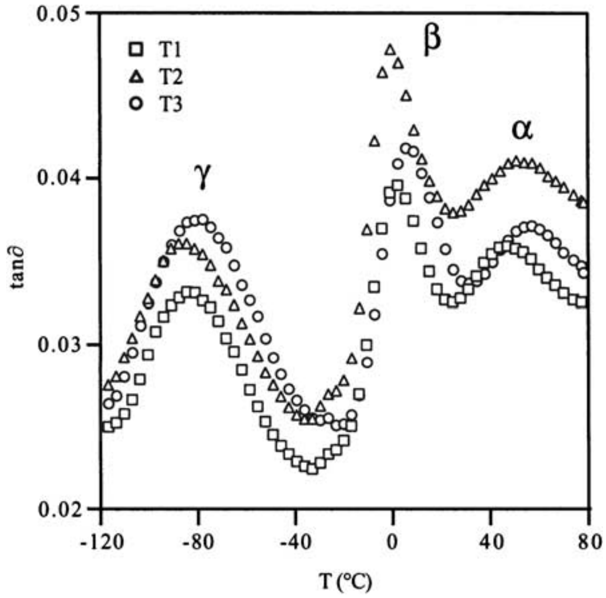

Figure 4 Three different tangential specimens (T1, T2, T3) conditioned in 33% RH prior to testing. Specimens T1 and T3 had narrower annual rings than specimen T2.

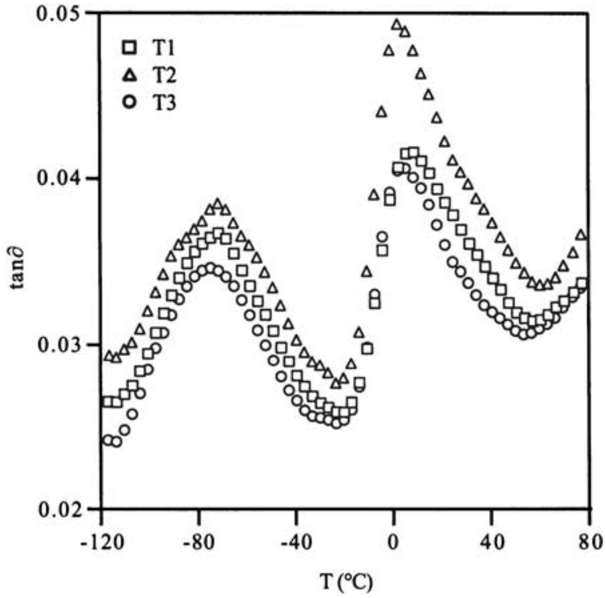

Figure 5 Three different tangential specimens (T1, T2, T3) conditioned in 11% RH prior to testing. Specimens T1 and T3 had narrower annual rings than specimen T2.

and tangential directions can be obtained from measurements on separate early- and latewood specimens [23].

This low tangential modulus in the earlywood is one plausible explanation for the difference in modulus between the two directions, though probably not the last explanation to be presented. A tentative theory proposed by the authors of the present paper is that the latewood could be considered as this stiff ribs which are already buckled at a small angle, with very soft earlywood lying between the ribs, thus resulting in the low tangential modulus that is observed.

TABLE I Loss factor peak temperatures for tangential (T) and radial (R) specimens conditioned in 11 and 33% RH

11% RH	R1*	R2	R3	R4	T1	T2	T3
α	—	—	—	—	—	—	—
β	16	9	—	34	8	3	4
γ	−82	−80	−82	−88	−72	−71	−75
33% RH	**R1***	**R2**	**R3**	**R4**	**T1**	**T2**	**T3**
α	40	42	—	57	46	50	56
β	2	−7	—	−7	2	−1	7
γ	−76	−84	−95	−89	−83	−87	−79

*Thermally treated above 80°C.

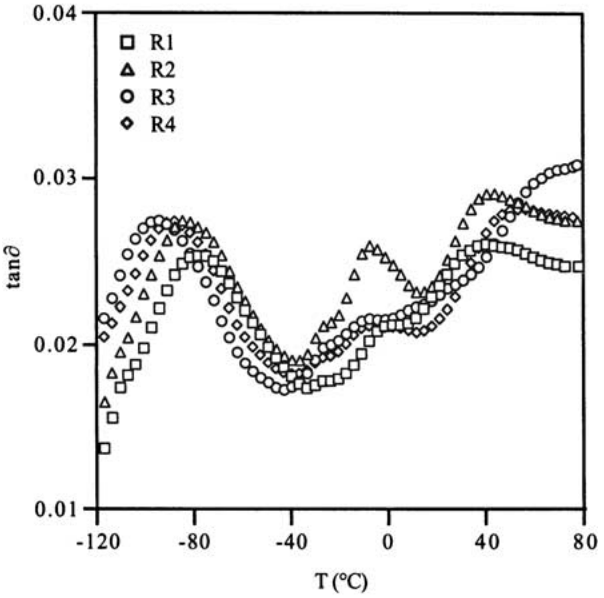

Figure 6 Four different radial specimens (R1, R2, R3, R4) conditioned in 33% RH prior to testing. All specimens were paired, and specimen R1 had been subjected to thermal treatment.

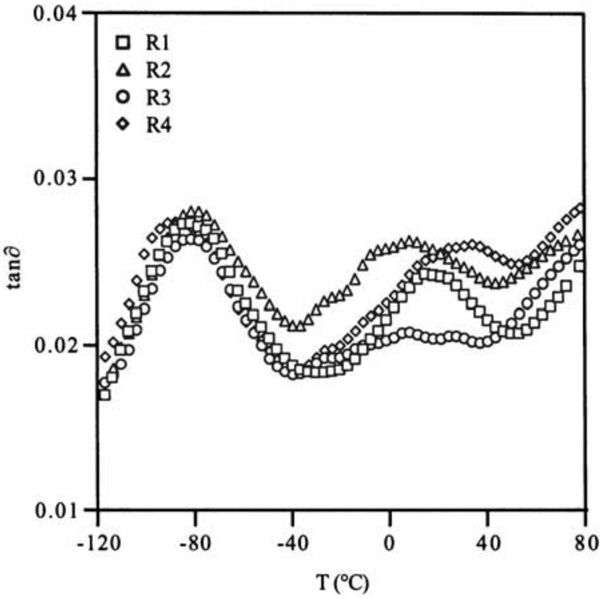

Figure 7 Four different radial specimens (R1, R2, R3, R4) conditioned in 11% RH prior to testing. All specimens were paired, and specimen R1 had been subjected to thermal treatment.

The radial and tangential directions also differed in their response as far as loss factor levels and peak temperatures are concerned, Figs 4–7. The peak temperatures are listed in Table I, peaks being labelled α, β and γ in order of decreasing temperature, Fig. 4. Several consecutive measurements on the same specimen were made, as mentioned earlier. Repetitive measurements on specimens initially conditioned in 33% RH were almost identical over many measurements, but the reproducibility was lower for specimens conditioned at 11% RH. The differences in γ-peak temperature between paired specimens were also reproducible. Since the specimens were conditioned in the same way and the measurements carried out using identical methods, the only possible reason for the differences are differences in initial moisture content.

Our results show that the specimens cut in the tangential direction had higher γ-peak temperature when conditioned in 11% RH than in 33% RH. The γ-peak temperatures found in the radial direction did not show any difference between 11% and 33% RH. The scatter in measurements was too large.

For absolutely dry wood a peak is situated at about −105°C, and with the slightest moisture contents (0.7%) another peak appears at about −40°C (30 Hz, dielectric) [7]. With increasing moisture content the −40°C peak moves towards lower temperatures whilst the peak at −105°C decreases in height and eventually disappears at about 2% m.c. The peak at about −105°C for dry wood is due to the movement of methylol side groups [7, 8]. The peak dependent on moisture content is assumed by many to be associated with movement of a methylol side group bonded to water molecules [7, 8]. The methylol group is present in all the three main polymers found in wood, although hemicellulose is assumed to adsorb most of the moisture.

The γ-peak which initially appears at −40°C could be due to adsorption of water on the methylol groups [7, 8]. However, if water molecules are adsorbed onto the methylol groups, the complex should become larger and stiffer with increasing moisture content and the peak shift towards increasing temperatures, not decreasing, which is the case. It is possible that water molecules are only adsorbed as a monolayer on the methylol groups, thus shifting the peak from −105°C to −40°C due to increase of the complex size. Further adsorption of water acts as a plasticizer making movement of the complex easier and lowering the peak temperature, which would better explain the movement of the γ-peak.

The γ-peak could also be due to site to site exchange of water [9], since one of the reasons proposed against a side-group movement was the absence of a drop in elastic modulus. In the present work a tendency for the modulus to fall was noted, Fig. 3. In Polyamide 6 several secondary relaxations are present, which all move with changes in moisture content. One of these, a peak which moves from about −40 to −80°C increasing from zero to 8% m.c., is argued to be due to the motion of chain segments and polymer-water complex [24].

Specimen R1 was the only specimen thermally treated above 80°C, being dried at 103°C for 48 hours and then used in two runs in the DMTA up to 150°C. The thermal history of specimen R1 was clearly visible as a change in the position of the γ-peak for 33% RH. The increase in temperature by at least 10°C for R1 compared to the untreated radial specimens indicates lower moisture content in the specimen. In [25] wood dried at 115°C for 120 hours showed a two percent points lower moisture content than wood dried at 82°C for 120 hours. Why the R1 specimen in the present work seems to have a higher moisture content following conditioning in 11% than in 33% RH is not clear.

The loss factor β-peak is seldom referred to in the literature. The tangential specimens showed this peak at 3°C to 8°C for 11% RH and −1°C to 7°C for 33% RH. The radial specimens had a much lower tan ∂ level for this peak. For one of the specimens the peak was missing entirely, Fig. 7. The peak temperatures for the radial specimens varied between −7°C and 34°C. The scatter was very large. No correlation between the peak temperatures and the moisture content or between peak temperatures and direction was apparent, Table I.

Only a few references to a peak similar to the β-peak were found. In [26] measurement in radial direction on hardwood with a torsion pendulum with damped oscillation revealed a small peak at 10°C. This was attributed to the local mode of wood components related to water. Also in [27] a peak at 10°C was seen in low-frequency torsional pendulum measurements on beech in the longitudinal direction with approximately 10% moisture content. In [8] a peak at 15°C was seen for longitudinal direction of Japan cedar with 7% moisture content. The peak was not discussed in the reference. It is possible that these references show the same peak as the β-peak in the present work.

In the tangential samples, Fig. 3, a clear drop in the modulus was seen at the transition temperature. This means that the peak was a true relaxation process and not merely related to movement of water molecules. The β-peak could therefore be a hemicellulose glass transition peak. The hemicellulose molecules consist of 150–200 sugar monomers in a heavily branched structure. Different compositions of hemicellulose have been found, and more than one type of hemicellulose is present in Scots pine. In low-molecular-weight amorphous polymers T_g is dependent on the molecular weight, a lower molecular weight giving a lower T_g [28]. If different types of hemicellulose with different molecular weights were phase separated this could lead to regions where the hemicellulose glass transition was lower, and thus produce the β-peak which was observed. Low-molecular-weight regions might also adsorb more water and are one possible explanation for the differences in the observed specimen moisture content.

The inconsistent appearance of the β-peak in the radial samples is not related to the presence, or otherwise, of certain molecules when testing. Radial specimens tested in the present work could sometimes show this peak in one measurement and not the following one. The peak at about −90°C is consistent, and the behaviour of the peaks is probably related to the measurement method used. It would seem that the method used to make the measurements on the radial samples does not produce consistent results. At low temperatures the modulus was high and the material apparently stable. However, at around 0°C the modulus of the material dropped and the DMTA tests ceased to give consistent results.

The specimens conditioned in 33% RH show an α-peak at 40°C to 60°C. According to Kelley [9] this is the glass transition peak of the hemicellulose. The specimens conditioned in 11% RH do not show the α-peak since they are drier and the α-peak therefore moved to temperatures above 80°C. Since the experiments were performed in a non climate-controlled chamber, the specimens could only be expected to maintain a relatively constant m.c. up to about 0°C. The scattering seen in the α-peak temperatures was therefore not surprising.

The radial specimens had lower tan ∂ values than the tangential specimens, Figs 4–7. A lower tan ∂ value indicates that less material is being moved. A tendency for the tangential direction to have higher peak temperatures for the γ-peak was observed. The longitudinal direction in wood and polymeric composites has a higher tan ∂-peak temperature than the transverse directions [29–31]. The difference in T_g between different structural directions is influenced by the underlying structure [31]. For wood, the stiffer radial direction had lower peak temperature. One possible hypothesis for this discrepancy may be that latewood was strained more in the tangential direction than in the radial direction, whilst most of the strain occurred in the earlywood in the radial direction. Most of the signals for E', E'' and tan ∂ then came from latewood when measured in the tangential direction and from earlywood in the radial direction.

Tangential specimens are shown in Figs 4 and 5. T2 is a specimen with wide annual rings whilst specimens T1 and T3 have narrower annual rings. The density of specimen T2 was higher than T1 and T3. T2 was between 0.53 and 0.54 kg/m^3 and T1 and T3 were between 0.48 and 0.49 kg/m^3. The radial samples had a density between 0.46 and 0.49 kg/m^3. The elastic modulus did not differ significantly, but the tan ∂ values at the α- and β-peaks are higher for the specimen with wide annual rings. The higher values were probably related to the higher density. The experiments were reproducible for the two similar tangential specimens, and the distance between annual rings did not have any marked effect on the dynamic behaviour.

4. Conclusions

The dynamical mechanical properties in radial and tangential directions of wood were different.

It is possible to measure the stiffness of wood by using DMTA and get good reproducibility and a relevant level of stiffness for radial and tangential directions.

The stiffness could easily be measured as a function of temperature up to room temperature. The measured radial stiffness was about two times the tangential stiffness, as expected.

Secondary loss peaks had lower tan δ levels measured in the radial direction than in the tangential direction.

The secondary transition peaks found testing wood in the tangential direction had higher temperatures than those measured in the radial direction did. This is in conflict with synthetic composites where the higher peak temperatures are found in the stiffer direction.

A loss factor peak at around 0°C was seen in the tangential direction. This peak has scarcely been reported in the literature before.

Measurements in the tangential direction gave reproducible values of loss factor, whilst measurements in the radial direction did not give enough signals to allow evaluation of the peaks from 0°C and above. All measurements were reproducible on the same specimen if temperatures did not exceed 80°C.

Acknowledgements

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References

1. M. F. KABIR, W. M. DAUD, K. KHALID and H. A. A. SIDEK, *Holzforschung* **52** (1998) 546.
2. K. B. KHALID, M. F. KABIR, W. M. DAUD and H. A. A. SIDEK, *ibid.* **53** (1999) 662.
3. M. F. KABIR, K. B. KHALID, W. M. DAUD and H. A. A. SIDEK, *Wood and Fiber Science* **29** (1997) 319.
4. M. NORIMOTO and T. YAMADA, "Wood Research" Vol. 52 (Kyoto University, Wood Research Institute, 1972) ISSN 0049-7916, p. 31.
5. M. NORIMOTO, "Wood Research" Vol. 59/60 (Kyoto University, Wood Research Institute, 1976) ISSN 0049-7916, p. 106.
6. Y. FURUTA, M. MAKINAGA, H. YANO and H. KAJITA, *Mokuzai Gakkaishi* **43** (1997) 16.
7. T. HANDA, M. FUKUOKA, S. YOSHIZAWA, Y. HASHIZUME and M. SUZUKI, in Proceedings of the 23rd Japan Congress on Materials Research-Non-Metallic Materials, March 1980, p. 338.
8. H. MAEDA and E. FUKADA, *J. Appl. Pol. Sci.* **33** (1987) 1187.
9. S. S. KELLEY, T. G. RIALS and W. G. GLASSER, *J. Mater. Sci.* **22** (1987) 617.
10. L. SALMÉN, *ibid.* **19** (1984) 3090.
11. L. E. NIELSEN and R. F. LANDEL, "Mechanical Properties of Polymers and Composites" (Marcel Dekker, Inc., New York, 1994) p. 141.
12. R. HAGEN, L. SALMÉN, H. LAVEBRATT and B. STENBERG, *Polymer Testing* **13** (1994) 113.
13. E. L. BACK and N. L. SALMÉN, *Tappi Journal* **65** (1982) 107.
14. A-M. OLSSON and L. SALMÉN, in Proceedings of the International Conference of COST Action E8, Copenhagen, June 16-17, 1997.
15. *Idem.*, in "Viscoelasticity of Biomaterials" (ACS Symposium Series, Washington, 1992) p. 133.
16. M. G. S. YAP, Y. T. QUE and L. H. L. CHIA, *J. Appl. Polym. Sci.* **43** (1991) 1991.
17. C. BIRKINSHAW, M. BUGGY and G. G. HENN, *J. Mater. Sci. Lett.* **5** (1986) 898.
18. D. R. LIDE, "CRC Handbook of Chemistry and Physics, 80th ed." (CRC Press, London, 1999).
19. I. ABSETZ and S. KOPONEN, in Proceedings of the International Conference of COST Action E8: Mechanical Performance of Wood and Wood Products, Copenhagen, June 1997, p. 89.
20. F. KOLLMAN and W. A. COTÉ, "Principles of Wood Science and Technology" (Springer-Verlag, Berlin, 1984) p. 294.
21. J. B. BOUTELJE, *Holzforschung* **16** (1962) 33.
22. L. J. GIBSON and M. F. ASHBY, "Cellular Solids, Structure & Properties" (Pergamon Press, Oxford, 1988) p. 304.
23. M. WÅLINDER, "Transverse Anisotropic Behaviour in Pine (Pinus Silvestris L.)," TRITA-TRÄ R-97-29 (1997), ISSN 1104-2117.
24. Y. S. PAPIR, S. KAPUR and C. E. ROGERS, *J. Pol. Sci.* **10** (1972) 1305.
25. E. W. PRICE and P. KOCH, *Forest Products J.* **30** (1980) 41.

26. T. NAKANO, S. HONMA and A. MATSUMOTO, *Mokuzai Gakkaishi* **36** (1990) 1063.
27. C. A. WERT, M. WELLER and D. CAULFIELD, *J. Appl. Physics* **56** (1984) 2453.
28. N. G. McCRUM, B. E. READ and G. WILLIAMS, "Anelastic and Dielectric Effects in Polymeric Solids" (Dover Publications Inc., New York, 1991) p. 37.
29. G. HOFFMANN and S. POLISZKO, *J. Appl. Pol. Sci.* **39** (1990) 153.
30. L. SALMÉN, in Proceedings of the Second Conference of European Rheologists, Prague, June 1986, edited by H. Giesekus, (Springer-Verlag, New York, 1988) p. 234.
31. P. S. THEOCARIS, G. SPATHIS and E. SIDERIDIS, *Fibre Science and Technology* **17** (1982) 169.

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Interaction between wood and polyurethane-alkyd
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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 *Tg* 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. Östman[4] 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 wood[7] 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 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]

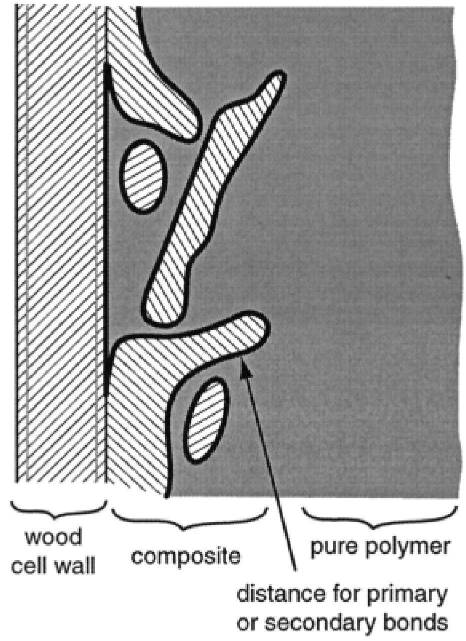

Figure 1 Model of interaction volumes.

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°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 $MgCl_2$,[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/m^2. 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/m^2.

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 δ) 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 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°C[18] has not clearly been assigned to any molecular movement.[15,19,20] This peak also decreases in height with increasing moisture content.

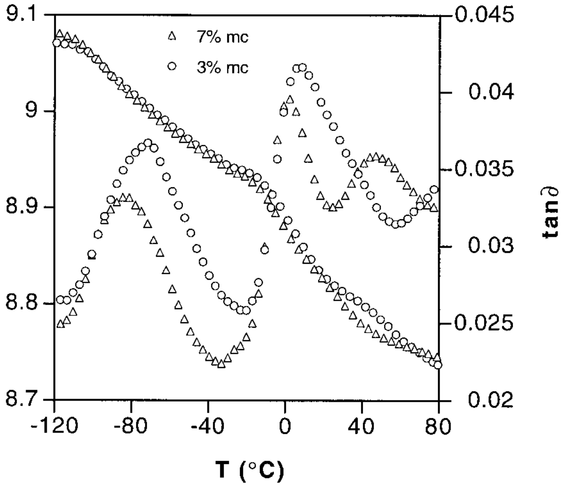

Figure 2 DMTA measurements in the tangential direction of wood with different moisture contents.

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

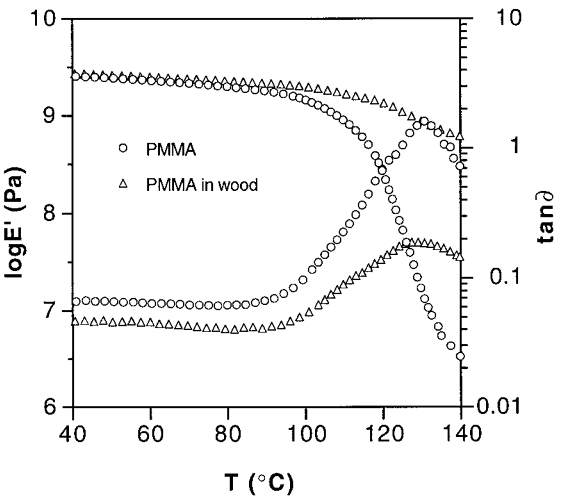

Figure 3 DMTA measurements of pure polymerized methyl methacrylate (PMMA) and PMMA impregnated in wood.

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 δ 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

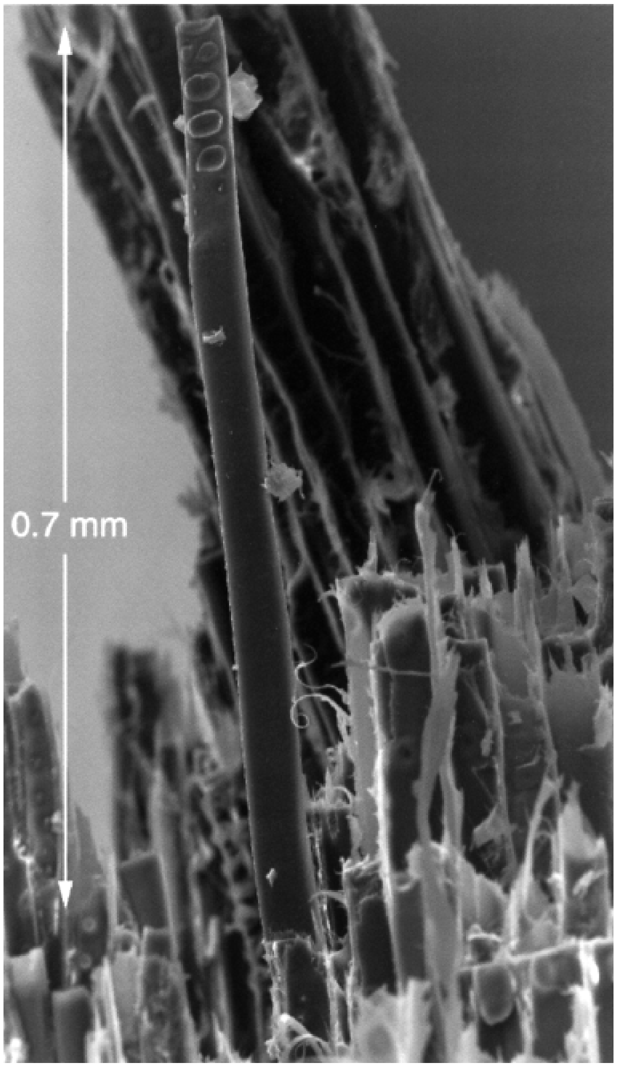

Figure 4 SEM micrograph of longitudinal fracture of composite showing a rod of PMMA.

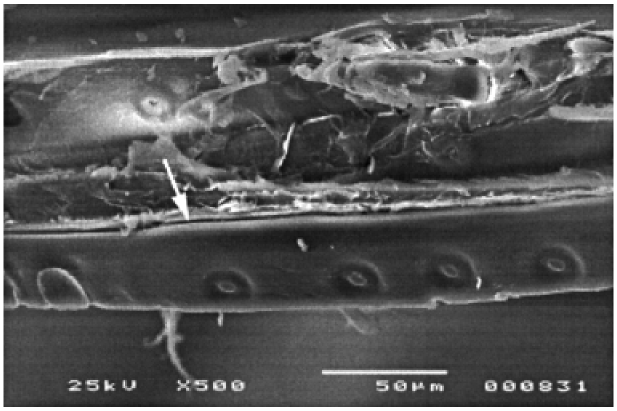

Figure 5 SEM micrograph of longitudinal fracture of composite showing poor adhesion between wood and PMMA. The arrow indicates a clear gap between wood and PMMA.

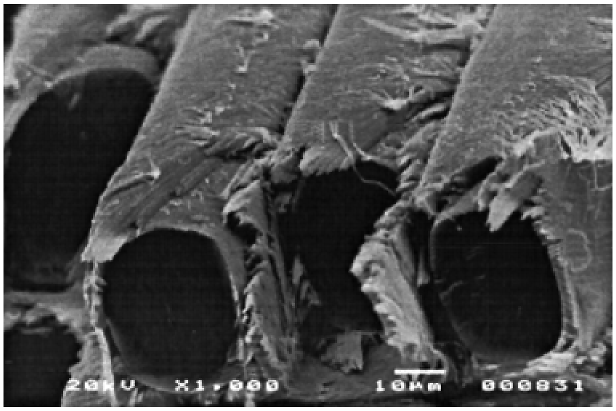

Figure 7 SEM micrograph of longitudinal fracture of composite showing good adhesion between wood and hydrophilic acrylate; the lumens are filled.

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 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-

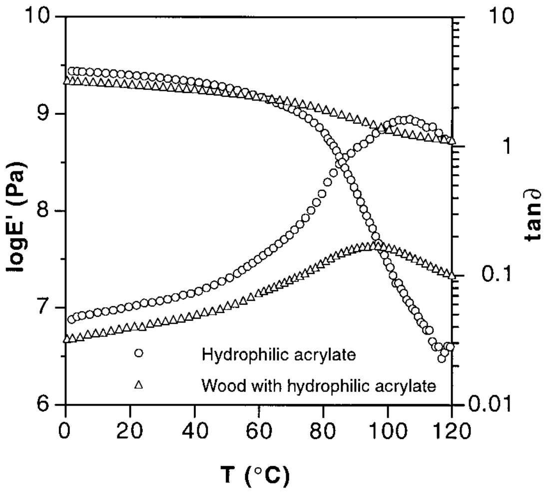

Figure 6 DMTA measurement of hydrophilic acrylate, pure and impregnated in wood.

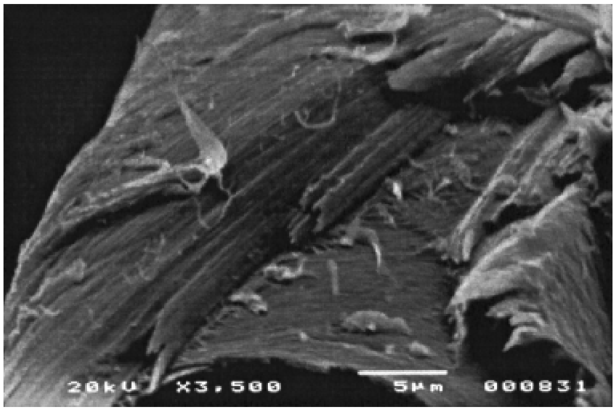

Figure 8 SEM micrograph, showing magnification of Figure 7.

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 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.

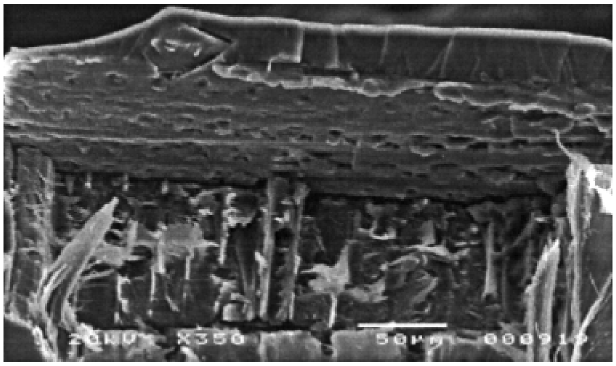

Figure 9 SEM micrograph of wood painted with polyurethane-alkyd (PUR1).

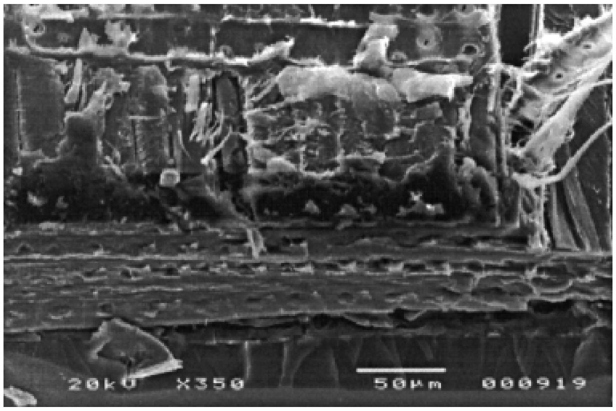

Figure 10 SEM micrograph of wood painted with polyurethane-alkyd (PUR1).

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-

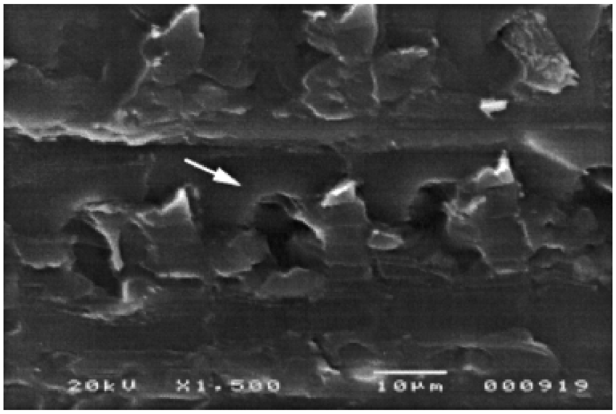

Figure 11 SEM micrograph of wood painted with polyurethane-alkyd (PU R1), a magnification of Figure 10.

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 ∂ 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 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.

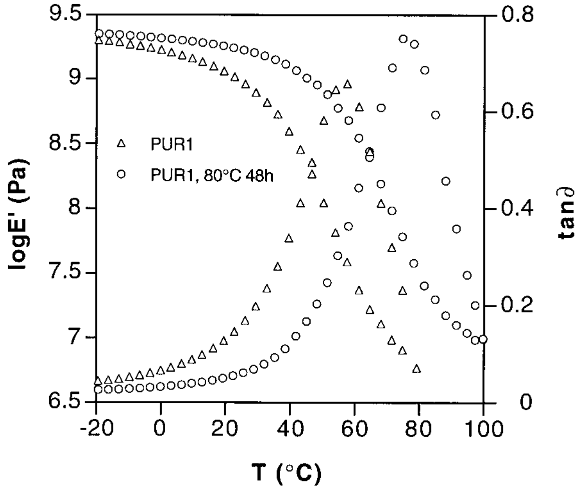

Figure 12 DMTA measurements of polyurethane-alkyd (PUR1) lacquer, with heat treatment at 80°C and without heat treatment (i.e., dried in 35°C for 1 week).

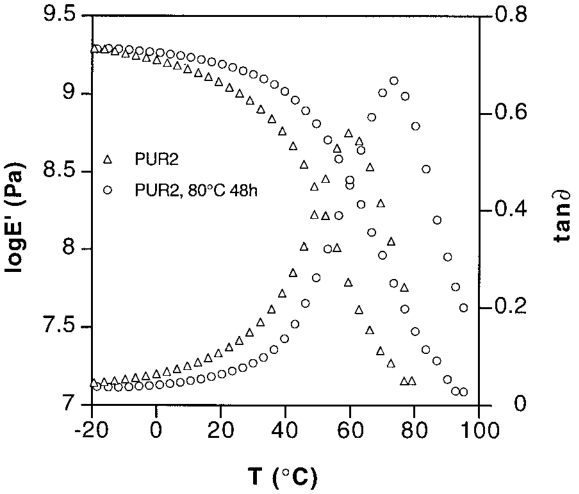

Figure 13 DMTA measurements of polyurethane-alkyd (PUR2) lacquer, with heat treatment at 80°C and without heat treatment (i.e., dried in 35°C for 1 week).

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-

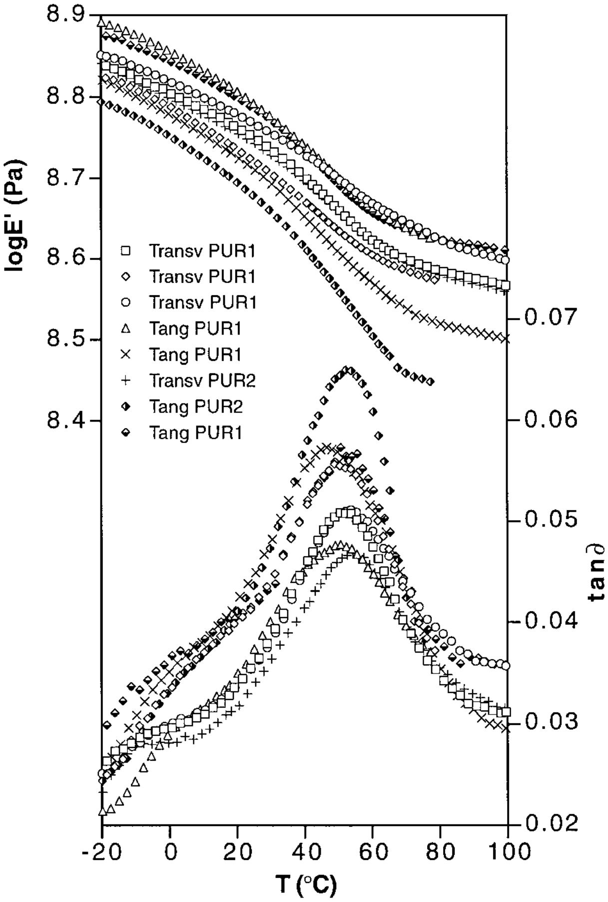

Figure 14 DMTA measurements of polyurethane-alkyd on transverse and tangential surfaces.

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 ∂ 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 ∂ 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 width[30]; 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 plasticizer[30]; at low levels of crosslinking, the tan ∂ 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∂ 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

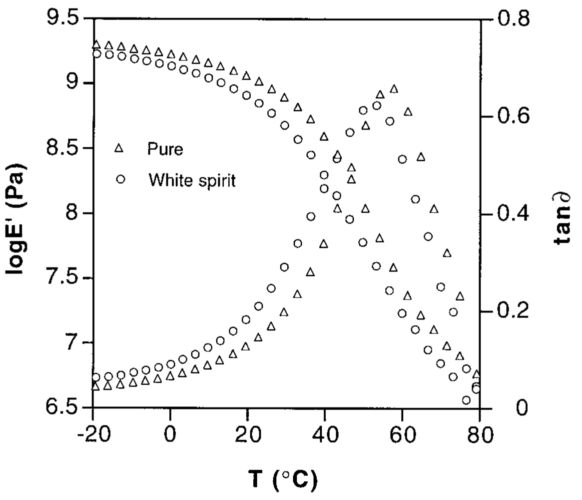

Figure 15 DMTA measurements of polyurethane-alkyd lacquer; white spirit content decreased from 4.4 to 3.2% during the experiment.

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.

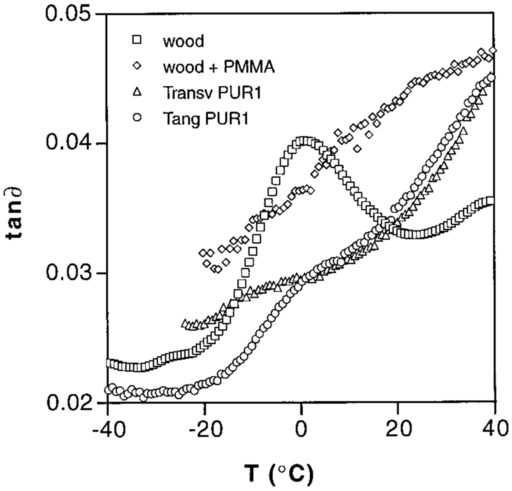

Figure 16 DMTA measurements in the tangential direction of wood, wood impregnated with PMMA, and wood painted transversely or tangentially with PUR1.

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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REFERENCES

1. Grundberg, S. A.; Hagman, P. O. G. Holz als Roh- und Werkstoff 1993, 51, 49–54.
2. Lindberg, K. A. H.; Ericson, M. L.; Backman, A. C. Measurement of polymer interfacial strength with an instrumented Ultramicrotome; in Proceedings of ECCM9: Composites from fundamentals to exploitation; 4–7 June 2000; Brighton, U.K.
3. Backman, A. C. SEM study of wood/paint interfaces; in Proceedings of Surface and Interfacial Phenomena in Macromolecular Systems; 21–24 July 1997; Prague.
4. Östman, B. A.-L. For Prod J 1983, 33, 35–42.
5. Backman, A. C.; Hiziroglu, S.; Lindberg, K. A. H., 1995, unpublished results.
6. Kollmann, F. F. P.; Côté, W. A. Principles of Wood Science and Technology, Vol. I: Solid Wood; Springer-Verlag: Berlin, 1984.
7. Thuvander, F.; Wallström, L.; Berglund, L.; Lindberg, H. Wood Sci Technol 2001, 34, 473–480.
8. Lewis, T. B.; Nielsen, L. E. J Appl Polym Sci 1970, 14, 1449–1471.
9. Oksman, K.; Lindberg, H. Holzforschung 1998, 52, 661–666.
10. Manson, J. A.; Sperling, L. H. Polymer Blends and Composites; Plenum Press: New York, 1976; Chapter 12, p 3.
11. Wirpsza, Z. Polyurethanes: Chemistry, Technology, and Applications; Ellis Horwood: New York, 1993; pp 114, 295–297.
12. Lide, D. R., Ed. Handbook of Chemistry and Physics, 80th ed.; CRC Press: London, 1999; pp 15–25.
13. Absetz, I.; Koponen, S. Mechanical Performance of Wood and Wood Products; in Proceedings of the International Conference of COST Action E8; Copenhagen, June 1997; p 89.
14. Handa, T.; Fukuoka, M.; Yoshizawa, S.; Hashizume, Y.; Suzuki, M. The dielectric properties of wood and wood-polymer composite (WPC) containing moisture at low temperature regions; in Proceedings of the 23rd Japan Congress on Materials Research—Non-Metallic Materials; March 1980; pp 338–342.
15. Maeda, H.; Fukada, E. J Appl Polym Sci. 1987, 33, 1187–1198.
16. Kelley, S. S.; Rials, T. G.; Glasser, W. G. J Mater Sci 1987, 22, 617–624.
17. Birkinshaw, C.; McCarthy, C. J.; Reagan, N.; Hale, M. D. C.; Cahill, D.; McCourt, M. Holzforschung 1999, 53, 459–464.
18. Backman, A. C.; Lindberg, K. A. H. J Mater Sci 2001, 36, 3777–3783.
19. Nakano, T.; Honma, S.; Matsumoto, A. Mokuzai Gakkaishi 1990, 36, 1063–1068.
20. Wert, C. A.; Weller, M.; Caulfield, D. J Appl Phys 1984, 56, 2453–2458.
21. Kawakami, H.; Taneda, K.; Ishida, S.; Ohtani, J. Mokuzai Gakkaishi 1981, 27, 197–204.
22. Wallström, L. Ph.D. Thesis, Luleå University of Technology, Sweden, 1998.
23. Ward, I. M.; Hadley, D. W. An Introduction to the Mechanical Properties of Solid Polymers; John Wiley and Sons: New York, 1993.
24. Diaz-Calleja, R.; Riande, E.; Guzman, J. J Polym Sci, Polym Phys Ed 1986, 24, 337–344.
25. Eisenberg, A.; Shen, M. Rubber Chem Technol 1978, 43, 156–170.
26. Handa, T.; Yoshizawa, S.; Seo, I. Org Coat Plast Chem 1981, 45, 375–381.
27. Klason, C.; Kubát, J. Sven Papperstidn 1976, 15-1976, 494–500.
28. Horiuchi, K.; Sato, K. J Coat Technol 1991, 63,55–61.
29. Sircae, A. K.; Chartoff, R. P. Measurement of the glass transition temperature of elastomer systems; in Assignment of the Glass Transition; Seyler, R. J., Ed.; ASTM: Philadelphia, PA, 1994; pp 226–238.
30. Nielsen, L. E.; Landel, R. F. Mechanical Properties of Polymers and Composites; Marcel Dekker: New York, 1994; pp 156–182.
31. Hagen, R.; Salmen, L.; Stenberg, B. J Polym Sci, Polym Phys Ed 1997, 34, 1997–2006.
32. Gibson, L. J.; Ashby, M. F. Cellular Solids, Structure and Properties; Pergamon Press: Oxford, 1988.

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Interaction between wood and polyvinyl acetate glue
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III

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 climates[2] 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 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 the manufacturer. According to the manufacturer the glue also contained unspecified filler.

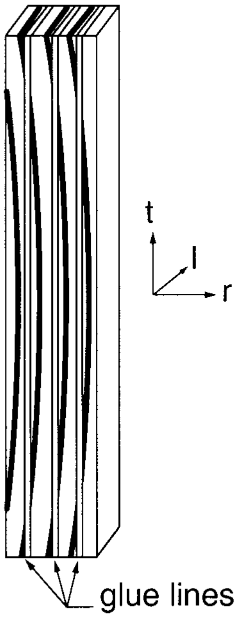


Figure 1 DMTA specimen with three glue lines. Measurement was made in tension in the tangential direction (*t*). *r*, radial and *l*, longitudinal directions of the wood.

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 purchased 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% bezoyl 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 × width × thickness) in the DMTA was for pure PVAc film 12 × 8 × 0.3–0.4 mm. Wood specimens glued with PVAc were 23 × 4 × 3 mm. Acrylate and acrylate impregnated wood specimens were 20 × 2–4 × 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 a 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.

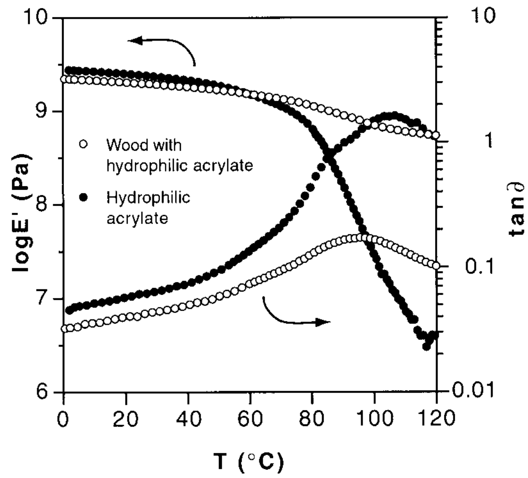


Figure 2 DMTA measurements on hydrophilic acrylate polymer and on wood impregnated with hydrophilic acrylate polymer. Polymer impregnated in wood had a T_g at 96°C and pure polymer had a T_g at 106°C.

RESULTS AND DISCUSSION

T_g as a tool to measure interaction between wood and polymers

In an earlier study[6] 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∂) 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 Lindberg[6]). 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

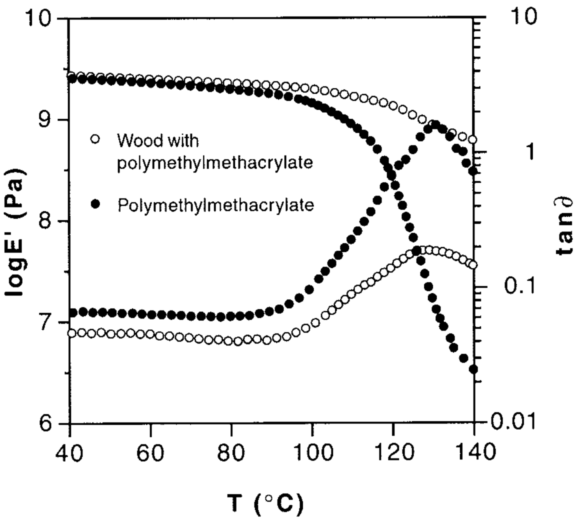


Figure 3 DMTA measurements on PMMA and wood impregnated with PMMA. PMMA in wood had a T_g at 127–129°C and pure PMMA had T_g at 129–131°C.

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 plastcizers 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

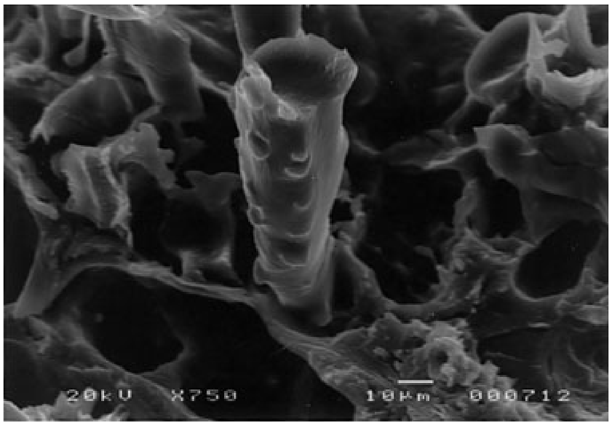


Figure 4 SEM micrograph of fracture surface of two transverse wood surfaces glued with PVAc, showing a protruding rod of glue.

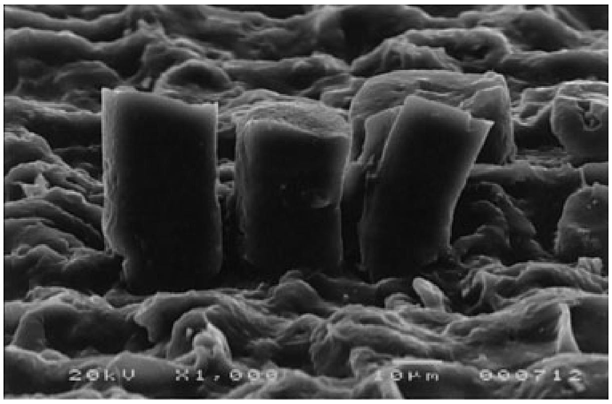


Figure 5 SEM micrograph of fracture surface of two transverse wood surfaces glued with PVAc, showing three protruding rods of glue.

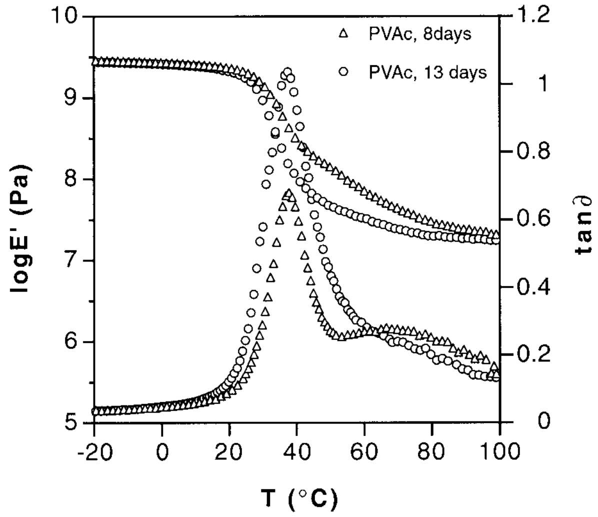


Figure 6 DMTA measurements of PVAc glue dried at room temperature for different drying times: 8 days and 13 days.

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 lumen[6], 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 ± 0.6°C. T_g was measured as the loss factor (tan∂) 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∂. It was probably related to the disappearance of the peak at 70°C, but, as stated above, the T_g peak 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∂ peak between 39 and 40°C. If a specimen of wood is tested,

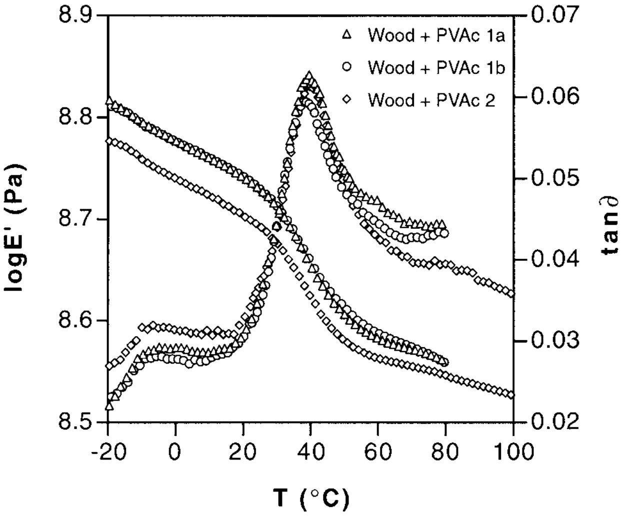
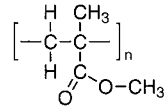
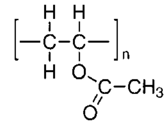
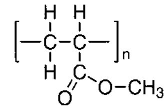


Figure 7 DMTA measurements of paired speciments of wood glued with PVAc. Specimen 2 and the first measurement of specimen 1 (1a) were made after drying for 17 days and measurement of specimen 1 was repeated the following day (1b).

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

Name	T_g (°C)	Structure	Hansen solubility parameters ($MPa^{0.5}$)			
			∂_D	∂_P	∂_H	∂
PMMA	105		18.64	10.52	7.51	22.69
PVAc	28		20.93	11.27	9.66	25.66
PMA	3		—	—	—	—

a tan∂ 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 ± 6°C with a peak height at tan∂ = 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°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∂ and E' almost identical to the first run (Figure 7, 1b). The difference of the peak temperature for PVAc in wood (39–40°C) from the peak temperature for pure PVAc (37–38°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 ∂ ($MPa^{0.5}$) 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 work[6] 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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References

1. Wu, Z-H.; Furono, T. J Wood Sci 1999, 45, 134.
2. Raknes, E. Holz als Roh- und Werkstoff 1997, 55, 83.
3. Handa, T.; Yoshizawa, S.; Seo, I. Org Coat Plast Chem 1981, 45, 375.
4. Oksman, K.; Lindberg, H. Holzforschung 1995, 49, 249.
5. Oksman, K.; Lindberg, H. J Appl Polym Sci 1998, 68, 1845.
6. Backman, A. C.; Lindberg K. A. H. J Appl Polym Sci 2002, 85, 595.
7. ; Thuvander, F.; Wallström, L. In Technical Report from The Royal Institute of Technology, Sweden, TRITA-TRΔ R-96–19, ISSN 1104–2117, Paper V.
8. Kuo, M-L.; DiCarlo, D. J Adhes 1984, 16, 257.
9. Packham, D. E. Handbook of Adhesion; Wiley: New York, 1992.
10. Pizzi, A.; Mittal, K. L. Handbook of Adhesive Technology; Dekker: New York, 1994.
11. McCrum, N. G.; Read, B. E.; Williams, G. Anelastic and Dielectric Effects in Polymeric Solids; Dover: New York, 1991.
12. Nielsen, L. E.; Landel, R. F. Mechanical Properties of Polymers and Composites; Dekker: New York, 1994.
13. Diaz-Calleja, R.; Riande, E.; Guzman, J. J Polym Sci Phys 1986, 24, 337.
14. Eisenberg, A.; Shen, M. Rubber Chem Technol 1970, 43, 156.
15. Birkinshaw, C.; McCarthy, C. J.; Reagan, N.; Hale, M. D C; Cahill, D; McCourt M. Holzforschung 1999, 53, 459.
16. Kelley, S. S.; Rials, T. G.; Glasser, W. G. J Mater Sci 1987, 22, 617.
17. Back, E. L.; Salmén, N. L. Tappi J 1982, 65, 107.
18. Backman, A. C.; Lindberg, K. A. H. J Mater Sci 2001, 36, 3777.
19. Brandrup, J; Immergut, E. H. Polymer Handbook, 3rd ed; Wiley: New York, 1989; vol 7, p. 530.

A. Backman Sandlund

Influence of surface structure on adhesion strength between wood and Melamine Urea Formaldehyde

IV

Influence of surface structure on adhesion strength between wood and Melamine Urea Formaldehyde.

Anna C. Backman Sandlund

Abstract

The structure of the adherend is important when joining two surfaces with a glue. The wood surface has a system of pores and lumens into where the adhesive can flow and anchor itself. The aim of the work presented in this paper was to compare the practical adhesion properties of melamine urea formaldehyde (MUF) glued beech and pine wood, with a circular sawn, rotary planed or sanded surface structure. The adhesion was measured using single and double overlap joint tests in tension and the as machined beech surfaces were also studied with scanning electron microscopy (SEM).

The sawn beech surfaces gave the highest failure stress and 100% wood failure. Most measurements on the sanded and planed specimens showed less than 100% wood failure. No apparent differences in failure stress and percent wood failure between the methods were found. Multivariate analysis was used on the data and could discriminate between sawn and sanded beech due to the dependence of both failure stress and percent wood failure. SEM showed more debris on sanded and sawn beech surfaces. The parts of tracheids still attached to these surfaces could act as a reinforcement to the unfilled MUF glue that was used. The sanded surface showed poorer glue penetration into the wood vessels than the sawn, which may be the reason why the sanded surfaces gave lower joint strengths than the sawn surfaces.

All pine sapwood specimens showed 100% wood failure, but the sawn and sanded samples had higher failure stress than the planed; a conclusion based on a limited number of planed specimens. The sawn heartwood tested with double overlap joint had a significantly lower failure stress than sawn sapwood. The double overlap test on sapwood specimens gave significantly higher failure stresses than the single overlap test, most likely because of the lower degree of peeling stress in double overlap test.

Introduction

The influence of surface structure on adhesion has been examined by many. If two solid surfaces are to be joined with a liquid adhesive, it is evident that the adherends play an important part. The surface of wood has a built in system of pores/lumens into which the adhesive can flow and anchor itself; giving a large contact area between adherend and adhesive. Mechanical interlocking is one of the adhesion mechanisms that has been proposed. Whilst this mechanism has at times been discarded for many materials, it is believed to have a significant influence on wood adhesion [1].

The perfect surface structure which would give the best possible anchoring of adhesives to wood has yet to be found; probably because of the many different species of wood, types of glue and influence of other factors such as the sharpness of the tools used for machining the surfaces, the age of the surface. Nor is there a standard way of describing or characterizing surface structure and appearance.

Knife or blade planed wood leaves clean-cut cells with very little distortion compared to abrasive planed or sanded wood which often exhibits a damaged surface and subsurface fibers which leads to more pronounced separation in glue line after aging [2]. Papers by Stewart and others [3, 4, 5] show the same results, i.e. that knife planed surfaces have higher bond strength than abrasive planed surfaces. This is thought to be due to the negative cutting angle of the grains in the sandpaper which results in the cutting force during sanding being more normal to the surface and thus causing more crushing of the cells.

The wettability and shear strength of karri and jarrah hardwoods, sanded by hand along the grain and glued with resorcinol-formaldehyde increased with increasing abrasive paper roughness (12000 to 80 grit)[6]. Control specimens, whose surfaces were planed, had shear strengths comparable to sanding with 6000 grit and significantly lower wettability. The shear strength loss when wet was much lower for the corse sanded (80 grit) than for the control / planed specimens. Significant improvements in dry shear strength were only achieved when sanding with 80 and 120 grit abrasive paper. This is probably due to the fact that sanding with finer grit sizes increases the possibility of clogging the wood surface with fine abrasive dust, preventing glue penetration and thus decreasing shear strength. The authors demonstrated greater glue penetration into the wood prepared using 80 grit-sanded specimens than the planed specimens.

A method using fixed-knife pressure-bar planing showed a 10 percent increase in the shear strength of glued sugar maple compared to those prepared using a conventional peripheral planing technique. For white spruce, no significantly different shear strength was detected, which indicates that the surfaces of these two woods have the same apparent roughness using both planing methods [7].

River [8] observed different shear strength in samples of yellow poplar and red oak prepared for gluing using sawing and planing. The sawed edge surfaces produced joints that gave lower values than those using planed edges surfaces. Severe crushing of wood cells was observed in the sawn specimens but very little damage was seen in planed latewood in red oak, which also had high shear strength values. These findings are though not to be directly comparable with the present investigation since this work is about end-grain glued wood. Several studies have also been made on surface structure and joint strength of glued wooden joints involving ablated end-grain surfaces [9].

Objective

Several authors have studied the effect of different machining methods on surface structure and glue line strength. However, no recent references have been found where comparisons between conventional machining techniques sawing and rotary planning have been made. The present work compares conventional machining techniques (circular sawing, rotary planing and sanding) and evaluates differences in glue line strength between wooden surfaces prepared using these methods. The aim of this work was to compare the practical adhesion strength for different surface structures when gluing beech or pine with melamine urea formaldehyde. Beech is the hardwood most commonly referred to in many European standards and pine one of the most commonly used softwood. The adhesion was measured using single and double overlap joint tests in tension.

Method and material

Material

The wood used was clear wood from Scots Pine (*Pinus sylvestris*) and Beech (*Fagus sylvatica*). Three different surface structures were produced using three commonly used machining / finishing techniques; sawing using a circular saw, planing with a rotary planer and sanding by hand in the longitudinal direction with 150-grade sand paper. No specific information was obtained regarding types of saws or planers and their normal cutting speed and blade sharpness. The samples tested were prepared using laboratory scale equipment. The microscopy studies of the cut surfaces indicated that the planer blade was not optimally sharp. The sanded surfaces were lightly blown free of debris after sanding. Samples of both wood species were prepared in the same machines using approximately the same settings.

For the Scots Pine the presence of heartwood was checked using a standard reagent[10]: Solution A: 5 g ortho-anisidine [2-methoxyaniline] in a mixture of 20 ml concentrated hydrochloric acid (HCl) and 1000 ml water. Solution B: 100 g sodium nitrite ($NaNO_2$) in 1000 ml water. Equal volumes of solution A and B were mixed and applied in drops on wood surface. The presence of heartwood was shown by a red colour appearing after approximately 30 seconds of exposure.

The resin used was a melamine urea formaldehyde (MUF), prepared according to the formulation reported in Pizzi [11], with a ratio (M+U):F of 1:1.9. The resin was prepared to a degree of advancement as defined by a water tolerance of 130%. The glue was used as prepared with a solid content of 59% and a viscosity of 500 mPas at 20 rpm measured in RT. The hardener used was 5 weight percent of 98% formic acid, giving a pH of 5-6 and a potlife in room temperature (RT) of ca. 3.5 hours.

Gluing

Surfaces for gluing were 46-96 hours old, having been conditioned at 20°C and 65% relative humidity (RH). An excess of glue was spread on both surfaces to be joined then assembled giving a bonded overlap of 25 x 25 mm. The joint was then clamped and left in the clamp for 22-38 hours followed by aging for 7-10 days at 20°C and 65% RH. The glued surfaces were not purely tangential with a 30° angle between the surface and the tangential direction being maintained. The same type of clamping assembly described by Properzi [12] was used with a clamping pressure of 0.5-0.7 MPa.

Fracture testing

The single overlap test (see Figure 1) is perhaps the most common test configuration for adhesive joints. It is cheap and easy to produce but will not test the joint in pure shear which is preferred. The double overlap test overcomes the loading eccentricity associated with the single overlap test and peel stresses are thus reduced [13]. Single overlap joint (SJ) specimens were made in dimensions of 115 x 25 x 3 mm (length x width x thickness). Double overlap joint (DJ) specimens for tensile testing were made with the same dimensions. The length of the specimens was in the longitudinal direction.

The adhesion of the specimens was measured using an Instron 4467 with cat# 2716-015 claws. The maximum force for fracture at a constant speed of 4 mm/min was recorded for each specimen. Loose pieces of 3mm thick Pine or Beech wood were used during fracture testing to centre the SJ in the jaws. For the DJ samples, a loose piece of pine or beech wood was inserted on the double side, see Figure 1. The percentage of wood failure was determined by visual inspection.

Microscopy

The Scanning Electron Microscope (SEM) used was a Jeol JSM 5200 at an acceleration voltage of 20kV. The glued wood specimens were softened in water at approximately 80°C for 15 minutes before samples for SEM were cut along the glue line across the fibers using a microtome. The specimens were dried and then sputter coated with gold.

Statistical analysis

A one sample analysis t-test was made with a confidence interval of 95% using StatView 4.01 from Abacus Concepts Inc. This shows with 95% confidence where the mean value for new measurements would lie.

Projection to latent structures (PLS) modeling (multivariate analysis) was carried out using SimcaP 8.0 from Umetrics, Box 7960, SE-907 19 Umeå, Sweden. For the multivariate analysis data was included for single overlap planed beech samples with 200 hours from planing to gluing and for double overlap sawn beech samples with 700 hours from sawing to gluing. The results for beech and pine were analyzed separately with dummy variables set for the different surface structures and dummy variable 1 for double overlap and 0 for single overlap test. A variable named heartwood was used for the pine, heartwood specimens were labeled with dummy variable 1, sapwood specimens with 0 and planed specimens consisting of both sapwood and heartwood had dummy variable 0.5. As dependent y-variables, failure stress and percent wood failure were used.

Results and discussion

Fracture tests on beech

Fracture tests of single and double overlap joints made from sawn, sanded and planed beech glued with melamine urea formaldehyde (MUF) were carried out (see Figure 2). For both types of joints, the sawn surfaces gave the strongest joint and the planed surfaces the weakest joint. The mean strength was also statistically different with a 95% confidence interval. The mean value for the double lap test using sawn samples was 65%

higher than that using the planed samples (58% higher for the single overlap test). Joints using the sanded surfaces failed at stresses somewhere between the other two. Belfas et. al [6] found the same tendency of higher joint shear strength for sanded wood compared to planed wood, in particular the wet shear strength was higher (only 80 grit sanded surfaces tested). This was explained as being due to greater penetration of the glue into the sanded specimens. The stresses for the double overlap tests were slightly higher than for the single overlap tests, but the difference was not statistically significant. The higher failure stress was expected since the peel stresses are lower in the double overlap test and should give higher failure values.

The proportion of wood that had failed during fracture was determined from manual inspection of the fractured wood surfaces (see Figure 3). These results were plotted against failure stress which showed a large difference between the performance of the different surface structures. No apparent difference was observed between the two methods (SJ and DJ). All the specimens prepared using sawing had 100% wood failure; the weakest point of the joint being the wood itself. The specimens prepared using planing and sanding showed a somewhat linear relationship between stress at failure and proportion of wood failure, with the curve leveling out at 100% wood failure. All the DJ specimens prepared using planing gave low levels of wood failure some SJ samples though gave 100% wood failure; two with failure stress of 4.5 and 4.8MPa respectively. The joints involving sawn surfaces gave the highest failure stress and percent wood failure in both single and double overlap tests.

Fracture tests on pine

Sawn, sanded and planed pine glued with MUF were tested in single and double overlap tests until failure (see Figure 4). The samples were of sapwood, heartwood and some with both sap- and heartwood. The first three data points in Figure 4 for SJ and DJ tests are for the sapwood specimens. It can be seen that the stress at failure was about the same for sawn and sanded specimens for both SJ and DJ. The planed sapwood appeared weakest from the limited number of measurements made; for the DJ tests only three.

The wood for these tests was originally intended to be sapwood. However, after all the tests had been made a test using heartwood reagent revealed that most of the planed specimens consisted of both heartwood and sapwood. The number of planed samples consisting purely of sapwood were too low for any reliable statistical analysis, but the t-test nevertheless showed a clear difference between the planed surface and the other two surfaces. This conclusion was confirmed by the comparison showing the dependence of failure stress on surface structure in the beech samples. Some specimens made from sawn heartwood were tested (see Figure 4), and it was clear that DJ made from heartwood have considerably lower adhesion strength.

The DJ measurements gave significantly higher failure stresses than for the SJ tests for all surface structures. For the beech, however, the differences were small. The double overlap test overcomes the loading eccentricity associated with the SJ tests which reduces peel stresses. It is plausible that pine is more susceptible to failure due to peel stresses than beech since the loading method had a greater influence on the results for the pine samples. It can be concluded that the SJ test is probably not appropriate for testing glued pine joints.

The percent of wood failure plotted against failure stress for pine (see Figure 5) shows a similar appearance to that seen in Figure 3 for beech; with a somewhat linear relationship leveling out at 100% wood failure. All of the sawn sapwood specimens, all but four of the sanded sapwood specimens and all of the planed sapwood specimens had 100% wood failure. Low levels of wood failure were seen in the sawn heartwood specimens, a few sanded sapwood specimens and the planed heartwood and mixed heartwood:sapwood specimens. The differences in proportion of wood failure appear to be almost exclusively dependent on the presence of heartwood. No dependence on surface structure could be observed with any certainty.

Multivariate analysis

It is possibile to analyse the failure stress and percentage of wood failure in combination to more accurately differentiate between the three different surface structures investigated. This is done using multivariate analysis. This technique also allowed the surface age before gluing, clamping time and conditioning time prior to fracture testing to be incorporated in the analysis. For the beech, additional data using older surface before gluing were included (6 planed SJ specimens stored for 8 days and 9 sawed SJ and DJ specimens stored for 29 days). The dummy variables used were 1 for double overlap and 0 for single overlap. The dependent y-variables used were failure stress and percent wood failure.

Multivariate analysis on beech

A PLS analysis (projection to latent structures) was made for the data obtained from the beech samples and gave one principal component (pc) with Q_2=0.445, R_{2X}=0.332 and R_{2Y}= 0.475 (see Figure 6). This is quite a good level of explanation on a single pc, at least for the dependent variables failure stress and percent wood failure. The description of x-data was low, indicating a low level of information in some variables, for example method, time to testing and pressing time. The sawn surfaces gave a high contribution to y-variables which separated sawn surfaces from sanded. This was not the case using traditional statistical analysis. The improvement was due to the incorporation of percent wood failure into the PLS model. Sanded and planed surfaces were not clearly separated and gave negative contributions in the model. As expected from Figure 2, the variable method (SJ, DJ) gave almost no contribution, and could have been excluded for the beech samples.

Multivariate analysis on pine

A PLS analysis on data from the pine samples gave three principal components; $Q_{2(cum)}$=0.636, $R_{2X(cum)}$= 0.640 and $R_{2Y(cum)}$= 0.513. A variable named heartwood was used, fully heartwood specimens were labeled with dummy variable 1, fully sapwood specimens with 0 and planed specimens having both sapwood and heartwood had dummy variable 0.5. As dependent y-variables failure stress and percent wood failure were again chosen.

In Figure 7 it can be seen that method gave a positive contribution for the y-variables, as it did in classical statistical analysis. A sanded surface gave a positive contribution to failure stress and percent wood-failure. Sawn, planed and heartwood gave negative a contribution. This is not a sound analysis, since the sawn sapwood gave y-values as high as those for the sanded. No data was available for sanded samples with 100% heartwood and the multivariate analysis is obviously not able to accurately discriminate between surface structure and heartwood contents. The presence of heartwood strongly decreases values of y-variables and this influences the model. If enough data for all surface structures with both sapwood and heartwood had been available, it is possible that the influence of surface structure on the y-variables could have been more accurately detected by the multivariate analysis.

An analysis of only sapwood is meaningless on this data since almost all sapwood specimens gave 100% wood failure and hence the possibility to extract more information with combination of two dependent y-variables is lost.

Scanning electron microscopy on beech surfaces

The beech samples showed a significant difference in the fracture stress and wood percent failure between the three different surface structures. The reason for this could be due to either physical or chemical differences in the surfaces. Scanning electron microscopy (SEM) was used to reveal differences in the physical structure of the ‘as machined’ surfaces. Chemical differences were not investigated in this work. For pine the difference was not so clear. The presence of heartwood in some of the samples clouded the analysis and the SEM study was therefore limited to only beech wood.

SEM micrographs of the tangential surface of sawn, sanded and planed beech are presented in Figure 8. Like the samples used for the fracture tests, the surfaces of the SEM samples were handled carefully after machining. The sanded surface was lightly blown free of excess dust. Deep gouges could be observed in the sawn surface where tracheids had been torn off (see Figure 8a) but a large percentage of the sawn surface had a rather smooth appearance (Figure 8b) but full of loose debris and parts of tracheids still attached to the wood. The sanded surface (Figure 8c) was smoother with no apparent gouges, but with an abundance of loose debris and some attached parts of tracheids. The planed surface (Figure 8d) was different in appearance with a smooth and plane surface, the tracheids had an almost smeared out appearance as can be seen in the left part of Figure 8d. There was very little debris on the surface and seemingly few places for the adhesive to penetrate the surface into non-damaged wood, except at the lumens which can be seen at the right hand side of Figure 8d.

The structure of the glue line for beech samples prepared for fracture tests was also examined in SEM. A cut was made along the glue line across the fibers. The sawn surface had a rather thick and irregular glue line, sometimes more than 50μm thick (see Fig. 9a). There was an abundance of filled vessels around the glue line, some were found at a distance of 400μm from the glue line. Fibers filled with glue was also found close to the glue line.

The sanded surfaces exhibited very low penetration of glue into vessels, very few filled vessels were found, at most 100μm from the glue line, and glue filled fibers close to the glue line were also observed (see Fig. 9b). A smoother glue line than for the sawn surface was observed with fewer glue rich areas. The low penetration could be explained by the presence of small particles or debris produced during sanding which was not removed prior to gluing which may have blocked openings and hindered penetration of the glue into the wood [6].

The planed surfaces gave the smoothest and narrowest glue line (see Fig. 9c). There was also good penetration of glue into vessels, similar to that for the sawn surface. Many vessels were filled with glue; at most about 350μm from the glue line. The penetration into fibers for the planed surface was at most two fibers deep which is the same as that observed in the sawn and sanded surfaces. The planed surface shown in Fig. 8d showed smeared fibers but the vessels are open for penetration. The lower penetration into the sanded surfaces compared to the planed surfaces is the opposite of that observed by Belfas el al. [6] who found a higher penetration into sanded (80 grit) surfaces than planed; probably because of the different grit size of paper used in the present work (150 grit). The sharpness of the blades used for planing has a significant effect on the microscopic structure of softwood. Singh et al. [14] showed a narrow glue line and penetration of PVAc glue up to three cells deep for Pinus radiata. When planing with dull blades, a thick glue line with severely distorted and crushed cells several cells deep were observed with low penetration of glue. The surface appearance of the planed beech wood in the present work suggests planing with dull blades results in a few layers of crushed cells but not the depth of damage seen for softwoods. The penetration of MUF glue into beech fibers would probably be very low even for a knife planed surface due to the small pit openings. The penetration path into beech seen in the present work is through vessels and rays which were not smeared out during the planing operation.

The lower strength and wood failure observed in planed surfaces compared to the sawn surfaces cannot be explained simply by lower penetration of glue into vessels since both structures had similar penetration; i.e. up to 400 μm. All three kinds of machined surfaces had glue penetration into fibers close to the glue line, with perhaps slightly higher penetration for the sawn surfaces. The presence of debris on the surface of the sawn and sanded surfaces but not for planed surface is one possible explanation for the lower adhesion strength of the planed surfaces. It is possible that the debris could act as a reinforcement in the glue; especially considering that the MUF glue used was not a commercial glue, and had no fillers as would usually be the case in normal commercial products.

The penetration of glue into the wood was primarily into vessels. If a damaged layer of wood cells covered the surface, it would be difficult for the glue to penetrate, giving low strength. For the planed surfaces the glue could penetrate into the vessels but not necessarily deep enough into fibers down to undamaged wood which would be necessary to give a high joint strength. A thin layer of wood on apparently wood free glue fractures would not be easily observed in the visual inspection used to determine percent wood failure. The reason for the sawn surface giving higher fracture stresses than the sanded surface cannot be satisfactory explained only by differences in penetration. The actual area of a sawn surface is larger than a sanded surface, which would give a larger bonding area and therefore the possibility of a higher fracture stress.

Conclusions

For beech the sawn surfaces gave the highest failure stress and percent wood failure for both single and double overlap tests. Most measurements on sanded and planed specimens showed less than 100% wood failure. No apparent differences in failure stress and percent wood failure between the methods were found.

All pine sapwood specimens showed 100% wood failure, but the sawn and sanded surfaces had higher failure stress than the planed; although this conclusion is based on a limited number of planed specimens. The double overlap test gave significantly higher failure stresses than the single overlap test, most likely due to the decreased amount of peeling stress in the double overlap test.

Multivariate analysis could discriminate between sawn and sanded beech due to dependence of both failure stress and percent wood failure on the results. For pine very little additional information was obtained with multivariate analysis compared to statistical analysis. This is mainly due to the few sapwood specimens tested and because almost all sapwood specimens had 100% wood failure.

SEM showed more debris on the sanded and sawn beech surfaces, which could act as reinforcement in the unfilled MUF glue that was used. Parts of tracheids still attached to the surface can also contribute to adhesion strength and were present on the sawn and sanded surfaces but far less on the planed surfaces. The sanded surface showed poor glue penetration into the wood at the glue line whilst the sawn and planed surfaces had similar penetration, which is one possible reason why the sanded surfaces gave lower joint strengths than the sawn surfaces

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References

1. A. Pizzi and K. L. Mittal, 2003, "Handbook of Adhesive Technology", second edition, Marcel Dekker Inc, New York, ISBN 0-8247-0986-1.
2. R. W. Jokerst and H. A. Stewart, 1976, Knife- versus abrasive-planed wood: quality of adhesive bonds, *Wood and Fiber* **8** pp 107-113.
3. H. A. Stewart and J. B. Crist, 1982, SEM examination of subsurface damage of wood after abrasive and knife planing, *Wood Sci.* **14** pp 106-109.
4. L. Murmanis, B. H. River and H. A. Stewart, 1983, Microscopy of abrasive-planed and knife-planed surfaces in wood-adhesive bonds, *Wood and Fiber Sci.* **15** pp 102-115.
5. L. Murmanis, B. H. River and H. A. Stewart, 1986, Surface and subsurface characteristics related to abrasive-planing conditions, *Wood and Fiber Sci.* **18** pp 107-117.
6. J. Belfas, K. W. Groves and P. E. Evans, 1993, Bonding surface-modified Karri and Jarrah with resorcinol formaldehyde, *Holz als Roh- und Werkstoff* **51** pp 253-259.
7. R. E. Hernandez, 1994, Effect of two wood surfacing methods on the gluing properties of sugar maple and white spruce, *Forest Prod. J.* **44** pp 63-66.
8. B. H. River and V. P. Minutti, 1975, Surface damage before gluing weak joints, *Wood and Wood Products* **80** pp 35-38.
9. M. Stehr, 1999, Adhesion to machined and laser ablated wood surfaces, Doctoral thesis, Royal Institute of Technology, ISSN 1104-2117.
10. Nordic Wood Preservation Council , 1998, Nordic requirements for quality control and marking of pressure-treated timber, Part 1: Pine and other permeable softwoods. NWPC Document no. 3: 1998 English Edition, Nordic Wood Preservation Council.
11. A. Pizzi, 1994, "Advanced Wood Adhesives Technology", Marcel Dekker Inc., New York, ISBN 0-8247-9266-1.
12. M. Properzi, A. Pizzi and L. Uzielli, 2001, Honeymoon MUF adhesives for exterior grade glulam, *Holz als Roh- und Werkstoff* **59** pp 413-421.
13. M. R. Groth, 2001, Structural adhesive bonding of metals - surface and fracture mechanics aspects, Doctoral thesis, Luleå University of Technology, ISSN 1402-1544.
14. A. P. Singh, C. R. Anderson, J. M. Warnes and J. Matsumura, 2002, The effect of planing on the microscopic structure of *Pinus radiata* wood cells in relation to penetration of PVA glue, *Holz als Roh- und Werkstoff* **60** pp 333-341.

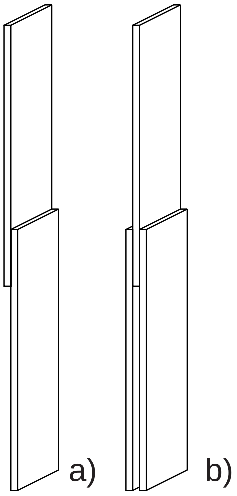

Figure 1: Specimens for a) single overlap joint (SJ) and b) double overlap joint (DJ) in tension.

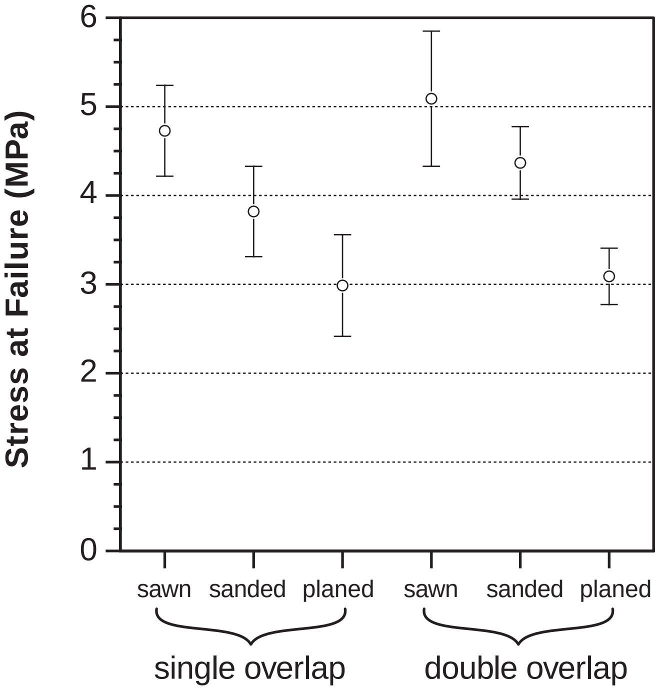

Figure 2: Fracture testing of glued beech. Bars represent 95% confidence interval of one-sample t-test. Number of specimens for each analysis from left is: 11, 11, 12, 10, 11, 11.

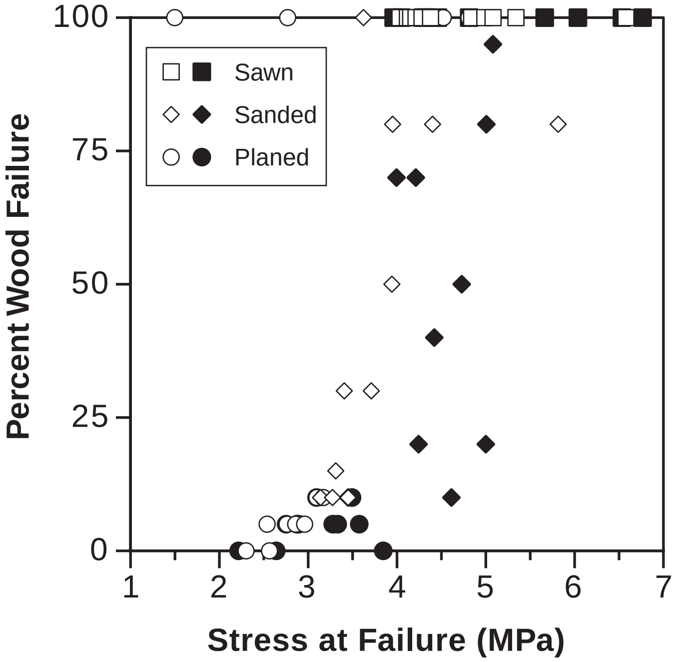

Figure 3: Percent wood failure in fracture test on glued beech. Open symbols are single overlap tests and filled symbols are double overlap tests.

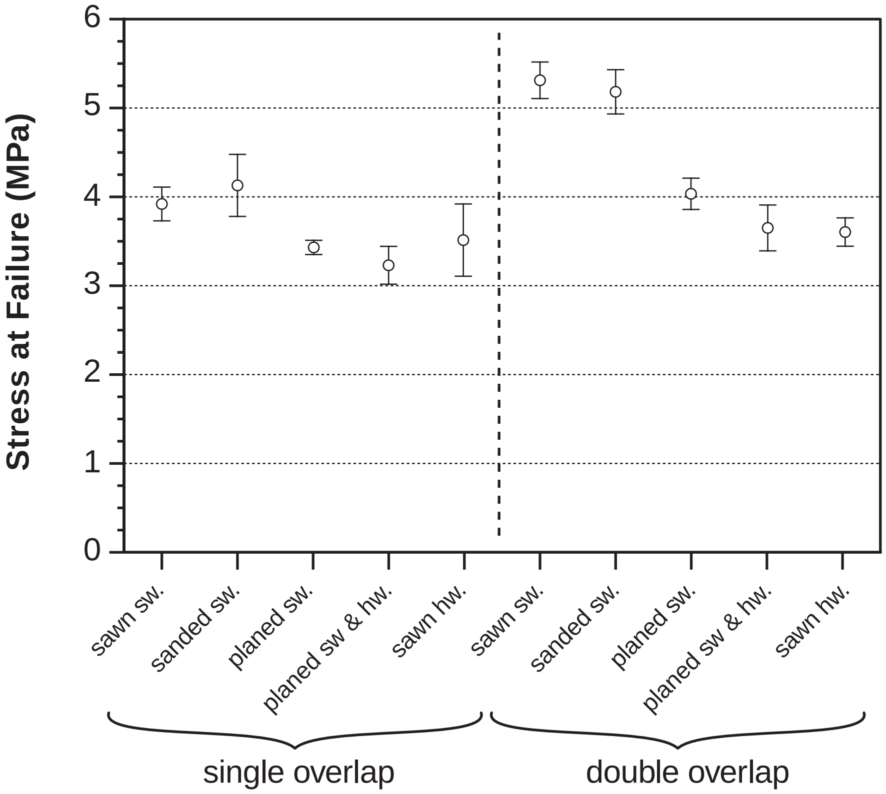

Figure 4: Fracture testing of glued pine with different surface structures. Specimens were made of sapwood (sw) or heartwood (hw). Bars represent 95% confidence interval of one-sample t-test. Number of specimens for each analysis from left was: 11, 20, 6, 14, 6 in single overlap joint and 12, 13, 3, 12, 8 in double overlap joint.

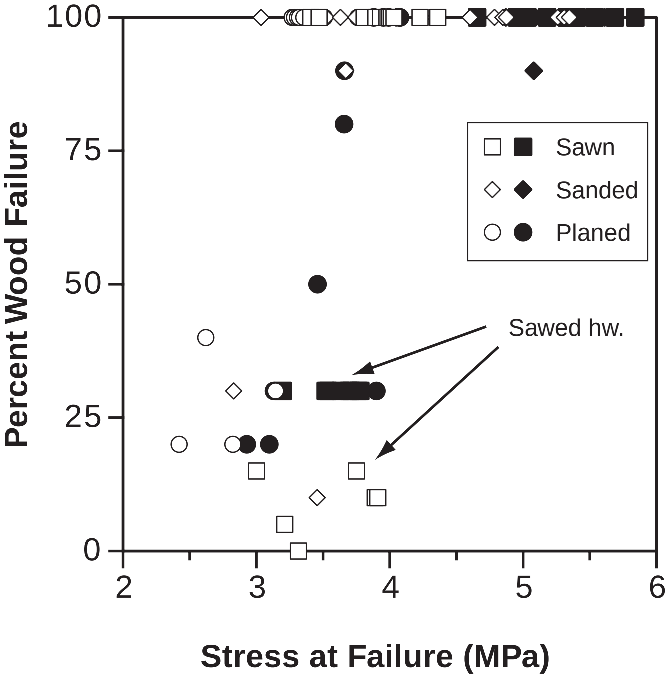

Figure 5: Percent wood failure in fracture test on glued pine. Open symbols are single overlap tests and filled symbols are double overlap tests. The sawed heartwood specimens had low level of wood fracture as marked in figure with arrows.

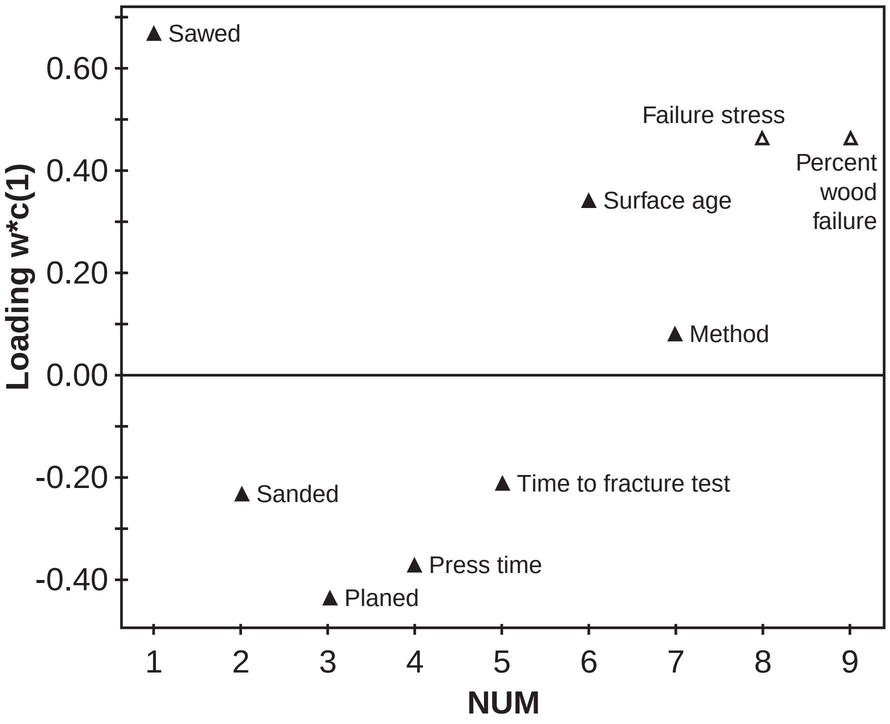

Figure 6: PLS analysis on beech showing loading plot of principal component 1 (w*c(1)). Dependent y-variables (Δ open symbols) were "Failure stress" and "Percent wood failure".

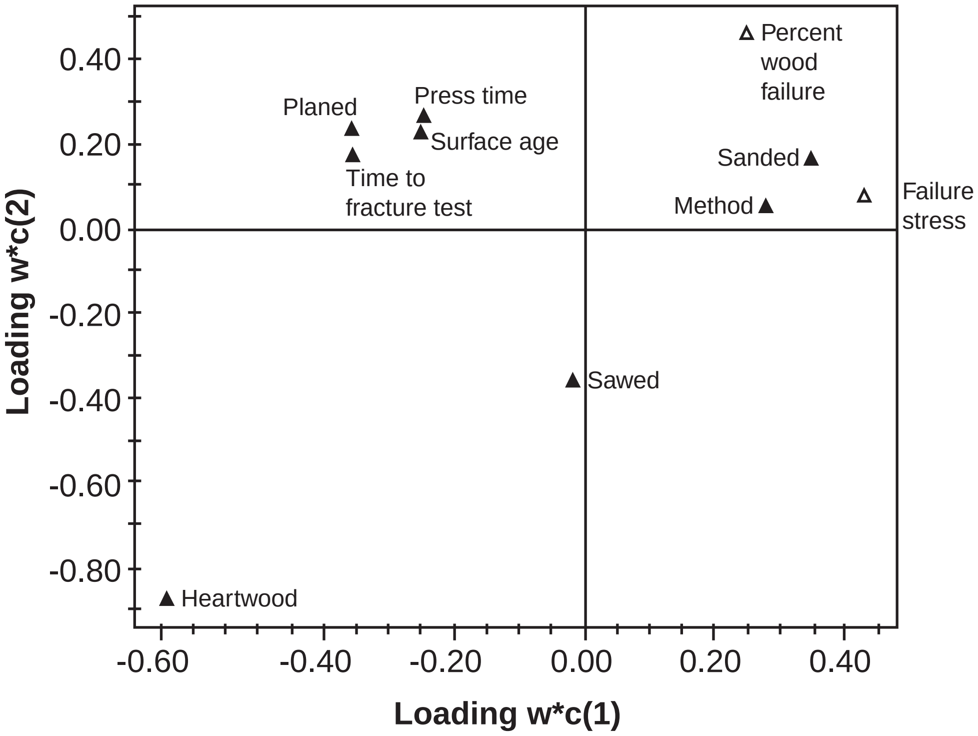

Figure 7: PLS analysis on pine showing loading plot of principal component 1 versus 2 (w*c(1) and w*c(2)). Dependent y-variables (Δ open symbols) were "Failure stress" and "Percent wood failure".

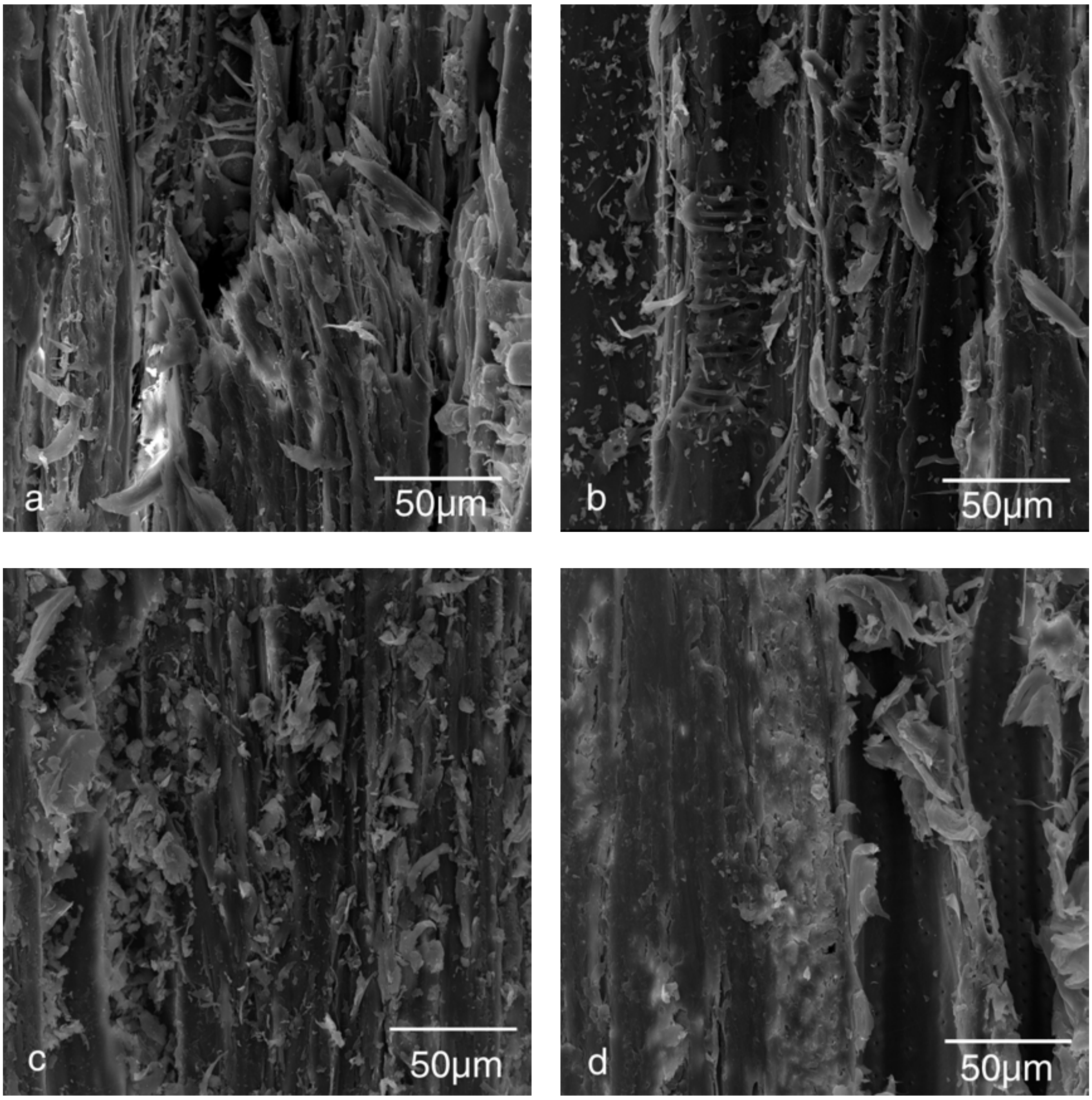

Figure 8: Scanning electron micrograph of tangential surface of beech, a and b) sawn c) sanded and d) planed. The longitudinal direction of wood was vertical in the micrographs.

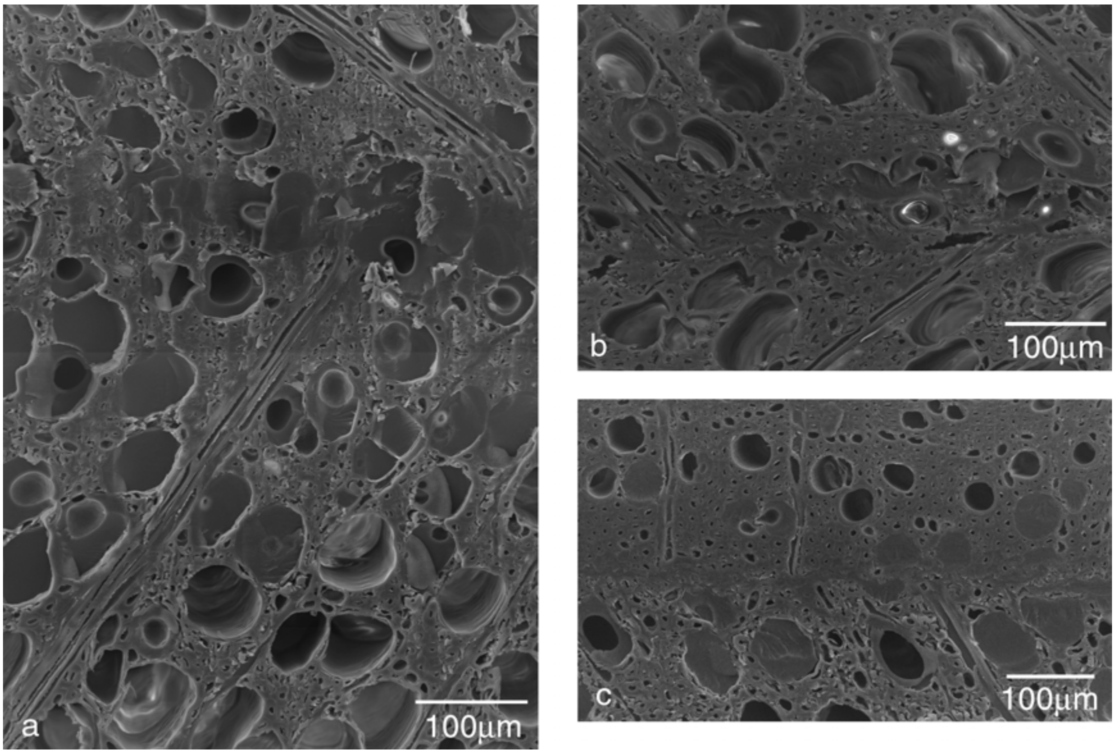

Figure 9: Scanning electron micrograph of glueline in beech. The glueline was horisontal in the micrographs. a) sawn b) sanded and c) planed surfaces glued with MUF.

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