CA.97.20768 CONFIDENTIAL

Code 25362301.500.70.623
(Chemicals)

CARILITE WOOD GLUE FEASIBILITY
Experimental evaluations of one-pot emulsion systems in plywood

(March-December 1997)

by

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Summary

Experimental work has been carried out on plywood production with CARILITE glue emulsions, water based glue systems developed from CARILITE (co- and terpolymers of propene, ethene and carbonmonoxide) and PDA as curing agent. Features of this system are the low viscosity, low free volatile diamine, very good stability and the fact that it is water washable. At curing a very stable network is formed via pyrrole cross-links, which are boiling water resistant and makes the glue suitable for outdoor wood applications.
At a major Swedish glue manufacturer (CASCO), an American wood institute and at SRTCA, a broad range of variables in the plywood manufacturing has been tested. The smell, handling and cleaning were rated as very good. With the most reactive CARILITE grade the waterboil resistant bonds and wood failure could be reached in up to 40% shorter pressing times than the reference phenol formaldehyde glue. Moreover the CARILITE glue appeared to be less critical in the assembly process, waiting periods within gluing and pressing up to 2 hours did not interfere with the product performance. Double the amount of residual moisture in the dried wood veneers could be tolerated, so less deep drying is needed. Cheap fillers could easily be blended in and the performance was not affected. On the other hand the CARILITE emulsion - uniquely for the industry - is truly one-pot. All alternative glue systems require a glue-kitchen to blend in hardeners and/or catalysts.
These advantages may lead to significant savings for the plywood producers due to higher throughput, lower energy input and less rejects in the processing.
Yet these studies made also clear that the industrial production of plywood is featured by numerous variables, and controlled warranted performance for each factory, wood species and local circumstances will require extensive skills to be developed or to team up with.

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1. Introduction

CARILITE polyketone oligomers of CO and olefins can be cross-linked by diamines to a pyrrole linked thermoset polymer network. That was found to form very good waterboil resistant bonds in glued wood products[1,2]). However the potential of a 2-pot system and the hexamethylene diamine cure used in those studies is limited because the operations in wood glueing factories set requirements w.r.t rheology, minimum pot-life and HSE aspects.

With 1,2-Propanediamine the difference in reactivity between the two amine functionalities enables pre-reacting of one of the amine-sides, while keeping the other more hindered amine group available for further cure later [3]). The polyamine thus formed can be made water-soluble by protonating. Blending of CARILITE with the aqueous solution gives an one-pot aqueous emulsion system with very attractive operational characteristics for the wood industry: low viscosity, water dilution and water washable, stable pot-life, and no free volatile diamine.

Plywood forms one of the most promising market segments for introduction of a new wood glue with water stable properties. Therefore, besides scouting many other applications, in 1997 the main effort in our product development work has been directed towards evaluation in plywood. In this report the experimental results have been compiled and integrated.

Experimental work has been carried out to establish the suitability of CARILITE glues in plywood and its manufacturing process. Commercially plywood is made of cross-plied veneers, which are peeled off from stems of wood, directly imported from the forest (55/45 water/solids) and stored in almost 100°C hot water. The in-line drying of the veneers is one of the critical steps in the process. Glue is applied either by rollers, two-sidedly on every 2nd veneer which is than covered by 2 clean veneers, or in more modern lines by spraying on top of each veneer, except the toplayer. The hot dried and glue coated veneers tend to deform and give voluminous packs of say 15 cm for each panel to become a 18 mm product. The cold pressing renders the packs of veneers compact, smooth and straight, so that they can be fed rapidly into the hot press (the second critical process step), undisturbed without delay. After continuous peeling, drying and glue application, the cold- and hot pressing is a batch operation, with twice a standing time of a stack of glued veneerpacks. The assembly procedure and the sensitivity of a glue to give the right performance in case of stagnation are important factors.

In the period March-December '97, three kinds of experiment series have been conducted for plywood at three locations: at Mississippi US, at Nacka Sweden and at SRTCA. The approaches and methods of the first two were distinctly different and in the SRTCA work we attempted to supplement the ranges of variables in a way to enable an integrated evaluation. In this report we combined the outcome of those studies and present an integrated review of the results.

2. Experimental

2.1 Plywood preparation test runs

Mississippi Forest Products Laboratory (MFPL)
MFPL is connected to the State University and Prof. Terry Sellers leads a recognised expertise centre. On a contract with SCC a trial series was organised aiming at testing the suitability of CARILITE PX-335 emulsion in the existing commercial (PF-based) plywood manufacture operations. With one grade of glue, one woodtype and thickness, one pressure, one temperature, the glue dosage, press-times and waiting time were varied. The performance was judged by the physical response of plywood product to hot water exposure, with a US commercial PF glue as reference.
CASCO Products Lab. Nacka, Sweden
CASCO is a major woodglue company, with probably the broadest range of products in the world, buying in base chemicals and converting those into turn-key glue formulations for end-users. In the course of a joint R&D programme CASCO evaluated CARILITE, mainly aiming at operational aspects. With one glue grade, on Pine wood only, in several typical commercial thicknesses, the main variables included the hot pressing, the cold pressing, the assembly procedure, the glue dosage and the depth of drying of the wood veneers were examined. Again the outcome was rated on basis of the plywood product performance in exposure tests. This programme was carried out using CASCO's own commercial PF glue for plywood as the reference
SRTCA
In order to achieve a more generally applicable quality assessment, at SRTCA more combinations have been tested: other wood species, commercially applied elsewhere, supplementary curing conditions, wider ranges of product dimensions and levels of additives in formulations. Different development grades of CARILITE glue emulsions have been compared, and the nature and curing performance of the products was analysed also as such, i.e. without all artefacts introduced by the plywood and its manufacture.

2.2 Test methods

For tests and analyses mainly international standard methods have been used and details are summarised in the Appendices. The main yardstick for outdoor resistant wood glue is the waterboil resistance and in case of plywood that is measured by EN-314, which prescribes either 72 hours boiling water at 100°C or a repeated cycle of 4 hours and drying steps in between. Both in the Nacka and MFPL work a time saving variant has been applied: impregnation and heating in hot water in a pressure-cooker at 120°C, 2 bars, for 17 hours.
Because the forces in cross-plied wood in non-stationary conditions are very complex, we were advised by WKI[1] that for a proper judgement of the contributions of glue itself to the performance it is better to also carry out EN-204 testing. In parallel grain glued samples, the response to boiling water gives more accurate insight in the adhesion and the hot water resistance, without the effects of the deformations of the cross plied wood. So at SRTCA for most of the glue formulations and relevant parameters also the EN-204 response was monitored.
In order to distinguish the glue curing behaviour from wood-induced effects, at SRTCA with analytical tools the curing reaction was also monitored as well as the cured resin network.
In addition for workability of the glue, the rheological properties have been measured, and their response to storage conditions and formulating the glue.

2.3 Description PX glue systems applied

Since the CARILITE-EP emulsion systems are based on materials of different compositions, the coding has been defined as follows:
PX-100 is the basic CO copolymer with propylene alone

PX-2x0 is the CO terpolymer of propylene and ethylene
First digit indicates CO ter-polymerisation with propylene and ethylene
The x stands for the ethylene content of total olefin, e.g. 30 % E becomes PX-230

PX-3xy code for the emulsion based glue system, i.e. polyamine based, with 2nd CARILITE batch added
the second digit E-content for CARILITE in the polyamine
third digit stands for E-content of the added CARILITE.
For example PX-335 is made of a PX-230 based polyamine with PX-250 added

Typical composition and characteristics of the PX-333, PX-334 and PX-335 glue batches made at SRTCA and WTC and used in the evaluations are shown in Table 1.
At the time the investigation started it was not known what kind of reactivity was feasible, therefore many batches were made and studied with different weight percentages of ethene in the emulsified CARILITE-EP (Table 2). A high percentages of ethene in CARILITE often goes hand in hand with higher molecular weights, higher melting points and higher viscosities , which makes the CARILITE more difficult to handle in the glue processing step. For that reason CARILITE types with up to 30% resp. 50%w ethylene content have been used.

2.4 Gluing operation considerations

The performance of glued wood products is the result of a complex of many variables and in order to achieve the adequate results, understanding of the most important issues in gluing wood is needed. Literature and brochures from DYNO,CASCO and BORDEN for PF glue have been consulted[6-10] and below a summary is given. As will be seen several operational limitations exist also for successful use of PF glues.

Wood type and structure:
Wood products are considered adequately bound when the strength of the joints matches that of the wood, which is observed as wood failure. So the stronger the wood species, the greater the glue line strength should be. Regions in the world historically apply different wood types: US pine, Canada maple, aspen, Mediterranean poplar, Far East and Netherlands tropical deciduous species, Germany beech. Deciduous wood types feature even more roughness than coniferous wood because of the more irregular cell structure. Wood is heterogeneous and anisotropic material, the veneers, planks and flakes are cut randomly oriented to the grain.
Higher density per species and per yearring will cause lower penetration, greater strength and dimensional instability. Adhesion in wood gluing is also dependent on the age of the wood surface. The wood surface is constantly changing both physically and chemically from the time the wood is machined until the adhesive is applied. This change is due to contamination and the chemical changes induced by exposure to heat, light and oxygen. The effect of age is generally more apparent in species rich in resins or extractive content (pine). In construction plywood industry there is no stock, all the wood processed is freshly cut.

Moisture content:
Moisture content of the substrate at the time of gluing is an important factor in producing bonds that will perform well in service. The wood particles, flakes and veneers are dried in-line in specially designed air dryers prior to gluing. Ideally wood should be dried to a moisture content desired in the finished product application (for interior use: 5-7w% and for exterior use 7-16w%). Large differences within the moisture content of wood (> 4%) that is to be glued together will result in considerable dimensional stresses on glue joints and cause delamination and warping. The faster the drying, and the greater the differences in wood structure between yearrings, the more probable differences in moisture after the dryer.
If the wood is very dry there is a tendency for the adhesive to bolt into the surface leaving insufficient for wetting which may lead to starved joints and bleed through of the resin. Too high moisture contents

may give steam blisters, and with PF glue the dilution effect within the woodsurface tends to weaken the bond and water also reduces the curing rate. The recommended moisture content of the timber to be bonded with an ambient RPF glue from Borden should be between 12 and 18w% and in between 3 and 8w% when hot glued with a PF glue from DYNO, the moisture content should be 5% for the PF resin from DYNO.

Assembly time:
Essentially the plywood process consists of continuously operated veneer peeling and drying lines, and a batchwise pressing.. Interruptions in the pressing would require stopping of the veneer line (economically unacceptable) or rejecting of glue coated veneers. Hence in the operation sometimes a stack of glue coated wood veneers is waiting to be pressed. The tolerance of a glue for such standing is important. The glue can e.g. dry out or penetrate into the wood causing starvation. These waiting times or so called assembly times can be subdivided in open (from glue application until the cold press) and closed assembly times (between cold and hot press). Open assembly time should be kept as short as possible. For PF, 5-10 minutes closed assembly may be beneficial, in particular when dense woods are being bonded penetration does not proceed fast and squeezing out of the glue during pressing needs to be prevented. Maximum assembly time depends first of all on the glue spread rate, further on wood species, moisture content and temperature and relative humidity of the air in the workshop. The lower the spread, the higher the temperature and the drier the air, the shorter will the assembly time be.
Cold prepressing at lower pressures improves the bond quality and facilitates further handling of the glued assembly hence shortening the hot pressing cycle. Under all circumstances the glue must not be dried out and be still tacky when the pressure is applied to ensure a good flow and wetting of the opposite veneer.

Glue dosage:
Depending on the veneer surface quality, glue is applied at a rate of about 100-200 g/m^2 single glue line for PVA, UF and PF type of glues. Thick veneers and rougher surfaces require a higher glue spread. When bonding thin veneers, it is important to keep the glue spread low to avoid penetration and blisters, especially when the veneer moisture content is high. For dense timber like beech and oak relatively higher glue spreads are to be used and double spreading is essential. For RPF glues from BORDEN and DYNO much higher glue spreads are advised: 200-500 g/m2.

Fillers and extenders:
In the plywood industry many different types of fillers and extenders are used, depending on local availability, experience, wood type and prices.. Some are needed to adjust the performance of resins which could not be applied without, e.g. liquid PF types have a low molecular weight tail would penetrate into the wood immediately without thickening. On the other hand some cheap fillers just help to fill up the gaps between the adjacent wood layers, in particular with rough surfaces. Very common fillers are based on nutshells, with its inherent moisture stability, but without the tool wear caused by a number of mineral fillers.

Extenders having some adhesive action themselves are added to reduce the amount of primary binder and improve processing properties such as: tackiness, overpenetration resistance, greater assembly time tolerance, faster and stronger prepress bonds.
Extenders like wheat flours (particulate) and starch (non-particulate) control the viscosity and contribute to the tackiness, but excess interferes with the moisture resistance of the glue bond in the product.
For the evaluation of the value of CARILITE, on one hand it is attractive that additives can be easily dispersed and CARILITE can be applied in existing operations without modifications, on the other hand, if some additives are not needed any more, the saving of the extra handling step, the material, the equipment and the logistics together, make CARILITE more economical.

3 RESULTS AND DISCUSSION

3.1 Rheology and pot-life

3.1.1 Viscosity of CARILITE emulsion systems and the use of fillers

Directly after the emulsion preparation relatively high viscosity's are measured (10-1 Pa.s at 25°C), and some air is entrapped as a micro-foam, strongly dependent on reactor and formulation conditions. In 2 weeks time the viscosity drops to its final value of 400-150 mPa.s. This viscosity would be ideal for spraying applications in the particle board and OSB industry. To meet typical PF plywood industry requirements various additives can be added to increase viscosity. Depending whether the glue is applied on the wood surface as a curtain or by a roller coater, the typical wanted viscosities are in between 1-2 and 5 Pa.s. (2.5 and 5 according recent Weyerhauser information)
For the evaluation of the value of CARILITE in existing operations various fillers and extenders have been used and were found to mix easily in the emulsion. The effect of various typical additives on the viscosity was studied at MFPL and at SRTCA (Tables 3 and 4).
Wheat flour was found to give a faster increase in viscosity than nutshell flour. To obtain a good ratio of additives to binder and a good viscosity, extra water can be added without any detrimental effect to the emulsion stability. Small amounts of water added to the finished emulsion steeply reduce the viscosity. Formulations number 8 and 9 in Table 3 were used to make the plywood. As a result of standing the formulated glue can slowly rise in viscosity (formulations 3 and 6), possibly due to the further thickening of the wheat flour. During processing the glue formulation on the roller coater (formulation 8) also a strong increase in viscosity can be found, which might be due to the foaming actions of the rollers in the glue bath. On standing again the viscosity returned to its original level, showing no gelation.
Table 4 shows a strong effect of both wheat flour and coconut shell flour on viscosity. In the plywood tests performed at SRTCA, formulations with and without additives have been used. Typical formulated emulsions consisted often of 30-35 phr coconut shell flour and 5 phr of wheat flour or just of 40 phr coconut shell flour. The consistency of these formulations was very pasty like and were put on the wood veneers with a putty knife or a handroller.
Tables 5 and 6 give the final compositions and characteristics of the glue formulations used by CASCO and MFPL in their trials with PX-335 and PF reference systems.

3.1.2 Temperature and storage stability

Since the emulsion is a water based 1-pot system, temperature and storage time could be of importance for the emulsion stability and reactivity. The smaller the particles are, the more stable the emulsions were found to be at room temperature and generally it takes weeks to months before a (clear brown) supernatant liquid is observed. Excellent room temperature stability is obtained with an average particle size of 0.3-1 µm. If after storage some settling was observed the emulsion could easily be homogenised again by stirring it.
The higher the temperature the faster an emulsion could set and at temperatures below zero the emulsion solidifies. A PX-335 emulsion has been stored at three different temperatures (-20°C, +40°C and 25°C) and its performance was followed as function of the storage time (Table 7). For this work a less stable emulsion had to be used because at that time no optimum emulsion was available. Viscosity, particle size measurements and gluing performance were checked in time. When the emulsion is frozen no effect of storage time at all has been observed. Storage at higher temperatures showed a decrease in viscosity and also smaller particle sizes were measured. More important however was the constant gluing performance. After a storage period of 4 weeks no differences were observed in gluing performance between the three batches stored at different temperatures.

3.2 Reactivity

3.2.1 Gelling measurements

As a yardstick for the onset of the cross linking reaction and gelation of resin systems hot plate gel time measurements are used. A major draw back of this method with aqueous systems however is that first the water has to evaporate before the reaction is believed to take place. Therefore Arrhenius types of curves (log gelation time as function of reciprocal temperature) could not be drawn.
PX-335 systems (Table 8) behaved differently than the PF based systems. With the PF systems first evaporation of water was observed after which a high viscous material was obtained, which starts to gel and becomes solid. With PX-335 glues no intermediate gel-phase was obtained and the sample turned unnoticeably into a dry solid after the water had disappeared. Time till no string or till dry solid were however for both systems very similar. UF systems, known to be much faster also showed a similar behaviour, although there were clear signs of water boiling but no gelation was observed. No evidence of any clear gelation and solidification steps for the PX-33Y systems have been obtained with this technique.
CASCO tried to determine the time to gelation via their standard test in which the glue is heated in a test tube at 100°C.The PF glue although water based gave a gel time of 34 minutes; no gel time could be determined with the PX-335 glue.

3.2.2 DSC and DMA experiments

DSC measurements (Table 9) in closed steel pressure cups have been carried out with small samples (10 mg) of PX-335 emulsion and commercial glue systems (RPF and PF) to determine the onset reaction temperature - a measure of reactivity- and exothermic heat of polymerisation reaction. Clear signals were seen at both competitor systems with a clearly higher reactivity, i.e. a lower onset temperature, for the RPF system compared to the PF system. At the PX-335 emulsion system no exothermic peak at all was observed, while in the past exothermic effects have been observed with pure CARILITE-EP and various diamines (onset temperature of 60°C-90°C). Although for the cure reaction no exotherm was measured, with the Phi-tec apparatus (from EOS/4 department) a clear exotherm was measured of 56 kJ /mole PDA for the primary reaction of PDA with CARILITE. DSC as well as the Phi-tec did not prove to be useful tools to monitor the secondary curing reaction of the present emulsion systems. The reason for the absence of a clear measurable exotherm is not known but could be caused by e.g. the presence or formation of water or by just the absence of any measurable or significant exothermic reactionheat of the already pre-reacted polyamine- and the emulsified CARILITE.

To try to understand the formation of cross links of polyamine with the emulsified CARILITE, glass transition temperature measurements of the glue before and after cure were measured . FTIR and NMR analysis were carried out to follow the cure reaction in terms of CARILITE ketone conversion into pyrrole rings.
Glass transition temperature of pure CARILITE (Table 10) depends on molecular weight and ethylene content. For CARILITE-EP used in the emulsion Tg's have been measured in between -18°C and -13°C, and for the prereacted CARILITE-polyamine +43°C. Apparently there is a strong increase in Tg when pyrrole rings are formed, which can be confirmed by calculations based on group contribution tables as explained by v Krevelen[11] .

DMA measurements on impregnated jute material (Table 11), pressed for different times at elevated temperatures showed two Tg's, a low one at about 30-70°C and a higher one at 110-200°C, both depending on the extend of cure, which might indicate the existence of two phases.
DMA measurements of thin (50 μm thick) cast films and cured for different times in an oven also showed two Tg's (Figures 1, 2 and 3). Both Tg's (5-20°C and 140-200°C) depend again on the extend of cure. No explanation was found for the difference in the low Tg-range for both type of materials. Films made with CARILITE/HMDA systems only showed one Tg (Figure 4), which could indicate that

pre-reacting the starting materials and emulsifying the second component, determine the final properties. Films made with the water based commercial systems did not show an extra low Tg peak (Figure 5) and it was also noticed that these films, except the PVAc one of course, appeared to be more brittle at handling. This extra flexibility of the PX-33Y systems may be valuable for the performance.

3.2.3 FTIR and NMR analysis to determine the state of cure

With FTIR analysis the cure reaction, the conversion of ketones into pyrrole rings, was followed in-situ (Figures 6 and 7). Peaks in the spectra at 1708 cm-1 (decrease in ketone group of CARILITE due to reaction), 1560 cm-1 (decrease in N-H group of polyamine-(acetic) acid salt) and at 3500 cm-1 (decrease of water due to evaporation) were followed as function of time and increasing temperatures. The water and ketone peaks were the most easy to follow. Unfortunately no clear N-H signals from the pure poly amine groups could be obtained.
In the first 300 seconds (Figure 6) water evaporates, which was followed by a decrease in absorbency of the ketone peak (Figure 7). The conversion of the ketone group stops however quite suddenly after 1200 seconds at about 140°C, leaving a high residual absorbency. The relatively decrease in absorbency is equal to the decrease in ketone groups (Lambert Beer), which is calculated to be only 16 % (100% x [1.2-1.0] / 1.2).
The drop in N-H absorbency at 1560 cm-1 was not only observed at the PX-335 glue sample but also at the pure polyamine/water sample (Figure 8) and might only indicate the decomposition of the salt at raising temperatures and decreasing water content.

Theoretically (Table 12) the total amount of ketone groups initially present in the emulsified CARILITE is 22 mole and the amount of hindered amine groups from the PDA is 5 mole. When all the amines are converted into pyrrole rings, 10 moles of ketone can be reacted, leaving 12 moles. The conversion can be defined as the ratio of converted to total ketone groups. In this particular case this can be maximal 10/22= 45%. The lower value (16% versus 45%) found at FTIR indicates that only 35% (16/45) has reacted which might have been caused by various reasons like an early lack of mobility of the molecules, inefficient contact exposure of the ketone groups in the CARILITE emulsified particles to the poly amines group or an inefficient coupling of the ketone groups to the amines, leaving many single and isolated ketone groups in the middle of two reacted ones.

The progress of the reaction was also studied by NMR (Table 13). Materials, pure or impregnated in Whatman cellulose paper, were cured under different conditions and measured afterwards. The percentage of conversion of all ketone groups in the formulation to pyrrole groups was calculated as formulated in the experimental procedures. As can be seen from the data the theoretical values and measured values for the ketone conversion match very well within 10% of accuracy, which is allowed for this method.
This means that a clearly higher degree of conversion was measured and/or reached compared to the FTIR experiments and even after curing under ambient conditions already 80% of the maximum possible conversion was reached.
The difference found between FTIR and NMR can be explained in terms of differences in material preparation, the scanning, and interpretation of the spectra. If further work is required to understand more of the conversion and cross linking both of these techniques could be of importance but have to be evaluated in more detail.

3.2.4 Boiling water resistance of thin glued wood products

The degree of cure is likely to be related to the performance of the glue. Glued panels and cross ply duplex materials, pressed under different conditions, were exposed to (boiling) water after which the samples were inspected. Inspection can either be a purely visual one in which the amount of successful samples after water exposure are noted or according to a standardised test method (EN-

204 and 314) in which the residual wet shear strength is determined. Two commercial available PF glues from CASCO and DYNO were used to compare with.

Table 14 shows the effect of pressing time on the boiling water resistance of glued Birch cross-ply material. In general better performance is obtained with longer pressing times and reached faster at higher pressing temperatures. Figure 9 illustrates to which extend the temperature at the glue line rises for two different press plate temperatures. PX 335 glue systems based on a CARILITE containing 50% ethene were found to be the fastest systems. At lower pressing temperature the effect of ethene content becomes even more evident. The effect was also studied at lower glue dosage. With lower glue dosage apparently shorter pressing times can be realised, which might be due to the inherently smaller amounts of water, which evaporate before the temperature rises above 100°C. Compared to the commercial PF systems the PX based systems showed an excellent and sometimes superior cure rate.

Table 15 shows the effect of pressing temperature, veneer type and veneer thickness for a PX-335 batch in more detail. With higher pressing temperatures boiling water resistant materials can be obtained faster. When thick materials (16 plies e.g.) are pressed at too high temperatures extra attention should be paid to steam formation and blistering. Southern Pine (SWP) veneers from the USA were twice as thick and appeared to need 4 times longer pressing times than the thinner Birch ply's. The effect of cure conditions on the performance of US pine plywood and of thicker Birch plywood panels will be discussed later in more detail.
Effect of pressing time on glue performance was also measured on glued parallel grain beech panels, using the standardised EN-204 test conditions (Table 16). Dry glue strength and cold water resistance is achieved already after 2 minutes of pressing at 140°C, though in that case at the glue line the maximum temperature reached only 75°C (Figure 10). Inspection of the fracture surface after shearing of non exposed dry panels showed however that about 5 minutes is needed to obtain a strong glue line, stronger than the wood shear strength of beech. Pressing times of at least 5 minutes are also needed to obtain boiling water resistance. Experiments were repeated with a formulated PX-335 glue and compared with the commercial PF glue from CASCO (Table 17). Under the used pressing conditions, with fillers the PX-335 glue reached a sufficient strength twice as fast (5 minutes compared to 10 minutes) as the PF glue from CASCO.

3.3 Pressing of thick multiplies

At SRTCA Birch and Pine wood, at CASCO Pine wood and at MFPL Southern Pine wood was used to examine different parameters and to compare the PX-335 glue with commercial PF glues. Thickness, number of veneers (determining the distance between press platen and furthest most inner glue line) and the type of wood determine the pressing conditions to obtain a water resistant plywood.

Tables 18 and 19 show that about 5 to 7 minutes of pressing at 160°C is needed to press a 11 mm thick 5 ply-Birch or 8 ply-Pine ply wood (furthest distance glue line and press platen is about 5 mm.). Table 20 shows that about 8 minutes pressing at 160°C is needed to obtain a fully boiling water resistant 16 mm thick Birch 7-ply. Layers which were under cured and do not pass the water boil test often show glue failure when with a sharp knife the layers were separated.
Physically the temperature equilibration follows the Fourier laws and the time needed to achieve a given temperature rise is a function of the square of the thickness. Yet for not too thick panels DYNO gives their customers a prescription to calculate the pressing time for the PF glue in the brochure which is linear with the thickness. In line with this from the data we can derive a rough rule of thumb to estimate the minimum pressing time for gluing an uneven number of veneers:(at 160°C):

<u>t(min) = ½ + 1 min / mm distance glueline-press.</u>

Table 20 shows that longer pressing times are needed for the PX-333 and PX-334 glues. In this comparison however both commercial PF glues show faster pressing times than the PX-335 glue. This is quite surprising in view of the results found earlier with duplex materials.

Figure 11 once more illustrates the slow temperature rise of the inner glue line layers but also clearly shows that after the panels have been taken out of the press, post-cure still can continue because of the very slow cooling down in the centre as well.

CASCO examined, using the knife test, the quality of the glue lines directly after pressing times at 150°C (Table 21). In their evaluation a formulated PX-335 glue showed to be much faster than their PF reference. Instead of 5 minutes only 3 minutes pressing was sufficient to obtain a 15 mm thick Pine 5 cross plywood, which had sufficient amount of wood failure (>40%). Reasons for the much better performance could be due to the different conditions used: Pine wood instead of Birch, fresher wood veneer surfaces, dryer wood (3% compared to 8%), different fillers for both PF and PX-335 and the way of application (roller instead of putty knife).

MFPL compared processing and performance of a PX-335 glue (made by WTC) with their commercial PF glue in their typical operation conditions. Southern pine cross ply panels, 12 mm thick, were exposed to boiling water according to their standard procedure and residual wet shear strengths and amount of wood failure were measured. Results were then compared with the EN-314 standard norm for outdoor application. Table 26 (part A and F) shows a comparable performance for both glues. With the PX-335 glue, 12 mm thick pine wood cross ply panels can be made at 150°C within 3-4 minutes, which pass the EN-314 norm for outdoor applications. The other parts of this table concerns the effect of processing conditions and will be discussed elsewhere in this report.

3.4 Formulation and processing parameters

3.4.1 Extra CARILITE in the emulsion

Emulsion processing studies had already shown that optimal emulsion stability and low viscosity are obtained when an excess of CARILITE is used in the emulsified phase. The mass ratio of the amount of CARILITE for the emulsified phase to the amount of CARILITE for the poly-amine synthesis was found to be optimal between 1.3 and 1.5 (Tables 1,2). This implies though that after curing a fraction of CARILITE will not be cured with the polyamine.

The effect of adding an additional amount of pure CARILITE was further studied (Table 22). In this evaluation maximum cure conditions were used to be sure that reactions have been completed and that solely the effect of extra CARILITE on the glue performance could be examined. Adding extra CARILITE together with extra water to keep the solid content constant showed detrimental effects on the emulsion stability. Adding just extra CARILITE, which could easily be emulsified in the present emulsion with a Turrax, showed an increase in emulsion viscosity and improved stability against settling. However with increased amounts of CARILITE the Tg and also the glue performance dropped. Maximum tolerated amount of extra CARILITE appeared to be 100%. This would make the total ratio of emulsified CARILITE to polyamine converted CARILITE: 2.3 / 1.

3.4.2 Formulation and glue dosages

Fillers and extenders are often used in the industry to improve processing, performance and costs as described in paragraph 2.4, based on local needs. At SRTCA the combination of filler (coconut shell flour) and wheat flour was in first instance chosen in the same way: introduce better tackiness without excessive viscosity increase and detrimental effect on the water resistance. To study the effect of filler and glue content on the water boil performance, experiments were carried out with duplex cross plies, pressed at 140°C for a certain period of time (Table 23 and 24). With low glue dosages best results have been obtained (Table 23), which is possibly related to the amount of water which is equal with the amount of glue applied and has to be removed first before the temperature can rise over 100°C.

The fillers appear to have a strong effect on performance and minimum press time to obtain a boiling water resistant Birch cross ply (Table 24). Starch and wheat flour can have a very strong negative effect if too much is used. Coconut shell flour and Kaolin appeared to have a positive contribution to the glue performance within the current dosage. The ability of additives for catalysing the cure reaction has to be kept in mind when they are used to formulate glues.

CASCO and MFPL also varied the glue dosage. CASCO used in their evaluation relatively smooth Pine wood veneers , typical PF pressing conditions with an open assembly time of 5 minutes and a pressing times of 9 minutes for 19 mm thickness. At the knife test of freshly pressed panels no significant differences were observed using 120-180 g/m2 with both PX-335 and PF glues (Table 25).

MFPL made plywoods of 3x4 mm with only 3 minutes press time with rough pine wood veneers and found a strong effect of glue dosage (107-210 g/m2) on EN-314 performance after boiling water exposure (Table 26, part B,D). Good results were obtained with the higher glue dosage and binder content. With a too low binder content (part D) an insufficient cold tack was obtained after pre-assembly and cold press period, as part of the planned programme those panels were not hot pressed.
The differences found by CASCO and MFPL can be caused by many parameters: type of wood, roughness and moisture content, temperature and relative humidity of surrounding air, assembly times which will be discussed later, glue application, type and amount of fillers. This illustrates that a new type of glue has to comply with many different customer operation conditions and that adaptations may have to be made for specific situation.

3.4.3 Moisture in formulation and wood

In making plywood products the depth of wood drying needed is a critical factor because of the high costs involved and the final quality and performance of the product. Tests have been carried out to test the effect of moisture, We varied the wood moisture content and extra water in the formulation on the performance of CARILITE PX-333.
Moisture contents of birch veneers varying between 1 and 11w% could easily be glued and passed all the EN-314 norm (Table 27). Wood containing 17w% of moisture could also be glued but did not fully pass the EN-314 norm. The reference PF glue from DYNO failed also. Such high wood moisture contents would also increase the risk of steam blistering as was explained to us by CASCO.
The effect of wood moisture content combined with formulation water content on the boiling water resistance of cross ply Birch duplex was examined with a PX-335 batch (Table 28). With increasing water levels in filled and unfilled formulations longer pressing times were needed to obtain 100% water boil resistant cross ply panels and the effect was more pronounced than the effect of wood moisture levels. Best results were obtained with dry Birch wood and low formulation water levels.

The effect of moisture content on the pressing time needed, was also examined with parallel grain beech panels according to the EN-204 norm. Panels were dried to moisture contents of 1w% or equilibrated to 8w% and glued with PX-333 (Table 29). With dried panels better performance and also a fully water resistant glue was obtained, faster than with higher moisture content panels.

CASCO varied the wood moisture levels between 4.5 and 9.5w% and found a significant difference between the PF and PX-335 glues (Table 30). PF appeared to be very sensitive to wood moisture compared to PX-335, which did not show a detrimental effect. This can be of great importance for the wood glue industry in terms of cost savings at drying the veneers.

3.5 Assembly operations

After bringing the glue on the veneers (continuously), the bundles for each panel have to be stacked cross-ply (semi continuously). If interruptions occur between those operations the glue may dry out. Subsequently the stacks have to wait till the batch-wise cold pressing step and again for the hot press. These typical operation conditions might effect the glue properties in both negative and positive way.

CASCO investigated the effect of open assembly time and cold pre pressing of filled and unfilled formulations on the tackiness of the glue. A good tackiness means that after cold pressing the veneers will stay glued together and will not come apart on standing. For the PF glue from CASCO a certain amount of open assembly time is required to obtain a good tack after a short cold press time. No open assembly appeared to be needed for the PX-335 glue (Table 31), which means more freedom and can make processing faster. Extra open assembly times between 5 and 120 minutes also appeared to have no significant different effect on the glue performance after hot pressing for both types of glue (Table 32).
The effect of cold press time on the tackiness was investigated by CASCO for an unfilled PX-335 formulation and compared with their standard (filled) PF glue. Superior tack behaviour was found for the PX-335 glue, even at very low pressing times and also for a Pine veneer with a high moisture content (Table 33). The PF glue did not perform well in this comparison. The cold pressed panels were found stable for at least 30 minutes between cold and hot pressing.
As a whole the window of operations for CARILITE was found to have much more freedom than for PF in the CASCO work

At SRTCA the effect of cold pre pressing and open assembly times have been briefly checked with a PX-333 and a PX-335 glue batch.
After an open assembly time of 10 minutes and longer no tack was felt anymore and when the glued panels were broken apart after the hot press operation only on one surface glue was seen.
A certain period of cold pressing clearly shows a positive effect on the water boil resistance of Birch cross plies, which might imply that shorter hot press times can be used (Table 34). Also somewhat better results were obtained with parallel grain beech panels (Table 35). After cold pressing no separation of the veneers were observed and at splitting the glued veneers at both sides glue was seen, indicating a good glue transfer.

The effect of the waiting period between the cold press and the hot press on the tackiness and water boil resistant was also examined by MFPL (Table 26, part C,F). Best results were obtained with waiting times between cold and hot press as short as possible. When 15 minutes was waited panels tended to come apart (and were not pressed further), other panels gave a decrease of boiling water resistance. With their PF reference glue 30 minutes could be waited between cold and hot pressing without any negative result. (Note: this was referred to as standard, but not measured under the extremely dry conditions of the CARILITE testing).These results are in contradiction with CASCO's results mentioned in Table 31.

3.6 Confocal analysis of the glue line between cross plies

With the aid of confocal microscopy the glue line and glue penetration into the adjacent wood layers after hot pressing could be visualised. In contrast with the reference PF glue (Figures 13 and 14), the CARILITE glues with (Figures 12 and 13) and without fillers (Figure 15) did not show penetration into Beech, Pine and Birch wood cells. Therefore it is believed that lower glue dosages can be used with the PX-33Y glues before starvation of the glue line occurs (Figure 12, below). On the other hand with PF the penetration is believed to be needed to give anchoring and bonding to the wood. Only the sap canals of the adjacent wood layers were filled, when no filler and high dosages were used (Figure 15). With Phenol formaldehyde (PF) glued materials a lot of penetration was observed, not only the spaces around the canals were filled, but also the solid wood cell walls show fluorescence as a sign that the resin is absorbed.

4. Evaluation and conclusions

In the total production cost of a volume of plywood panels, the resin costs amounts to 5-10 % according to different sources[4, 5]. The wood veneers form 30-50 % of the product costs. Hence the further operation and capital related costs are almost 50 %. For a new glue there are basically 2 routes to be competitive: A-on the resins costs and B- on the operations costs, i.e. improved output for a given cost or reductions on the operations costs. If the price per kilogram glue is lower, or if the adequate performance can be reached at a lower glue dosage, the new glue would be competitive, though related to the panel volume the gain is a part of the 5-10 % resin share of the production cost. Advantages in the throughput and operations can influence the capital and operation related share of the plywood costs. The competitive argument on the glue price or dosage can be more easily demonstrated to a potential customer. The operational advantages may give more gain, but for convincing an end-user, more technical arguments are needed. CASCO Products delivers glue formulations to end-users together with the technology for optimal performance and possesses the kind of special expertise, calculation models and know-how to demonstrate relative advantages in the glueing operations and its effect on the economy.

The fact that the CARILITE glue is truly a 1-pot system with the hardener and catalyst already present, makes it unique. It may save the costs of a glue-kitchen and its operation at the customer. Cheap fillers could easily be blended in, so CARILITE can also be applied in the existing schemes, even up to high amounts. Nutshell flour nor kaolin did deteriorate the product properties. High levels of hydrolysable starches and some types of wheat flour will affect waterboil resistance. Moreover it was found that once formulated, the glues were stable for a considerable time. This may make it possible to formulate the glue in advance and deliver instant formulations.
The glue emulsion is very stable, it does not deteriorate in storage for more than 3 months. Also exposure to extreme temperatures from -20 to +40°C did not damage the performance. These factors may mean a significant cost saving for customers in terms of logistics operations and savings on otherwise rejected glue volumes as a result of disturbances in transport or production. Yet the strong tendency to form micro-foams and the accompanying rise of viscosity, may be a drawback in some operation conditions. Anti-foam agents have to be tested.
The facts that the CARILITE glue emulsion is easily diluted with water, and that the addition of small amounts of water to the finished glue cause a steep reduction of the viscosity, make the removal of uncured glue very easy. Both CASCO and MFPL commented as an important advantage that the cleaning was very convenient. The profiled rubber rollers of the coater at MFPL, after a full day of rolling with formulated glue, were cleaned instantly just by means of the cold water fire-hose.

In the SRTCA studies it was demonstrated that with very thin glue layers good bonding could be achieved on laboratory scale. If such thin layers can be applied industrially, and the bonding performance confirmed for large panels, it would mean a strong competitive point versus PF glue. The CSLM studies revealed a clear distinction in the behaviour at the glue lines. PF has a strong tendency to penetrate the wood, while the CARILITE from the emulsion stays on the surface. Some penetration is believed to contribute through anchoring, however for PMDI it was also found that without penetration adequate bonding could be reached at lower glue dosages.

Comparing the different CARILITE grades, the cure reaction rate was faster for the PX-335, in line with earlier findings that the cure becomes faster with increasing ethylene content and increasing molecular weight. The network formed features two Tg's. The high Tg may be the basis for the strong hard material properties, the low Tg may cause the flexibility. An explanation might be that the product network consists of two phases, possibly resulting from the CARILITE droplets between poly amine. Though with DSC no heat of reaction could be measured upon heating the emulsion till 200° C, the cure reaction can be monitored by FTIR/NMR techniques. However the actual conversion level of C=O groups into pyrroles and the accurate relationship of that and the cross-link density with the product performance requires further study.

In comparison with a commercial PF glue used in plywood, in the Swedish comparison the PX-335 was found in several series to reduce the required press time by about 40 % repeatedly: 3 minutes compared with 5-7 for a 15 mm thick 5-ply.

In the US tests the plywoods qualifying for EN-314 water resistance had the same range of press times as the reference PF glue ,3, 4 and 6 minutes for a 12 mm thick 3-ply. The fact that the press time did not differentiate, might be a signal that another factor (dry out of glue on wood) was more important.
In the SRTCA studies also similar pressing times for PX-335 and the PF glues were observed, when thick ply woods were pressed.

CARILITE accepts double the amount of moisture left in the wood normally as shown by CASCO and SRTCA. An even higher wood moisture content can be accepted for several wood species, and the moisture can even have a beneficial effect on the glueing performance. However systematic variation of the moisture contents showed that addition of extra water to the glue has a detrimental effect, also when the total moisture present during pressing is the same.

In the Swedish tests it was demonstrated that CARILITE allows for standing times up to 2 hours between glue application and cold pressing, and again 2 hours between cold press and hot press. This is much more than usual for PF glue. Unfortunately the American work showed equally clear that the conditions of the climate and the wood material are important and with the extremely dry wood and hot and dry air circumstances at the MFPL experiments, hardly the minimum assembly time (15 minutes) could be allowed. Similar to other glues, the open assembly time, with the glued surface in the open, before stacking the next veneer, is still limited to 5-10 minutes, in particular with high filler contents the glue surface will otherwise dry out.
Reviewing the whole series of experimental results it is clear that many complex and interacting variables play a role in successful plywood production. Small variations on one aspect may completely eliminate previously found improvements. Controlled warranted performance for each country, wood species and local circumstances will require extensive skills to be developed or to team up with.

Amsterdam, March 1998

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Table 1: Components to make the CARILITE glue batches and the characteristic of the emulsion

composition (pbw)/ Analysis	Poly amine	Emulsion SRTCA-PX-335 used by CASCO	Emulsion WTC 30/50 used by MFPL
preparation polyamine:			
CARILITE 30% E	1000		
1,2 propane diamine	370		
acetic acid	120		
reaction water	-180		
additions to make emulsion:			
extra water		2700	
CARILITE 30,40 or 50% E		1500[1)]	
Salicylic acid		28	
Characteristics:			
% dry		50	50
average droplet size, µm		1.05	2.53
viscosity, mPa.s		320	900

1): For the first batches made this value was 1300 grams, making the ratio CARILITE-polyamine to emulsified CARILTE 1000/1300 (1/1.3); see Table 2.

Table 2: CARILITE batches used in the SRTCA evaluations

Glue batch code	CARILITE-amine (I)		Properties of (I)		Emulsified CARILITE (II)		Properties of (II)		Mass ratio[1] mixture I/II
	%E	batch code	Mn	Mw	%E	batch code	Mn	Mw	
JF9611S	30	35214C	1810	3560	30	35214C	1810	3560	1/1.3
JF9619	30	35214G	1785	3348	30	35214G	1785	3348	1/1.3
JF9623S	30	35214G	1785	3348	30	35214G	1785	3348	1/1.3
JF9703	30	35239	1830	3117	30	35239	1830	3117	1/1.3
JF9704	30	35239	1830	3117	30	35239	1830	3117	1/1.3
JF9707	30	35240	1720	3020	30	35240	1720	3020	1/1.3
JF9717	42	35241	2048	3502	42	35241	2048	3502	1/1.3
JF9718S	30	35214G	1785	3348	30	35214G	1785	3348	1/1.3
JF9727	30	60018	2248	4153	30	60018	2248	4153	1/1.5
JF9728	30	60018	2248	4153	40	35249	3288	6362	1/1.5
JF9729	30	60018	2248	4153	50	35250	3548	6834	1/1.5
JF9733	30	60018	2248	4153	50	35250	3548	6834	1/1.5
JF9763	30	60003	1938	3535	50	60005	3151	6319	1/1.5
JF9764	30	60004	2153	3938	50	60024	3763	7388	1/1.5
PX335 for CASCO	30	60018	2248	4153	50	35250	3548	6834	1/1.5

1): I/II = [mass of CARILITE I used for the polyamine] / [mass of emulsified CARILITE II]

Table 3: Receipt screening and viscosity measurements at MFPL plywood testing

receipt	1	2	3	4	5	6	7	8	9
CARILITE WTC 30/50, phr	100	100	100	100	100	100	100	100	100
wheat flour		5	10	2	2	2	2	4.5	2
pecan nut flour				8	11	14.5	14.5	37	14.5
water							4	25	2
total	100	105	110	110	113	117	120	167	119
dry binder	50	48	45	45	44	43	41	30	42
dry solids	50	52	54	54	55	56	54	55	56
VISCOSITY/ spindle#4, 20rpm									
measured directly, Pa.s	0.9	2.6	8	2.7	4.5	8	2.5	3.4	6
measured after time Pa.s			8.9[1)]			9.0[1)]		10.3[2)] 2.9[3)]	

1) after 1 hour
2) after 4 hr's on roller coater
3) plus standing 20 hr's at rest.

Table 4: Viscosity of pure and formulated emulsions used at SRTCA

Filler I	Extender	Temperature (°C)	Viscosity (Pa.s) at different shearrates (s^{-1})			
phr of PX-333			5	9	19	37
-	-	25	0.35		0.3	
-	-	20	0.4		0.37	
coconutshell						
20	-	20	2.1	1.9	1.7	1.5
27	-	20		2.7	2.5	2.2
35	-	20		4.6	4.1	3.5
40	-	20		10	8	
coconutshell	Wheat flour					
20	13	20	35	27	22	
27	5	20	9.4	8.3	7.7	
35	5	20	15	13	10	
35	5	25	8	7	5.5	3
	Wheat flour					
-	13	20	1.3	1.2	1.1	1
-	20	20		4.5	4.1	3.8
Kaolin						
35	-	20	2.3	2	1.8	
phr of PF-1550						
-	-	25		0.18		0.17
		20		0.24		0.22
coconutshell						
27		20	5.5	4.4	3.8	3.2

Table 5: Formulations with PX-335 and PF glue used by CASCO

Glue system	Components	Remarks
Shell PX-335	glue as such or with 12 phr wheat flour Prima-T and an additional 5 phr water.	Viscosity of the unfilled formulation = 320 mPa.s filled formulation = 2300 mPa.s Solid content of filled formulation = 53w%
CASCO PF 1550 (55w% water, 45w% phenol-formaldehyde)	Phenol resin PF-1550 with 1.6 phr hardener (Na_2CO_3) and 15 phr wheat flour Prima-T and 7.5 phr water	Viscosity of the filled formulation = 1550 mPa.s Solid content of the filled formulation = 50w%

Table 6: Formulations used by MFPL

Glue system	Components (phr)			Remarks		
Shell PX-335 (WTC)	EMULSION code	(8)	(9)	EMULSION code	(8)	(9)
	wheat flour	4.7	2	dry solid content (%)	55	30
	pecan nut flour	37	15	dry binder content (%)	56	42
	water	25	2	Viscosity (mPa.s) (spindle#4, at 20 rpm)	3400	6000
MFPL PF resin BORAD of Georgia Pacific	47w% solids in water 28w% Binder					

Table 7: Stability of glue emulsion at different storage temperatures

storage temperature (°C)	Storage time (days)	Viscosity at 25°C (mPa.s)	Particle analysis (μm)			Boiling water result after 2' 140C hot pressing success rate
			mean ± SD	< 50%	<90%	
+20	0	124				
	7	125	1.63±0.60	2.57	1.68	
	28[1)]	122	1.49±0.60	2.33	1.60	100 % Pass
+40	0	124	1.63±0.60	2.57	1.68	
	7	100	1.74±0.61	2.76	1.73	
	28[1)]	75	1.41±0.65	2.17	1.53	100% pass
-20	0	124	1.63±0.60	2.57	1.68	
	7	126	1.71±0.70	2.56	1.70	100% pass
	28	120	1.65±0.57	2.35	1.65	

1): Batches needed to be stirred again to mix the settled material with the liquid material.
Glue batch used: PX-335 (JO-107).

Table 8: Hot plate reactivity; a measurement for gelation speed

Temperature (°C)	Time to evaporate water (sec)	Time to string (sec)	Time to no string (sec)	Remarks
CARILITE **PX-335** emulsion				
100	no water boil seen	-	130	from liquid to viscous to dry solid,
120	,,	-	80	,,
140	,,	-	60	
160	,,	-	50	
water based **PF** system ex CASCO (PF-1550)+ 1.6 pbw H2601 (Na_2CO_3)				
100	-	75	130	no water boil seen
120	-	70	100	no water boil seen
140	30	60	80	boiling water
160	30	50	70	boiling water
water based **PF** system ex DYNO S576+H630				
100			130	
120			100	
140			85	boiling water
160			75	boiling water
water based industrial **UF**/1.25w% NH4CL system ex EPINAL; U/F=1/1.2				
120	no water boil seen	(45)	52	
140	22		32	from liquid to dry solid
160	15		20	from liquid to dry solid

PX-335 glue batch used: JF 9763

Table 9: DSC measurements on emulsions and competitor resins

System		DSC results	
		Exothermic heat of reaction (J/g total intake)	Onset temperature of Exotherm (°C)
PX-335 emulsion	50w% CARILITE	-	-
PF DYNO (S576/H630);	38w% PF	66	130
RPF Borden (RS12/RXS22);	83w% RPF	150	60

PX-335 glue batch used: JF9733
DSC conditions: heating ramp 20°C/min from 20 to 250C

Table 10: Glass transition temperatures of the glue components

CARILITE material and batch number	Molweight Mw	Glass Transition Temperature (°C) onset	midpoint
CARILITE -P 29330/5	1490	-34	-18
CARILITE-P 29348/D	4180	-25	-21
CARILITE-EP(30%) 35248	3841	-22	-18
CARILITE-EP(40%) 35249	6362	-17	-15
CARILITE-EP(50%) 35250	6834	-16	-13
Polyamine salt powder (based on CAR-E 30%)		32	43

DSC conditions: heating ramp 20°C/min from -50 to 150°C

Table 11: Glass transition temperature (DMA) of jute impregnated emulsions

JF batch	Cure time/temp (min/°C)	DMA signals (°C)			
		E'onset	E'midp	E"peak	tan d peak
PX-333	1000/23	0		12/110	14/111
	2/140	6	50	30/111	33/115
	5/140	12		49/145	49/152
	20/140	14			
	60/140	16			
	5/200	23		62/175	69/175
	20/200	24		77/ >200	79/ >200
polyamine-salt	5/120	52		75	90
PF ex DYNO	2/160	170			

PX-333 batch used: JF9717S

Table 12: Theoretical conversion values of ketone and amine groups at synthesis and cure.

Component in emulsion[1)]	Amount of reactive groups (mole)			Amount of reactive groups left over (mole)		
	ketone	NH2	NH2 hindered	ketone	NH2	NH2 hindered
<u>synthesis of poly-amine</u> 1000 grams CARILITE-E 370 gram PDA	15	5	5	5	0	5
<u>completing the emulsion</u> with 1500 gram CARILITE-E and 2700 gram water	22	0	0	27	0	5
after cross linking reaction				17	0	0

1) for extra information see tables 1 and 2

Table 13: Cure of PX-333, as such or in cellulose paper, followed by C-13 NMR.

Material	Cure conditions	Converted C=O measured (%)	Converted C=O theoretical (%)
CARILITE	-	0	0
poly amine powder	-	72-75	66
glue system as such	no cure		28
	fully cured		57
thin film casting	over night 23°C	45-47	
thin film casting	over night 23°C/3 hr 110°C	60-63	
impregnated Whatman			
impregnated Whatman	over night 45C	55-58	
	45°C plus 5 min 200°C press	60-66	

PX-333 glue batch used: JF9623S

Table 14: Effect emulsion grade, press temperature and glue dosage on Water boil resistance of Birch duplex cross plies.

			Percentage of samples past the boiling water test							
Pressing time (min)			1	1.5	2	3	4	5	8	12
System grade	Glue dosage[1)] (g/m2)	Pressing temp. (°C)								
PX-333	170	140	0	0	0	50	100	100		
PX-334			0	0	0	100	100	100		
PX-335			0	0	50	100	100	100		
PF1550				0	75	100	100	100		
S576/H630				0	25	100				
PX-333	170	120			0		0		25	100
PX-334					0	0	25	75	100	100
PX-335					0	0	100		100	100
PF1550			nG		0	0	25	100	100	100
S576/H630			0		0	0	50			
PX-333	110	140	0	0	50	100	100	100		
PX-334			0	0	0	100				
PX-335			0	0	100	100	100	100		

PX glue batches used: JF 9727 (PX-333) , JF 9728 (PX-334), JF 9729 (PX-335)
1) Glue formulation: filled with 35 phr coconut shell and 5 phr wheat flour)
Moisture content wood 6w%
nG= time too short to glue

Table 15: Minimum pressing times for different temperatures and wood veneers to obtain boiling water resistance

Type of Wood and thickness	Glue dosage (g/m^2)	Temp=120°C	Temp=140°C	Temp=160°C	Temp=200°C
		minimum pressing times for water boil resistance (min)			
cross duplex Birch; 4.5 mm	110		2	1-1.25	
	170	4	3	1.25-1.5	
cross duplex SWP; 8 mm	110		8-10	6-8	3

PX-335 glue batch JF9733
Glue formulation: filled with 5 phr wheat flour and 35 phr coconut shell flour

Table 16 : Minimum pressing time to obtain EN-204 qualified beech panels with PX-335

Cure time at 140°C (min)	Max temperature reached (°C)	Dry shear strength (MPa)	% Glue failure at dry shear	Cold water resistance	Boiling water resistance
				success rates	
0	20	0	100	0	0
1	45	0	100	0	0
1.5	55	0	100	0	0
2	75	9.1	100	4 / 4	3 / 4
3	95	9.2	100	4 / 4	2 / 4
4	110	10.7	45	4 / 4	3 / 4
6	125	--	--	-	--
8	130	12.7	0	4 / 4	4 / 4
12	135	--	--	--	--
16	140	11.7	0	4 / 4	4 / 4

PX-335 batch same as for CASCO
Moisture beech planks 7 w%; glue dosage 110 g/m2 without fillers

Table 17: EN-204 testing of PX-335 and PF from CASCO; Effect press time at 140°C

formulation (170 g/m2)	Pressing time,min	EN-204 test results					
		dry testing after no exposure		wet testing after 4 days cold water		wet testing after 6 hr's boiling watei	
		Strength (MPa)	Fracture type	Success rate	Strength (MPa)	Success rate	Strengt (MPa)
PF+	3	0					
1.6 pbw Na_2CO3+	5	5.6±2.4	glue	0/3	0	1/5	0.15
40 pbw Coconutshell	7	10±0.7	glue	2/3	0.9±0.4	4/5	3.6±1.
	10	7.9±1.8	wood	3/3	4.8±0.3	4/5	4.3±1.
	3	14.6±1.2	G/Wood	3/3	3.4±0.4	3/5	4.4± 2.
PX-335 (JF9763)+	5	11±4.4	wood	3/3	4.9±0.6	5/5	4.4±0.6
40pbw coconutshell	7	13.5±0.4	wood	3/3	5.9±0.7	5/5	7±0.52
	10	12±0.8	wood	3/3	4.8±1.7	5/5	6.1±1.
	15	10.2±0.9	wood	3/3	6.3±0.7	5/5	6.1±0.2

wood moisture = 10 w% ; no assembly time

Table 18: EN314 testing of 5-ply Birch panels, glued with PX335;Effect pressing time

System	Pressing time at 160°C	Knife test dry material failures type	EN 314 success after boiling/drying 63C/boiling cycle	
			success rate	strength (MPa)
PX-335	3.5	glue	0/6	
	5	wood-glue	2/6	
	7.5	wood-glue	5/5	1.0± 0.3
	10	wood / wood-glue	5/6	1.2±0.1

PX-335 batch JF9763
Glue dosage 170 g/m2 with 30 phr coconut shell and 5phr wheat flour
No assembly times
Total product thickness is 11 mm

Table 19: Effect cure time PX-335 on boiling water resistance of 8-ply Pine multiplex

Pressing time at 160C (min)	Knife test results: type of fracture surface	Boiling water resistance
3	glue failures	0
4	wood-glue failures	0
6	mainly wood failures	100%

Glue batch PX-335: JF 9763
Glue dosage: 170 grams / m^2
Glue formulation: 5 phr wheat flour and 35 phr coconut shell flour
No assembly times
Total product thickness is 11 mm

Table 20: Development of boiling water resistance of a 7 ply Birch cross ply panel

Glue batches	PX-333	PX-334	PX-335	PF DYNO S576/H630	PF CASCO PF-1550/ 2601
Press time at 160°C (min)	type glue layers in between the 7-ply, which failed				
4	1,2,3	2,3	3	**none**	too short to glue
7	1,2,3	2,3	**3**	**none**	**none**
10	2,3	**3**	**none**	-	none
13	**none**	**none**	none	-	none
16	none	none	none	-	none

Glue batches used: JF9727 (PX-333), JF9728 (PX-334) and JF9729 (PX-335)
Glue dosages: 170 grams / m^2
Glue formulation: 5 phr wheat flour and 30 phr coconut shell flour
Moisture content wood= 8%
Total product thickness is 16 mm

Table 21: Effect of pressing time on PX-335 glue performance.

Glue batch	PF 1550 CASCO	PX-335, filled
pressing time at 150°C (min)	Knife test results: Percentage wood failure in the middle glue layers of the 5 ply (%)	
7	80	80
6	80	90
5	65	80
4	20	60
3	0	70
2	0	10

Glue dosage: 180 g/m2
thickness veneers: 3.1 mm
Moisture content: 2.9w%
Product: 5-cross ply
No assembly time

Table 22 : Effect extra emulsified CARILITE in glue formulation on performance

Percentage CARILITE in addition (w%)	Viscosity (mPa.s)	drop size (µm) mean diameter D[3,2]	Tg (DMA) (°C)			EN-204 test shear strength (MPa)	
			E'onset	E"	tan d	dry	after boiling water
0	50	1.9	39	88	102	9	5.2
50	100	2.2	28	69	80	8.5	4.7
100	200	1.8	20	50	69	8	4.8
150	450	1.4	15	39	45		
200	1000	1.3	8	30	40	6.5	2.5

Glue PX-333 (JF9619S)
Glue dosage: 140 g/m2
Pressing at 200°C for 10 minutes;

Table 23: Effect of PX-335 glue and filler dosage on water boil resistance of Birch cross duplex.

	Percentage of the samples passed the boiling water test							
PX-335 Glue dosage (g/m^2)	40	45	50	55	60	65	80	100
Filler dosage (g/m^2)								
0	100%		100%				0	0
9		100%						
18							0	
22					0			
30	100%		50%				0	
34		50%						
40	100%					50%		0
50					50%		50%	
60							50%	0
80							0	
100								

Pressing at 140°C for 2minutes
Grey area: Formulations with a too high filler content to apply easily.

Table 24: Effect of fillers on the water boil resistance of Birch cross duplex glued with PX-335

	Percentage of samples past the boiling water test				
pressing time at 140°C (min)	1	2	3	4	5
Fillers / amount (phr)					
No fillers	0	25	100	100	100
Bakers Wheat flour					
5	0	0	50	100	100
15			0	0	0
30			0	0	0
Starch					
10	0	0	0	0	
Kaolin					
10	0	75	75	100	
30	50	100	100	100	
Coconutshell flour					
30	0	100	100	100	
Wheatflour/ Coconutshellflour:					
5/30	0	50	100	100	
Starch / Kaolin					
7 / 35	0	0	100	100	

Glue batch PX-335 (JF9763)
Wood moisture = 8w%
Glue dosage is such that amount of glue and water remains the same:
100 g/m2 if no fillers are used, 110 g/m2 (5-10 phr fillers) and 120 g/m2 (30-40 phr fillers) :

Table 25: Effect glue dosage on PX-335 glue performance

Glue batch	PF 1550 CASCO	PX-335, filled
Glue dosage (g/m2)	Knife test results: Percentage wood failure in the middle glue layers of the 5 ply (%)	
180	75	65
150	60	75
120	65	65

thickness veneers: 3.8 mm thick
Moisture content: 4.5w% moisture
Product: 5- cross ply
Open assembly: 5 minutes
Hot press (150°C): 9 minutes.

Table 26: MFPL plywood test results: Effect of press time, glue dosage and assembly time on Performance of 12 mm thick SWP ply wood. (part A t/m F)

Glue dosage g/m2		Glue mix receipt [1]	Time between cold-hot Press time (min)	Hot press time (min) at 150°C	Boiling water results	
total	Binder				wood failure (%)	shear strength (MPa)
results with a formulation with total solid / binder ratio = 1.33 [1]						
part A: Effect press time						
166	69	9	0	3	38	0.61
166	69	9	0	4	46[2]	0.60
210	88	9	0	3	92[2]	0.74
210	88	9	0	4	84[2]	0.97
210	88	9	0	6	79[2]	0.89
part B: Effect total solid content in glue line						
107	45	9	0	3	<20	0.31
166	69	9	0	3	38	0.61
210	88	9	0	3	92[2]	0.74
part C: Effect time between cold and hot press						
210	88	9	0	4	84[2]	0.97
210	88	9	15	4	49[2]	0.60
Results with a formulation with a total solid / binder ratio = 1.83 [1]						
part D: Effect press time						
195	59	8	0	3	20	0.31
195	59	8	0	4	<20	0.26
195	59	8	0	6	0	0.03
part E: Effect time between cold press and hot press						
195	59	8	0	6	0	0.03
195	59	8	15	6	<20	0.26
part F: Results with a PF reference						
205	60		15	4	95[2]	0.79
205	60		30	4	95[2]	0.83

1) See tables 3 and 6 for more detail on formulations
2) Passed the EN-314 norm for outdoor applications

Table 27: Effect of wood moisture on boiling water resistance of birch triplex cross ply

Type of glue and Moisture content in birch veneers (w%)	EN 314 exposure test result: success rate	Wet shear stress (MPa)	Type shear failure
PX-333			
1	6/6	1.4	Glue failures
6	6/6	0.8	"
8.5	6/6	1.1	"
11	6/6	1.1	"
17	2/6	0.7	"
DYNO PF glue			
17	4/6	0.8	"

Glue dosage: 160 g/m^2, PX-333 glue batch JF 9718S
Press conditions: 140°C for 5 minutes at 12 bar ; No pre assembly
Formulation with 35 phr coconut shell flour and 5 phr wheat flour
Exposures: 4hr boiling water /18 hr 63°C drying /4 hr's boiling water/ 1 hr cold water

Table 28: Effect wood moisture and formulation water on boiling water resistance of Birch cross duplex glued with PX-335

Glue dosage g/m2	43		43	43		40	50	40	60
filler dosage g/m2	34		34	34		0	0	0	0
water dosage g/m2	43		60	77		40	50	60	80
Total dosage g/m2	120		137	154		80	100	100	140
Wood moisture (w%)	2	8	8	2	8	8	8	8	8
	Boiling water resistance: % samples successfully passed test								
Pressing time (min) :									
1	0	0	0	0	0	0	0	0	0
2	75	0	0	75	0	25	25	0	0
3	100	100	100	75	75	100	50	75	50
4	100			50	100				

Glue PX-335 batch used: JF 9763
Fillers: 35 phr coconut shell flour and 5 phr wheat flour
Press temperature 140C, no assembly time used

Table 29: Effect of moisture and pressing time on EN 204 results of panels glued with PX-333

Moisture content (w%)	Pressing (time / temperature) (min / °C)	Shear strength (MPa) after exposure	
		Cold water	boiling water
8	5 / 145	3.4	2.0
	10 / 145	6.3	4.1
	20 / 145	7.5	7.3
1	5 / 145	7	4
	10 / 145	6.5	6.5
	20 / 145	8.2	7

Glue PX-333 (JF9717S)
Glue dosage: 120-140 g/m2 ; unfilled formulations
Cold pressure 15 bar

Table 30: Effect of wood moisture content on PX335 glue performance

Glue batch	PF 1550 CASCO	PX-335, filled
wood moisture content (w%)	Knife test results: Percentage wood failure in the middle glue layers of the 5 ply (%)	
4.5	75	65
7.5	20	55

Glue dosage was 180 g/m2
veneer thickness: 3.8 mm
product : 5 cross ply
Press: 9 minutes / 150°C ; open assembly time: 5 minutes

Table 31: Effect open assembly time on PX-335 glue layer tackiness after a short cold pre-press cycle.

Glue batch	PF 1550 CASCO		PX-335, filled	
Open assembly time (min)	Percentage of release after a standing time of 10 or 30 minutes (%)			
	10	30	10	30
0	5	15	0	0
11	0	0	0	0

Glue dosage: 180 g/m2;
veneer thickness: 3.1 mm
Wood moisture: 2.9w%
Product : 3- cross ply
Cold press conditions: 4 minutes at 11 bar

Table 32: Effect of open assembly time on PX-335 glue performance

Glue batch	PF 1550 CASCO	PX-335, filled
Open assembly time (min)	Knife test results: percentage wood failure in the middle glue layers of the 5 ply (%)	
5	75	65
30	75	75
60	60	60
120	60	60

Glue dosage: 180 g/m2;
Veneer thickness: 3.1 mm
Wood moisture: 4.5 w%
Product : 5- cross ply

Table 33: Effect of cold pre-pressing time and wood moisture content on the unfilled PX-335 glue layer tackiness.

Glue batches		PF-1550 CASCO		PX-335, unfilled	
cold pressing time (min)	wood moisture content (w%)	Percentage of release after a standing time of 10 or 30 minutes (%)			
		10 min	30 min	10 min	30 min
4	4.9	50	50	0	0
3	4.9	20	30	0	0
3	9.5	40	70	0	0
2	4.9	20	35	0	0
1	4.9	25	60	0	2

Glue dosage: 180 g/m2
Thickness veneers: 2.4 mm thick
Product: 3- cross ply
No open assembly time

Table 34: Effect cold pre pressing on boiling water resistance of triplex cross ply

Cold press time (min)	Success rate after EN314 exposure [1)]	Wet shear strength (MPa)	Type failures
0	3/6	0.8	glue
5	4/6	1.1	glue
10	6/6	1.3	wood-glue
20	3/6	1.3	wood-glue
60	6/6	1.5	wood

Glue PX-333 (JF9718S) with fillers
Glue dosage was 160 g/m^2.
(35 phr coconut shell and 5 phr wheat flour)
Cold pressing : 1.2 bar
Hot Pressing: 5 min / 140°C / 12 bar
1) exposure: 4 hr's boiling water/18 hr 63°C drying/ 4 hr's boiling water/ 1 hr cold water

Table 35: Effect of moisture and cold pressure times on EN 204 test results of parallel grain beech panels

Moisture content (w%)	Cold Press time (min)	Shear strength (MPa) after exposure	
		cold water	boiling water
1	30	6.8	6.0
1	0	5.8	4.7
8	30	5.6	5.0
8	0	6.0	4.1

Glue : PX-333 (JF 9717S)
Glue dosage: 120-140 g/m2 ; unfilled formulations
Cold pressure 15 bar
Pressing: 10 minutes 145°C

Figure 9: Temperature profile of a birch duplex

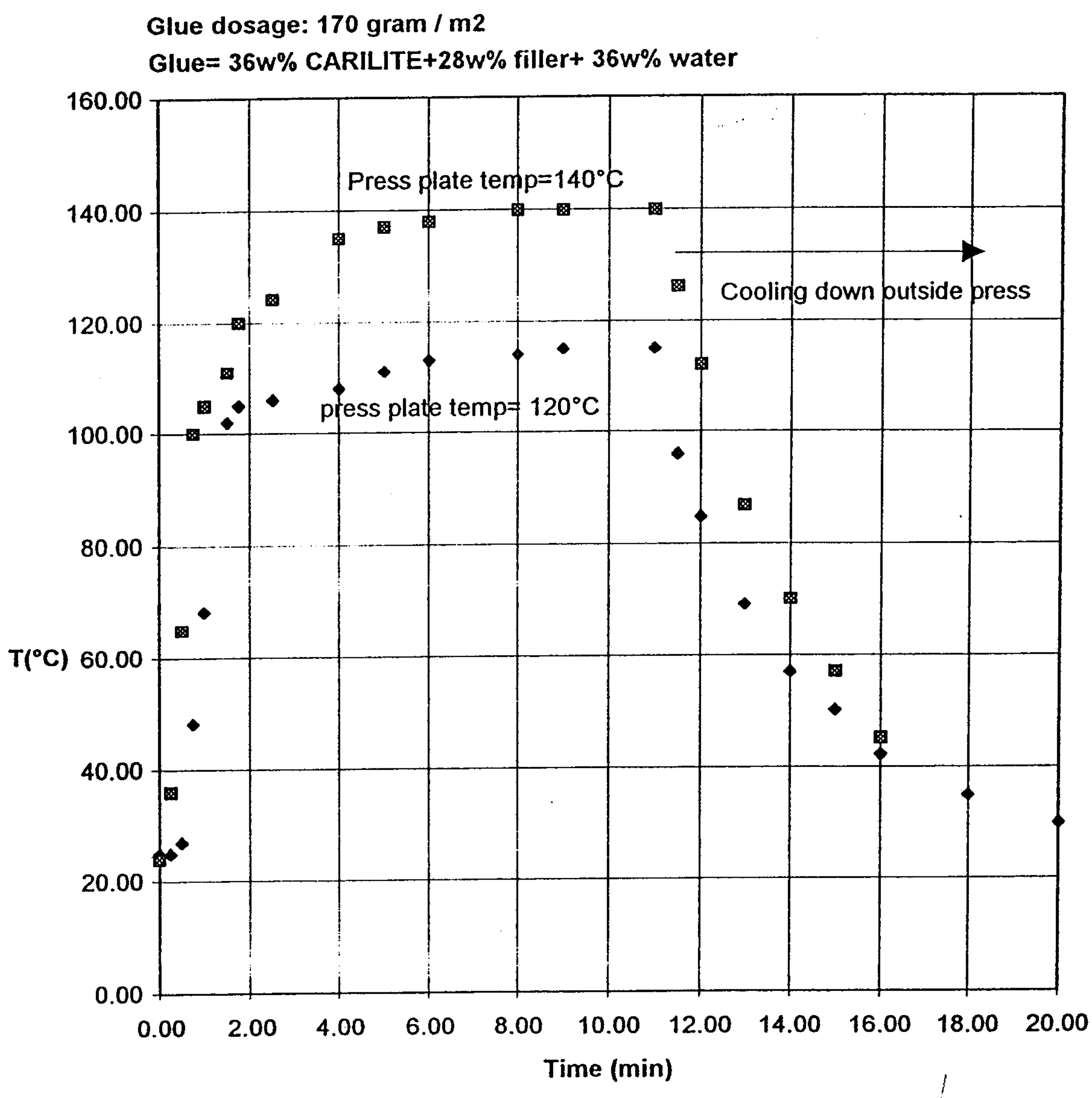


Figure 10: Temperature profile between two Beech panels

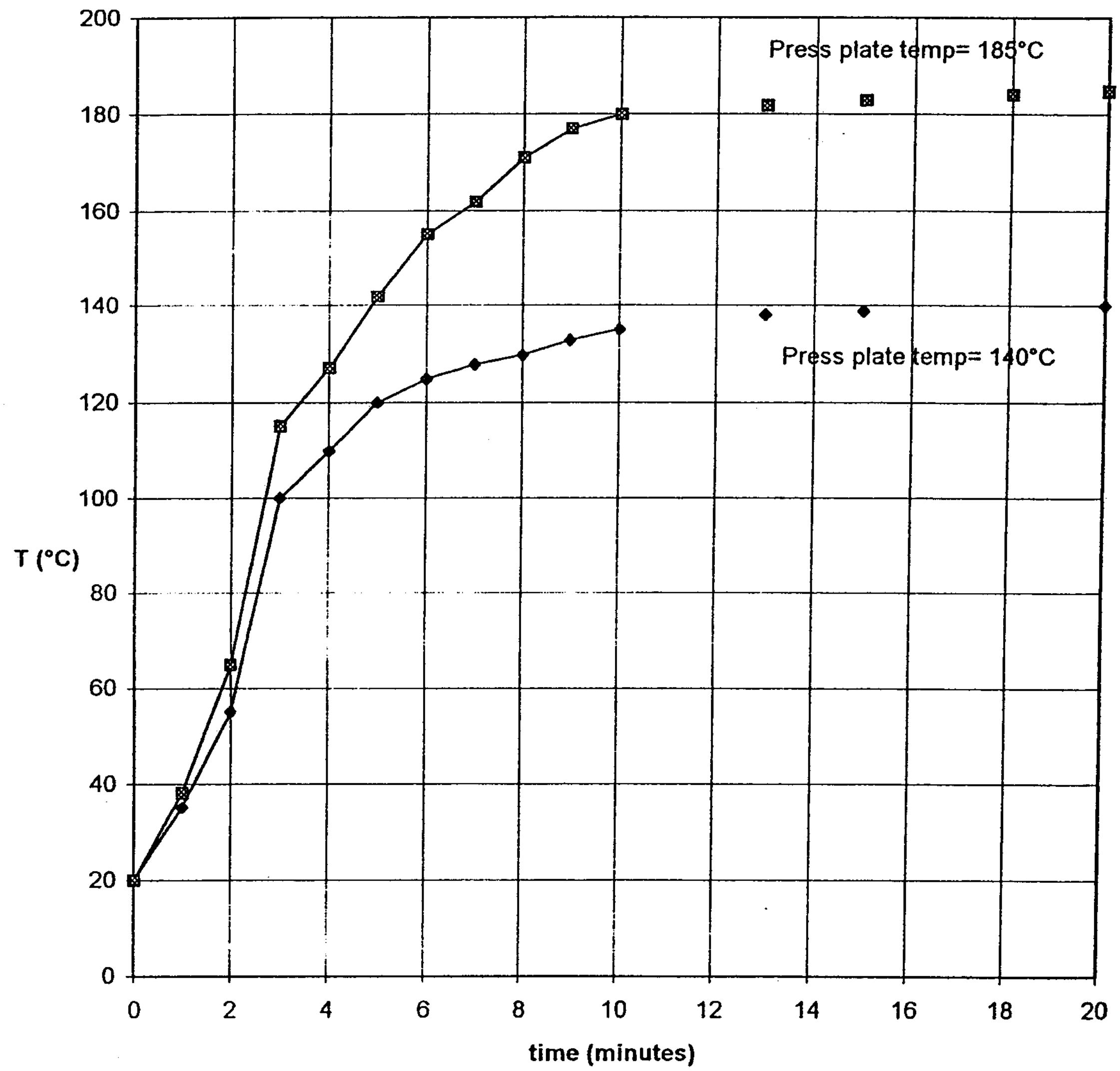


Figure 11: Temperature profile of a birch 8-ply

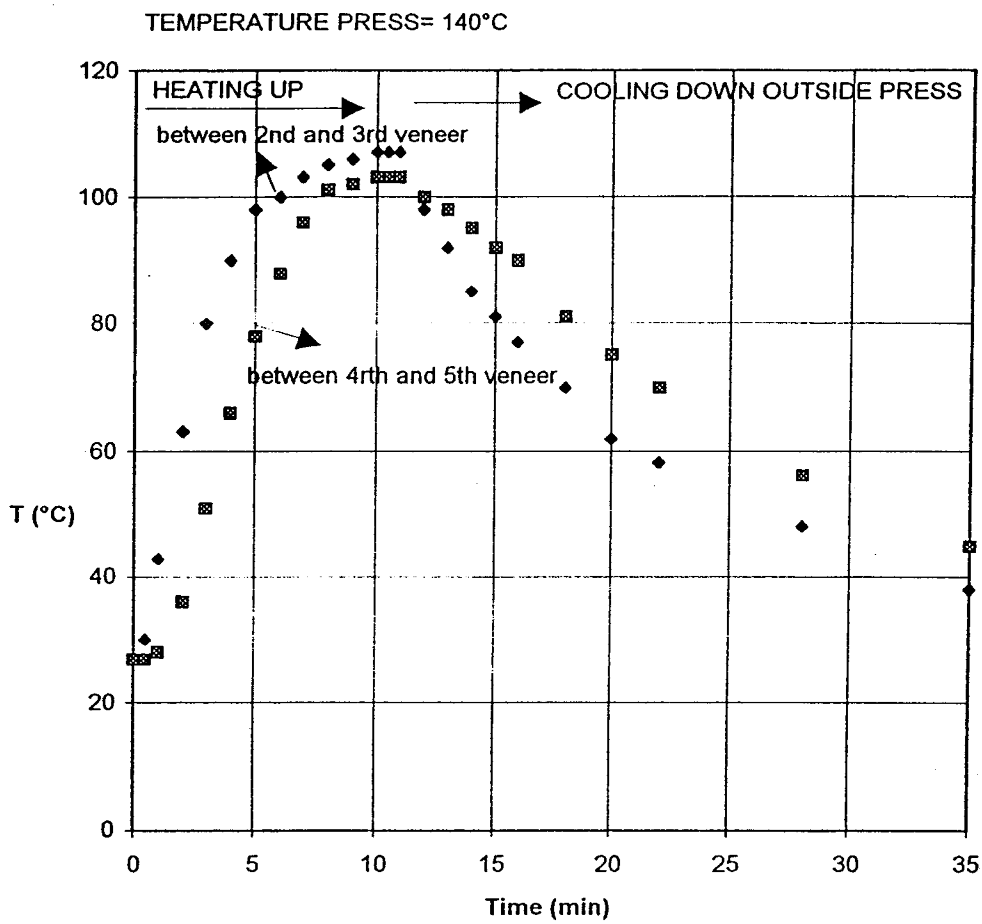
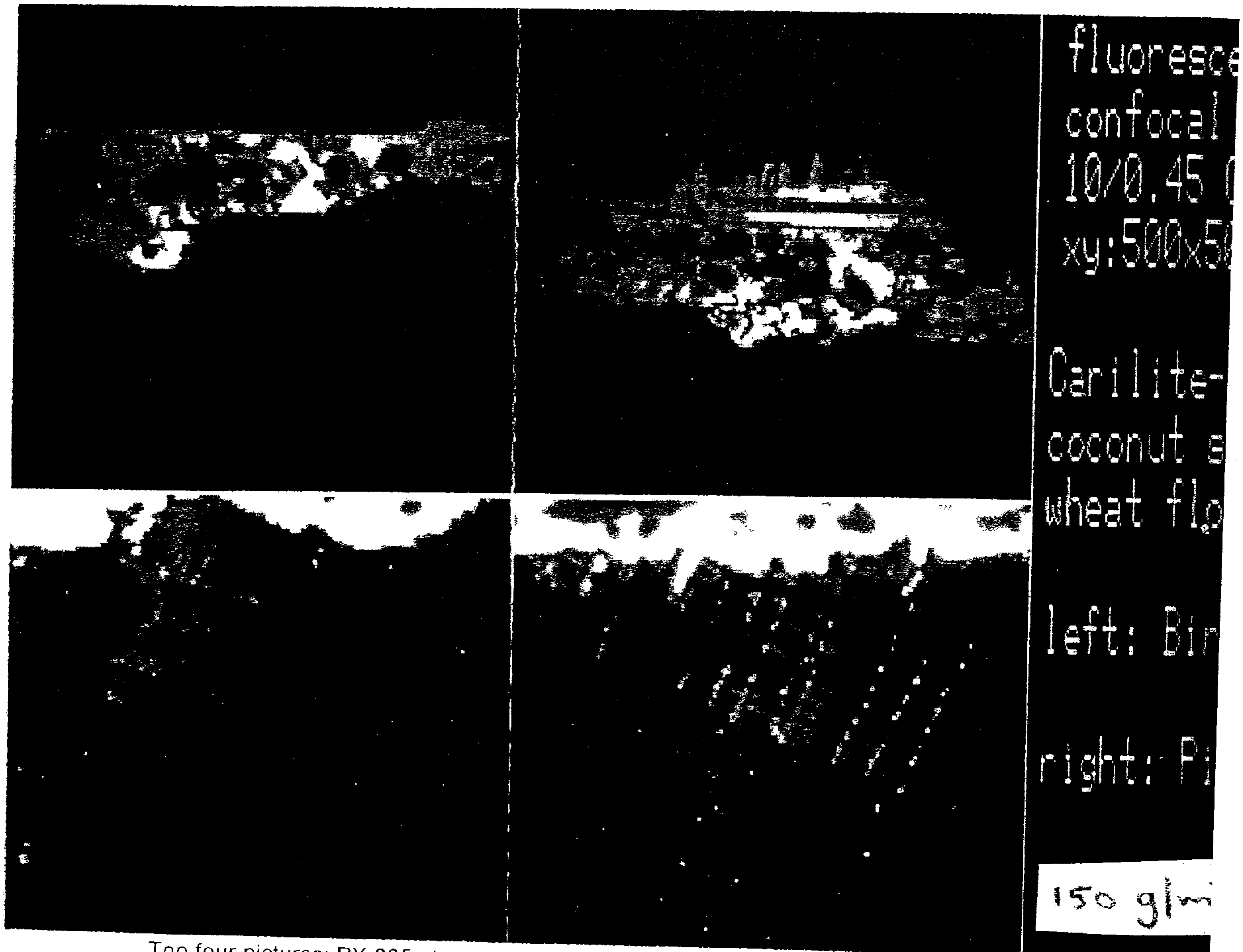
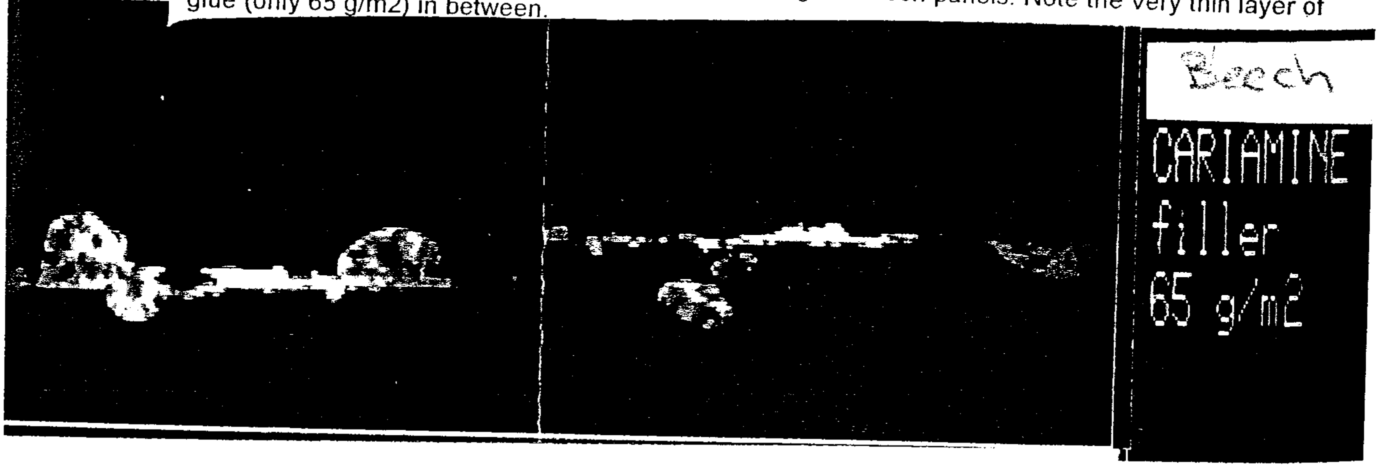


Figure 12 : CONFOCAL ANALYSIS OF GLUE LINES I



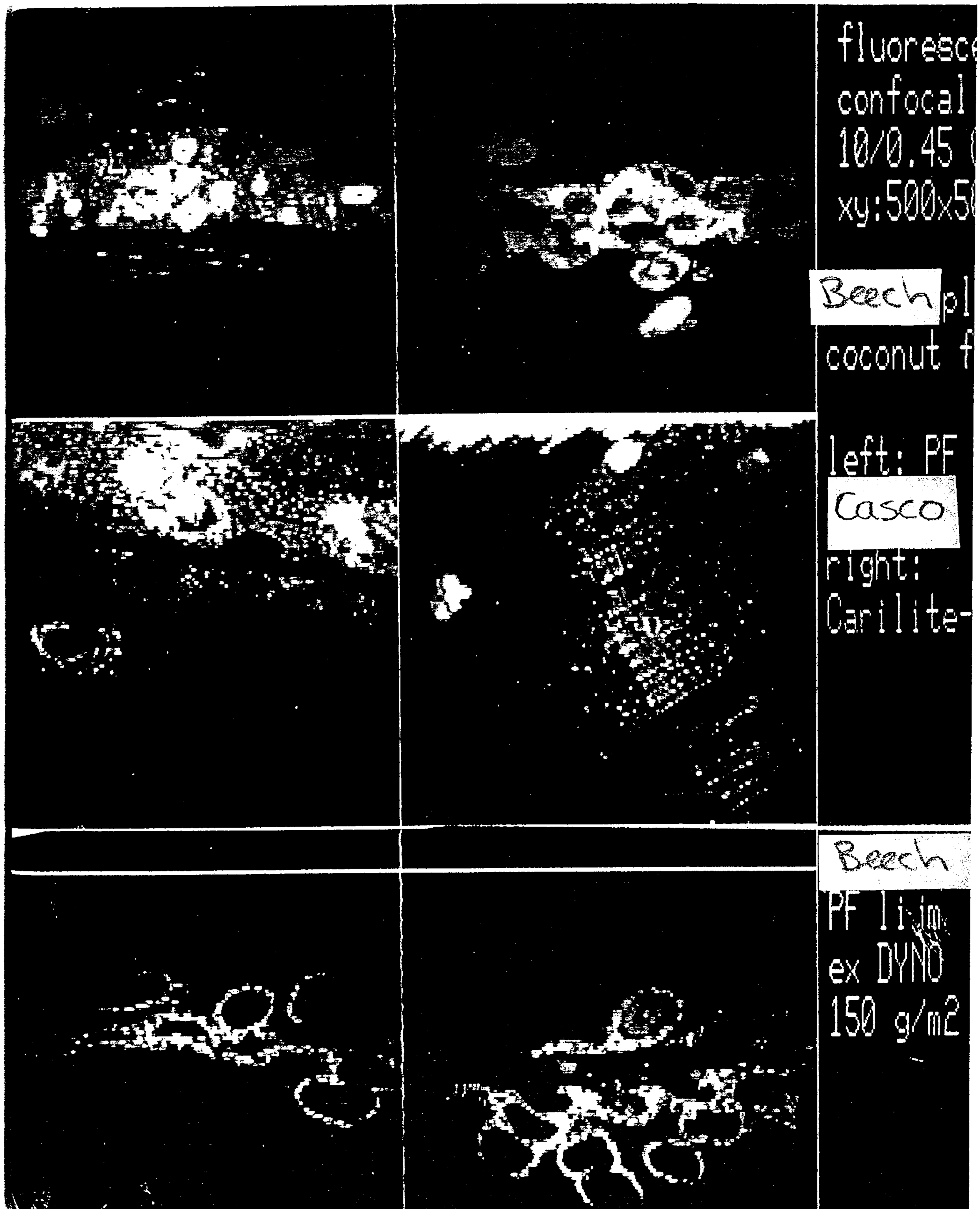
Top four pictures: PX-335 glue with fillers used to glue Birch (left) and Pine (right) wood veneers
Photos represent the glueline (top row) and the wood cell layers below the glue line (bottom row).

Bottom two pictures: PX-335 glue with fillers used to glue Beech panels. Note the very thin layer of glue (only 65 g/m2) in between.



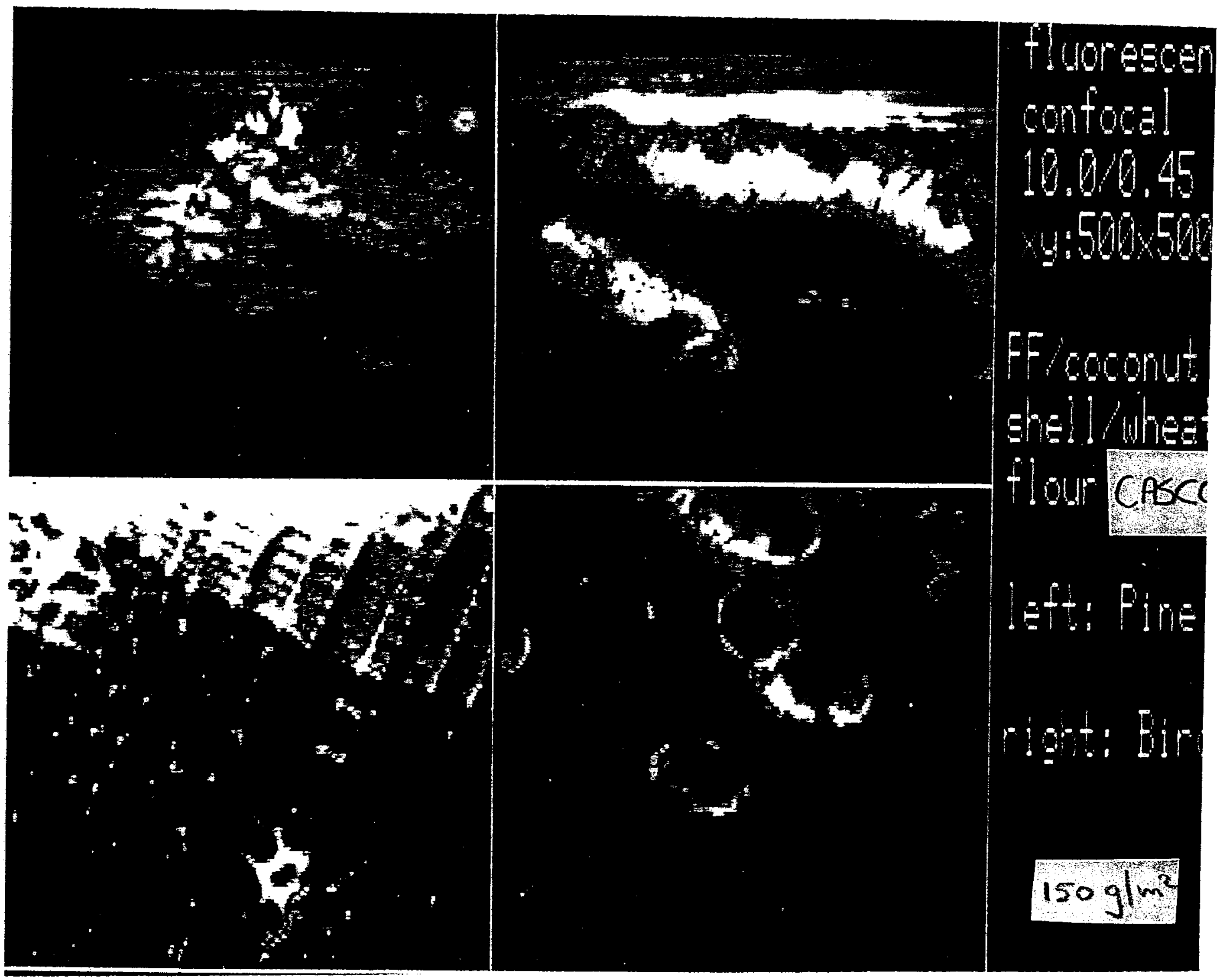
Beech par
(horizonta

Figure 13 : CONFOCAL ANAYLSIS OF GLUE LINES II



Beech panels glued with PX-335 (top right) and PF from CASCO (top left) and PF from DYNO (horizontal row). Especially note the penetration of the PF glue from DYNO into the cells.

Figure 14 : CONFOCAL ANAYLSIS OF GLUE LINES III

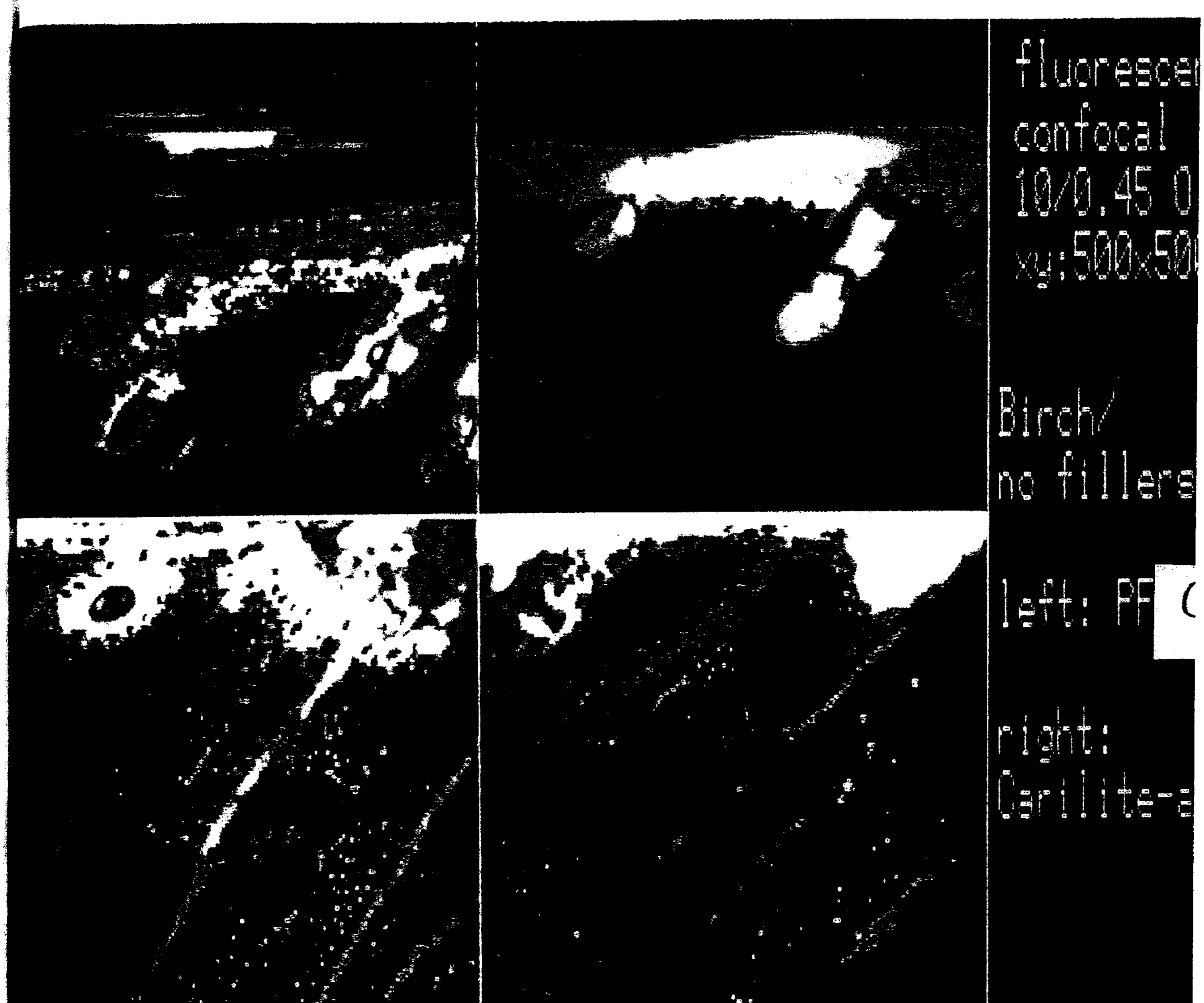


PF Casconol PF1550 with our fillers used to glue Pine (left) and Birch (right) wood veneers.

Photos represent the glueline (top row) and the wood cell layers below the glue line (bottom row).

Note the penetration of the glue into the wood cell layers which makes the glueline in the middle of two wood veneers almost invisible.

Figure 15 : CONFOCAL ANAYLSIS OF GLUE LINES IV



Comparison of PF Casconol PF1550 (left) and PX-335 glue (right) without any fillers used to gluc Birch wood veneers.

Photos represent the glueline (top row) and the wood cell layers below the glue line (bottom row).

Note the clearly visible glue line at the PX-335 glued sample in comparison with the PF glued sample. Several wood layers are penetrated by the PF glue.

FIGURE 1: TYPICAL DMA diagram of a PX-33X film cured at room temperature for 2 days

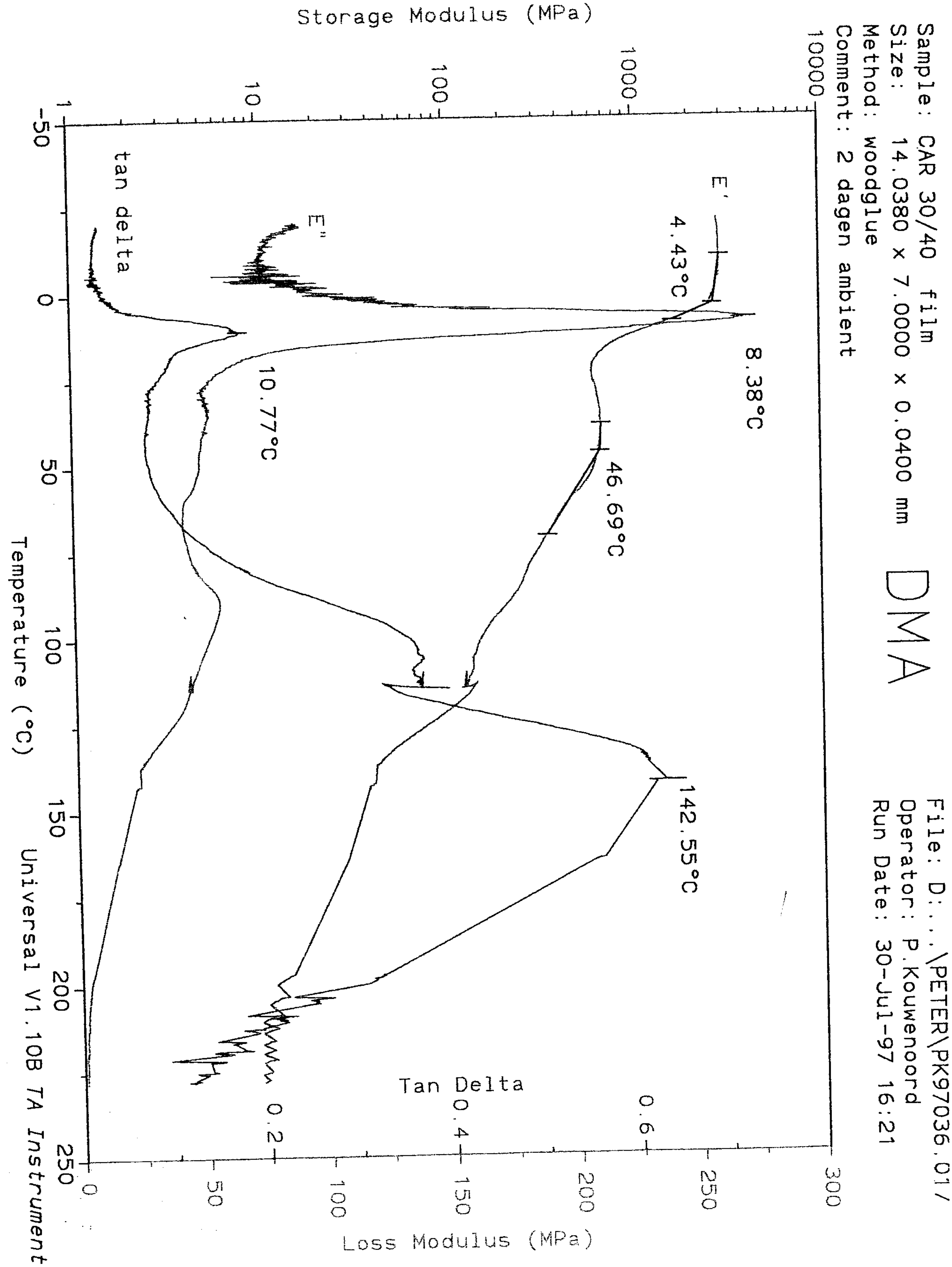


FIGURE 2: TYPICAL DMA diagram of a PX-33X film cured at elevated temperatures till 150°C

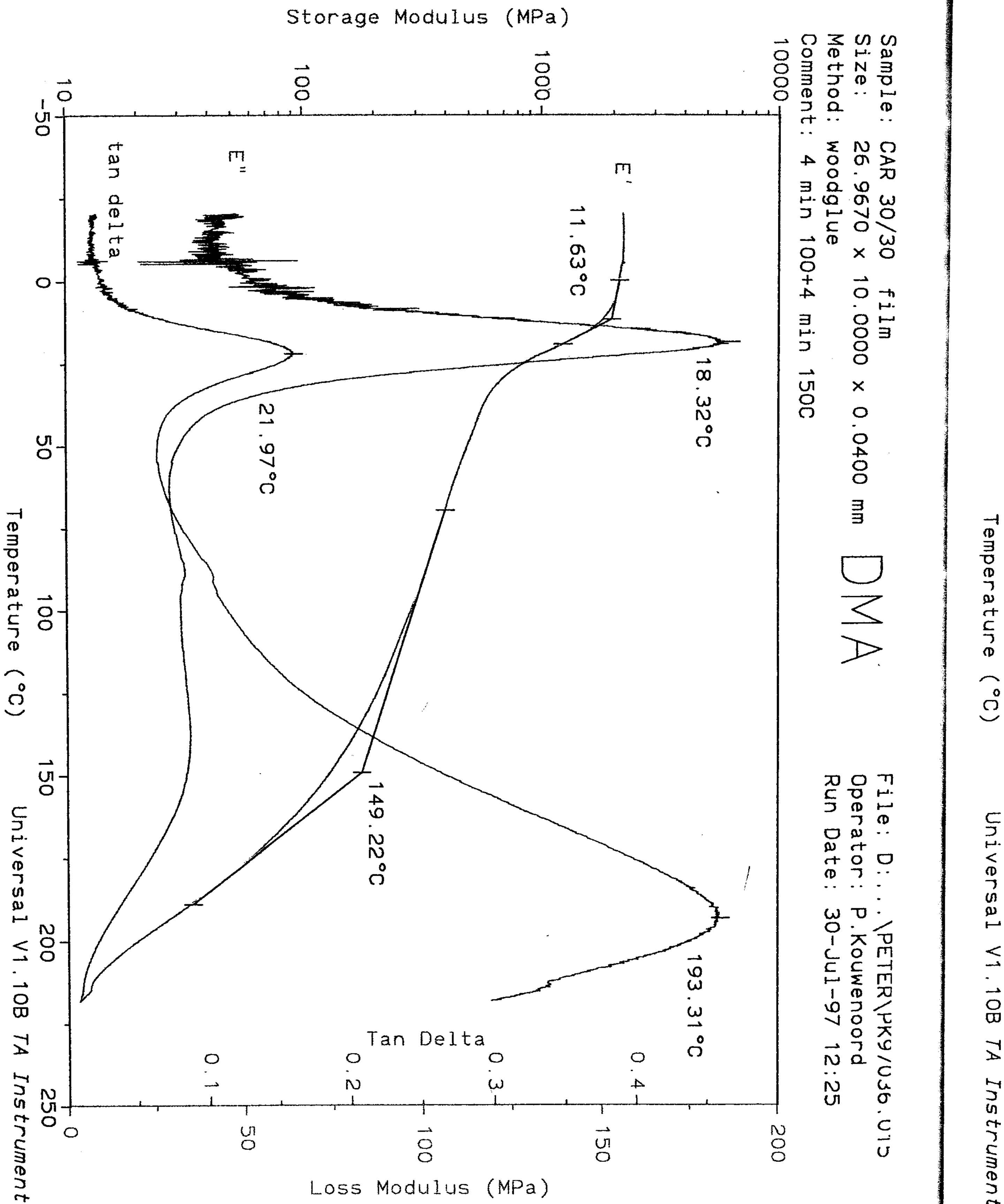


FIGURE 3: TYPICAL DMA diagram of a PX-33X film cured at elevated temperatures till 175°C

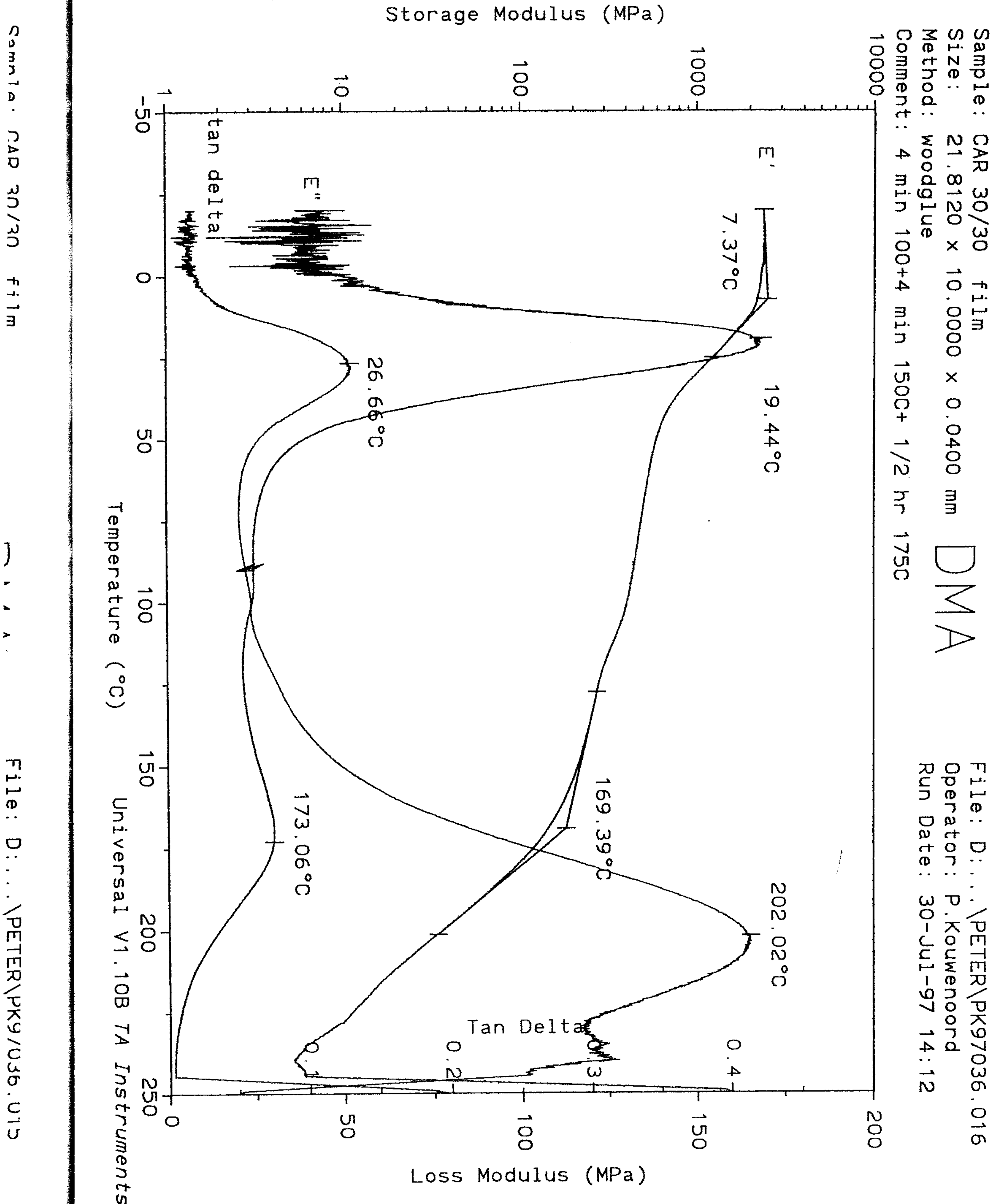


FIGURE 4: TYPICAL DMA diagram of a CARILITE EP (PX 230) / HMDA film cured at elevated temperatures till 175°C

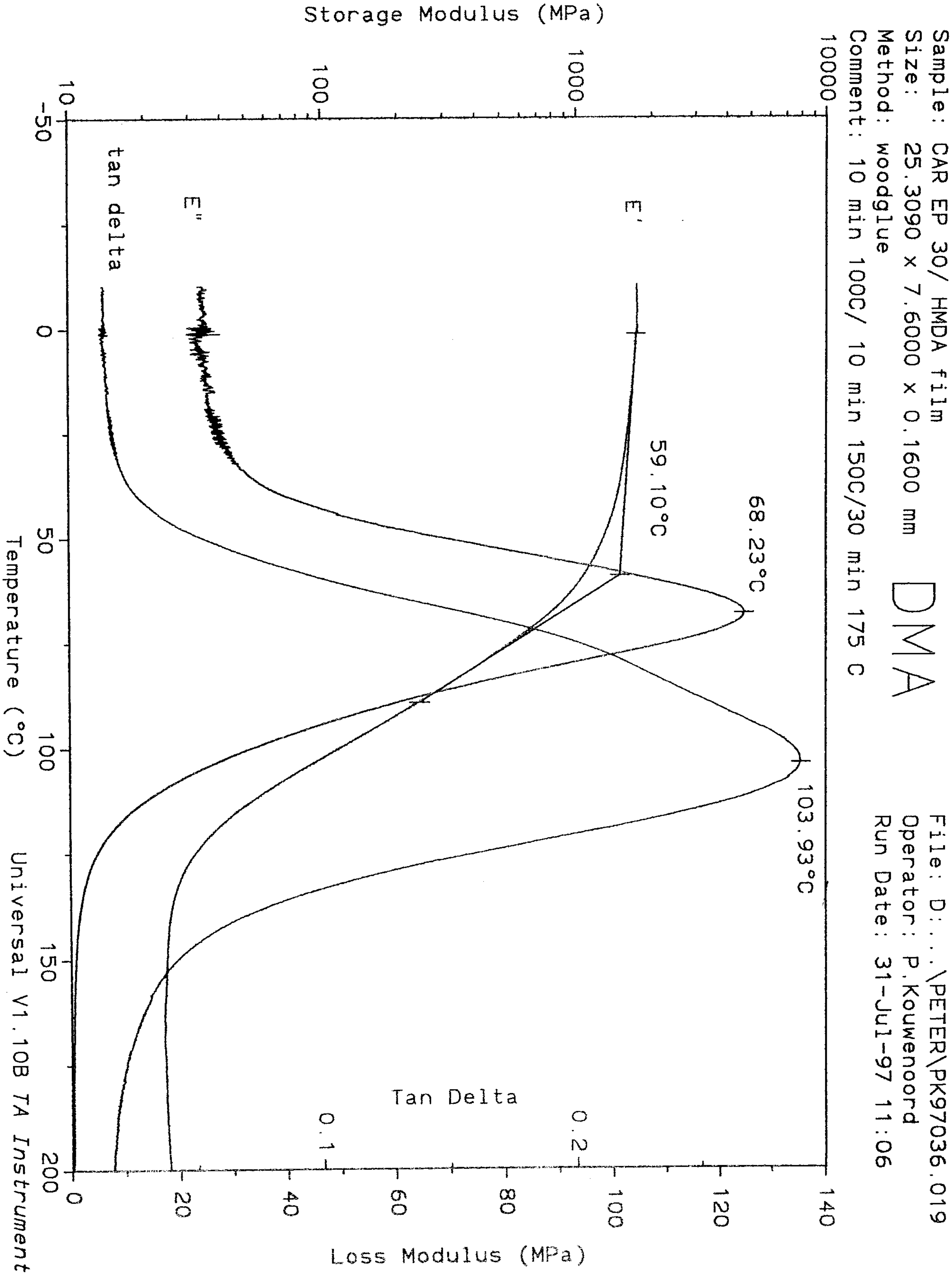


FIGURE 5: DMA diagrams of some commercial glue films compared to PX-33X system

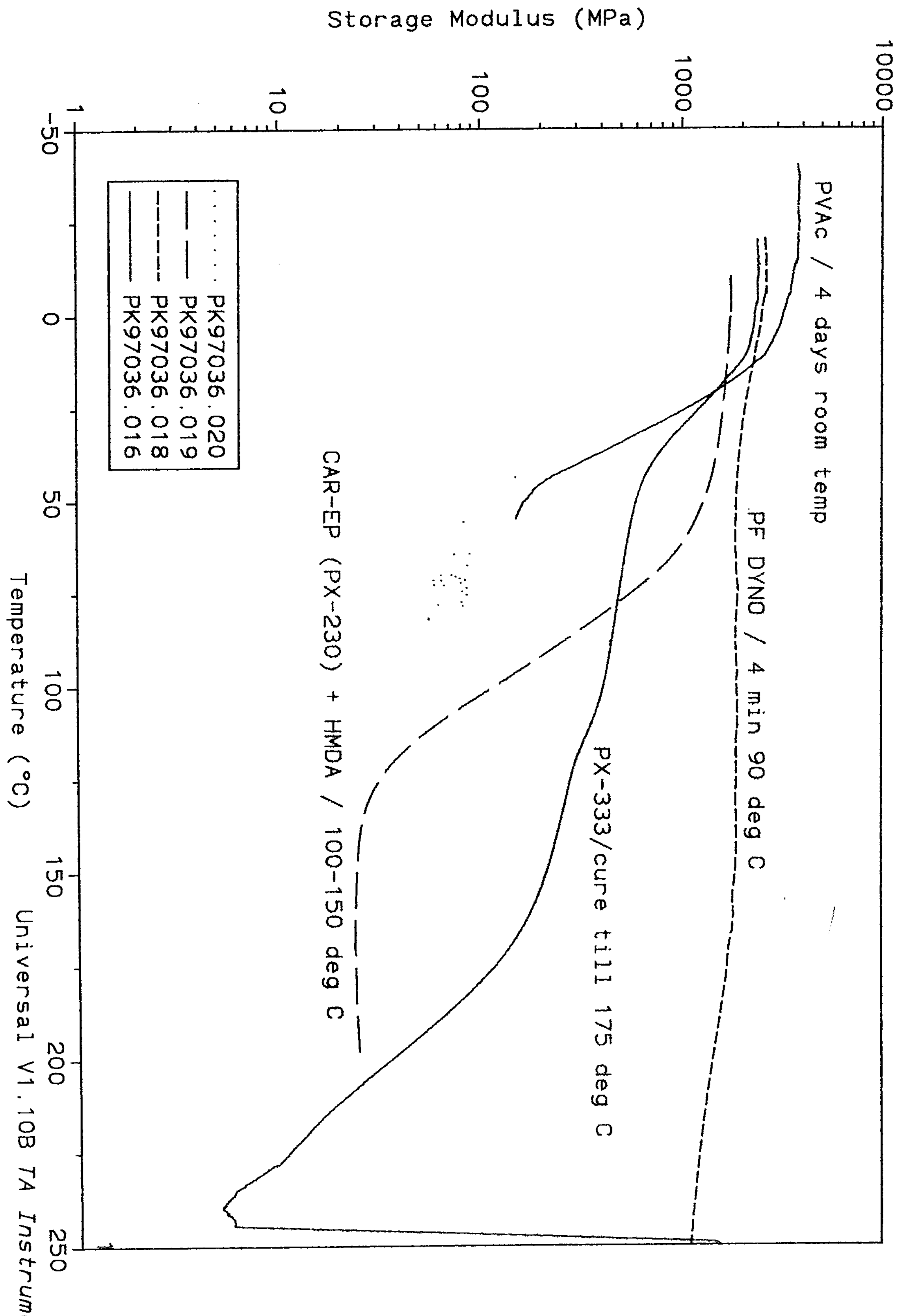


Figure 6 : Curing of PX335 followed by FTR

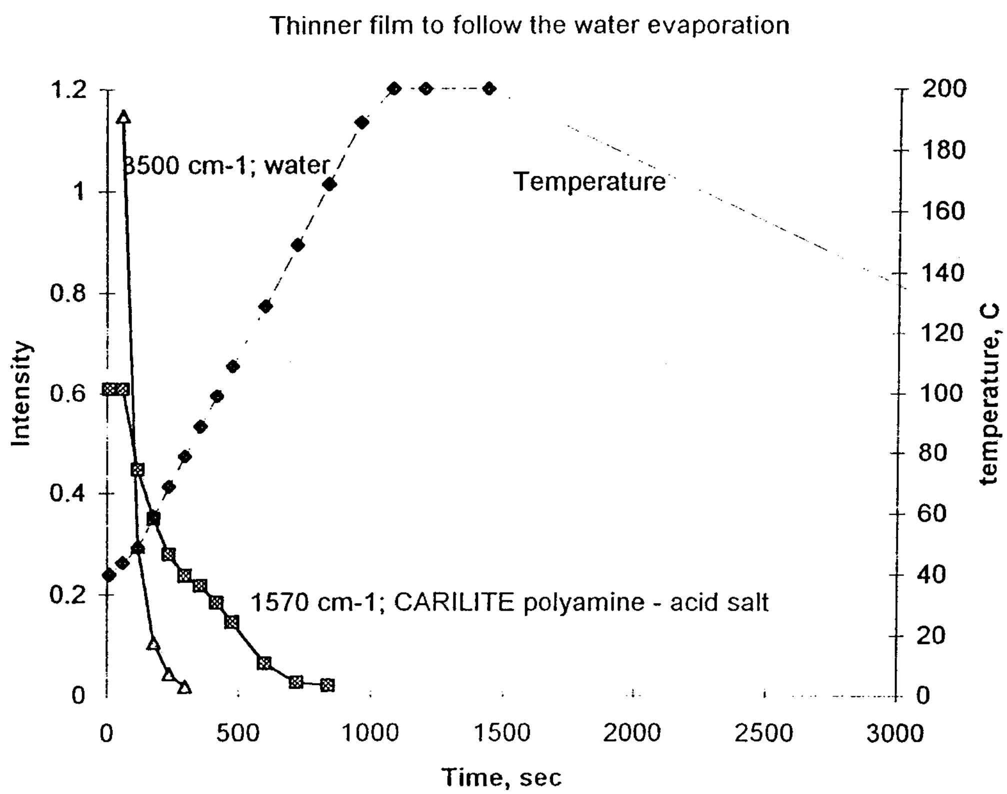


Figure 7 : Curing of PX-335 followed by FTIR

a relatively thick film layer in order to follow the keton conversion

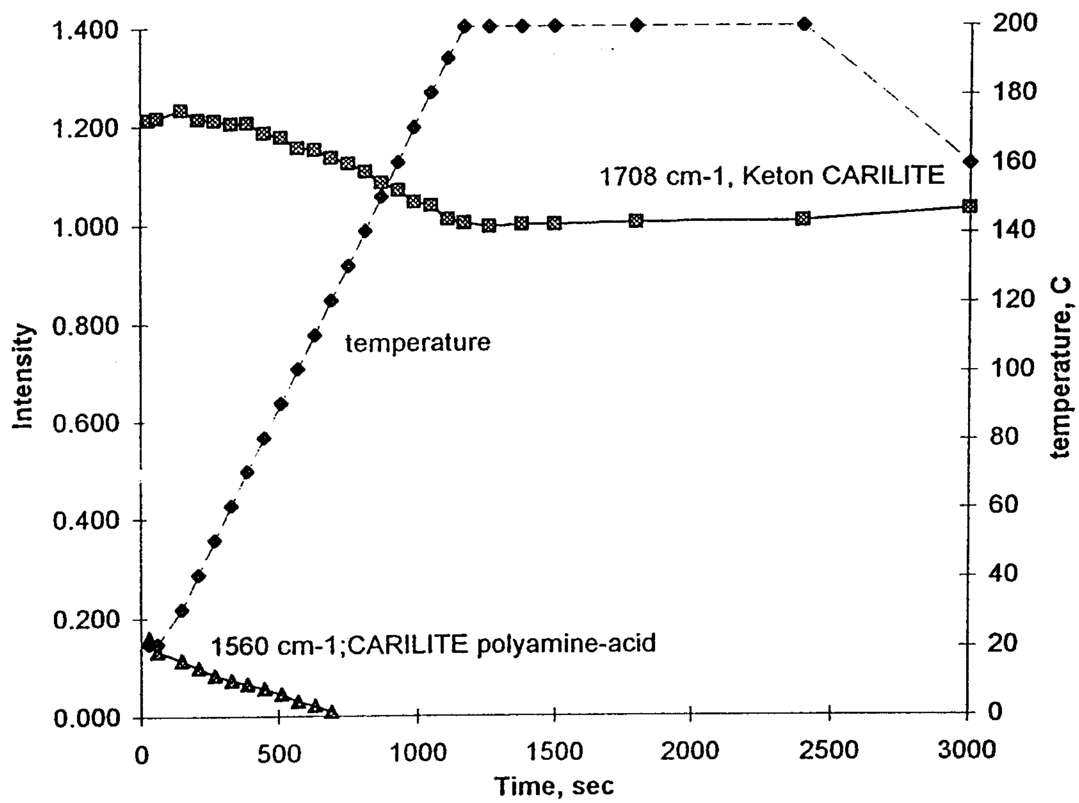
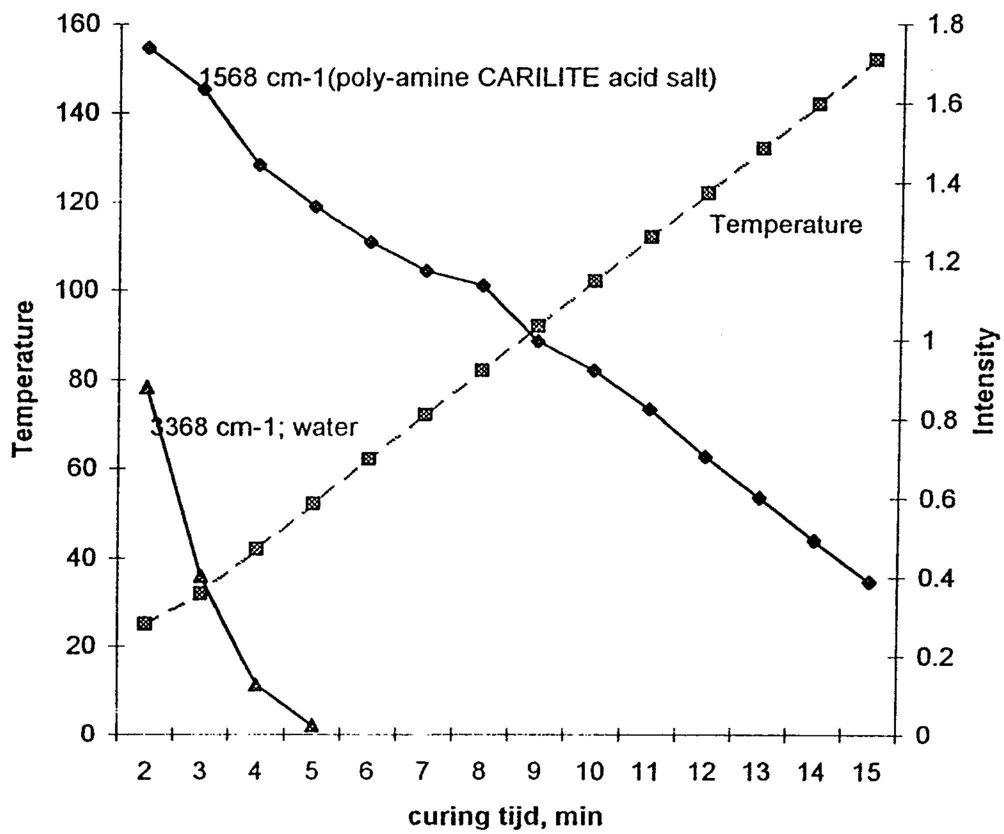


Figure 8: heating of polyamine/water followed by FTIR



Appendix 1

Experimental procedures

Viscosity measurements
Viscosities were measured with a Brookfield digital viscometer RV DII+ and spindle no's 21,24 and 28. The isothermal measurements were carried out on 8 grams samples in a small metal vessel. Most measurements were carried out at 20-25°C.

Particle size measurements of emulsion
Particle size measurements were carried out with a Coulter LS particle analyser (small volume model LS230). Demi water was used as medium and the results were analysed with the psl.rfd software.

Hot plate geltime measurement
Hot plate geltime measurements (HPGT) is a measure of gelation speed and reactivity and is determined according to "Resin Test Methods Series no 48". Small quantities (1 gram) of mixtures were put on a heated plate (Tetrahedron, USA) and occasionally stirred with a wooden rod. The state of cure of the system was checked over time by trying to pull out strings of gelled material. At "time to no string (ttns)" it was not possible anymore to pull out strings of gelled material and the time was recorded as such. Tests were carried out at temperatures between 100 and 160°C.

Gluing and pressing of wood materials for mechanical and water boil testing

1. At MFPL in Mississippi triplex cross plies of southern pine wood were made using an automatic roller coater machine. A veneer was coated on both sides and placed between two other empty veneers to make a triplex. Each veneer was 4 mm thick and contained 3w% of moisture. Local operation conditions were very hot and dry (35°C and a very low humidity). Their standard operation procedure, similar to that of PF commercial operations, was as follows:
   - 2-sides glue spreading of a veneer by roller, 1 minute waiting in the open
   - cover top and bottom by unglued veneers, covered waiting 8 minutes. (open assembly)
   - cold pressing at 10 bars for 5 minutes.
   - Waiting 1 to 15 minutes for the hot press (closed assembly)
   - Hot pressing at 14 bars at 150°C for 3,4 and 6 minutes.

2. At CASCO cross-plied plywoods have been made with 5 veneers of 2.4-3.8 mm thick pine wood. Wood moisture content was varied between 2.9 and 9.5w%. The glue was applied manually with a roller and glue dosages between 120 and 180 g/m^2 were applied as a single glue line. Open and close assembly times varied between 0 and 120 minutes and hot pressing was done at 150°C/12 bars for 2- 9 minutes. Panels were made of 30x30 cm^2 square. To compare the PX-335 glue with the commercial PF glue, each veneer was glued with both the reference and the PX-335. To that purpose the surfaces of the plies were divided into two areas of equal size.

3. At SRTCA parallel grain beech panels (size of each : 30x12x0.5 cm^2) were used for EN-204 testing. Beech planks were obtained from University of Ghent and were stored under room conditions (18-24°C // 20-60% RH) . Moisture content of the planks was between 6-8w%, except for tests where the planks were dried at 40°C/50mbar/N_2 flow prior to use. For these test series the planks were not abraded with a 3M 622 P400 sandpaper as is prescribed in EN-204 and was done in previous experiments[1]. With a putty knife the glue formulation (80-170 g/m^2) was evenly spread over one surface (single glue line) and another empty plank was laid on top. Immediately after assembly- if not mentioned otherwise- the panels were pressed at 20 bars in a heated press (PHI) at temperatures between 140 and 185°C. After a certain pressing time the glued product was taken out of the press and was allowed to cool down at room temperature and stored at 25°C/50% RH for a number of days (usually longer than 1 week) and cut to the shear test geometry before testing.

4. At SRTCA cross plied multiplex products have been made with 2 to 8 veneers of 2.5 mm thick Poplar wood (Dutch), Birch wood (Sweden), 2 mm Scandinavian pine or 4.5 mm thick Southern Pine wood (from USA). Materials were treated and glued in a similar way as described under (3). Pressure applied was 12 bars. The glued multiplies were used for water boil resistance measurements and EN-314 testing.

Quick water boil test screening
For a quick screening of glued multiplex panels, only small (10x10cm^2) panels were pressed which were subsequently cut into 4 small pieces (20x20 mm^2) and immersed in boiling water for a period of 6-24 hours. The response in terms of coherence was monitored visually .The results of these tests were noted as the percentage of samples which did not fall apart and therefore have passed this boiling water exposure test.

Water boil test by MFPL
Water boil resistance was measured in an autoclave at 2 bar pressure ,120 ° C for 17 hours. The exposed samples were tested on their wet shear strength according to the EN-314 norm.

Water boil test by CASCO
Same exposure conditions in the autoclave were used as was done by CASCO. After the exposure however the amount of wood failure was tested with the knife test.

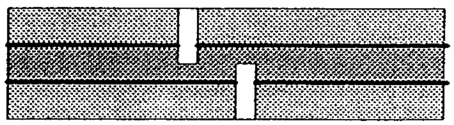
Water resistance measurement and Mechanical testing
To determine whether glued products are suitable for outdoor applications accelerated tests exist in the market . Samples are exposed to cold or boiling water for a certain length of time. Two of these tests- EN 204 with parallel grain glued beech panels is considered by the industry as a general yardstick for wood glue quality, the other, EN-314 is especially for ply wood materials, with any type of wood - have been used to determine the value of the CARILITE emulsions. A third type of test is the "knife test", which is mainly used by CASCO to do a quick check of the glue performance.

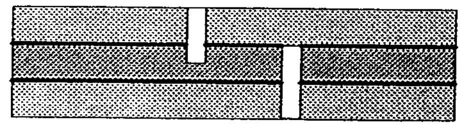
Knife test by CASCO
Directly after pressing the panels were tested according to a so called "knife test". The amount of wood failure as opposed to glue failure was determined by comparison with standard photo's of fractured panels, shown in the BS 1455 or EN-314 test procedures. A wood failure percentage of higher than 40% was considered to have passed the test. All 4 glue lines in the 5-ply panel were tested and the result of each glue line individually reported by CASCO. The middle two glue lines appeared to be the most sensitive ones to changes in the operation conditions. For reasons of convenience only the results of the middle two glue lines were taken from which the average was reported.
This simple test enables an experienced panel tester to determine whether a PF glue line is sufficiently strong to withstand (boiling) water exposure. A high amount of wood fibres in the fractured layer often means that the panel also would have had a good boiling water resistance

INSTRON Shear testing of exposed samples
The mechanical testing of water exposed samples was done in an INSTRON machine at a test rate of 50mm/min for the EN-204 test and 2 mm/min for the EN-314 test. Serrated clamps were used to clamp the samples and the distance between clamps was 50 mm. At the EN-314 test the cross-head speed was determined to be about 2 mm/min to ensure failure in about 30 seconds, as was pre described in the test procedure.

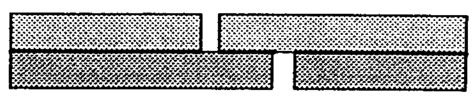
EN-314 shear strength testing
Each cross ply panel (variable sizes and thickness) was cut into samples (100x20 mm^2) and should be provided with saw cuts as shown in the picture left on page 51. In our testing procedures however the saw cuts were cut in a way that the shear was located only on one glue line (picture right), making the test more severe than necessary. This resulted in fractured surfaces, consisting mainly out of glue.
Samples used for the EN-314 tests were exposed for 72 hours to boiling water or to a cycle of 4 hr's boiling water,16 hrs drying at 63°C in oven and once again 4 hrs boiling water.

About 6 samples were subjected to testing The number of samples which did not fall apart were noted and the averages of the remaining shear strengths were determined of the samples which passed the tests.
Demands for outdoor durable plywood are wood failure or sufficient high wet shear strength. If the shear strength is larger than 1 MPa there is no demand for wood failure; If the shear strength is in between 0.6-1 MPa, amount of wood failure should be higher than 40%; If the shear strength is in between 0.4-0.6 MPa, higher than 60% and if in between 0.2- 0.4 MPa higher than 80%.
The estimation of the amount of wood failure was done by comparison with standard photographs of fracture surfaces shown in the test procedure.





EN-204 shear strength testing
Each panel (30x12x1 cm) was cut into 10-12 samples (15x2x1 cm) and provided with saw cuts 1 cm apart from each other and on opposite sides of the wood sample, as shown in the figure below.
Samples used for the EN-204 tests were exposed for 4 days to cold water or 6 hours to boiling water in a specially designed 10 litre vessel or in a heated water bath containing metal inserts to hold the samples.
About 6 samples per condition investigated were subjected to testing (the certified use of EN-204 for commercial application requests 20 shear bars).The amount of samples which did not fall apart were noted and the averages of the remaining shear strengths were determined of the samples which passed the tests. To pass the test for unprotected outside durable applications the remaining wet shear strength should be above 4 MPa



Glass transition temperature (Tg) analysis by DMA and DSC
Glass transition temperatures of the liquid glue mix components were determined by DSC (Perkin ELMER DSC7). A scan rate of 10°C/min was used between -50 - +150°C. The Tg was determined on the first scan.
Two Dynamical Mechanical Analysers (DMA) from TA-Instruments have been used to determine glass transition temperatures (Tg) of cured materials. First experiments were carried out with the DMA xxx , while later experiments were carried out with a newly purchased DMA 2980 analyser.
On 2 types of materials DMA analysis were carried out:

- thin films (20-50 μm) spread on PP and removed after curing in oven or at room temperature, Materials were measured in the tension mode with a fixed frequency. (DMA 2980)
- jute material- consisting of the same components as wood - was impregnated with the glue emulsion and pressed in a hot press between two Teflon coated aluminium foils. Materials were tested in a sinusoid tensile mode in the resonance frequency mode (DMA-983).

Typical measurements conditions are:
1) Temperature ramp: -50°C-240°C at 4°C/min
2) Tension mode for the films.
3) Specimen size: 40x10 mm (thickness varied between 20μm-500μm)
4) Fixed resonance (1-2 Hz) or resonance mode at the DMA-983.
5) Oscillation amplitude 10 μm for the tensile mode; 0.6 mm for the sinusoid mode
6) tensile measurements were done in the autostrain mode at 110%

For the calculation of the Tg different curves were used: From the storage modulus E'(T) curve the onset and midpoint values were determined, from the loss modulus E"(T) and tan delta (tan E"/E') curves the peak values were measured.

FTIR analysis

With the aid of a heated sample holder mounted in a FTIR the curing of a polyamine-CARILITE emulsion film layer on top of ZnSe surface was followed.

On a ZnSe substrate a thin (20 µm) film of PX-335 was coated and immediately scanned at different peaks. Spectra at 1708 cm-1 (C=O CARILITE), 1560 cm-1 (C=O polyamine salt) and at 3500 cm-1 (water) were followed as function of time at increasing temperatures. The disappearing of the water , the decrease in C=O CARILITE signal and the decrease in C=O polyamine -acetic acid salt signal could be followed in time and in temperature. This analysis was carried out by our analytical department.

NMR analysis

C^{13} CPMAS NMR experiments have been conducted trying to determine the amount of converted carbonyl as function of cure conditions. Several C^{13} NMR signals were used to determine the conversion from carbonyl to pyrrole. Typical signals for the CARILITE ketone group was found at 211 ppm and for the pyrrole group at 126 and 136 ppm (the average of both intensities is used).

The conversion of ketone could be defined as the ratio of two integration values:

I (avg. of 126+136 ppm) / [I (211 ppm) + I (avg. of 126+136 ppm)].

Measuring time is taken long enough to compensate for differences in the efficiency for the magnetic transfer of protons to carbon atom of both different groups.

Pure cast films and impregnated WHATMAN cellulose paper (which did not show any disturbing peaks) have been analysed. All samples were ground into very fine powder with the aid of a freezer milling machine from SPEX). Samples were stored in a refrigerator to minimise further curing. Analysis were done by ANL.

Confocal microscopy of glue lines

Confocal (CSLM) experiments were carried out by the analytical department. The glue line and the wood layers at opposite sides of the glue line were examined for wood cell defects and glue penetration. Small samples have been cut from the panels and abraded with 3M Whatman coarse and fine paper after which they were cleaned with compressed air. In order to make the wood cells clearly visible higher fluorescence light intensities were needed, which explains differences in intensities of the wood cells in both type of pictures (glue line and wood cells): The top photo represents the glue line and the bottom photo the woodcell layers just under the glueline.

List of non-standard Abbreviations

APA	American Plywood Association
CSLM	Confocal laser microscopy
DMA	Dynamic mechanical (thermal) analysis
EN	European testnorm
FTIR	Fourier transformed Infrared spectroscopy
HMDA	Hexamethylene diamine
HPGT	Hot plate gel time
MFPL	Mississippi Forest Products Laboratory
MLB	Multilayer laminated beam (from planks)
PF	Phenol formaldehyde glue
phr	part per hundred
PVA(c)	Polyvinylalcohol(acetate) glue
PW	Plywood
RF	Resorcinol formaldehyde glue
RH	Relative humidity
RT	Room Temperature
RPF	Phenol diluted resorcinol formaldehyde glue
Tg	Glass transition temperature
WKI	Wilhelm Klauditz Institute, Braunschweig