

# Wood Adhesives Made with Pyrolysis Oils

**Panagiotis Nakos, Sophia Tsiantzi, Eleftheria Athanassiadou**  
**A.C.M. Wood Chemicals plc**

Phenol-formaldehyde resins represent an important type of adhesives employed in the production of wood-based panels of superior water resistance (exterior use products). Phenol is a petrochemical product and the increased oil prices together with the need of reducing the demand on fossil fuels and promoting environmentally friendly products have encouraged developments in the use of alternative raw materials derived from renewable resources. Efforts in this field have accelerated in the latest two decades. The research group of A.C.M. Wood Chemicals plc in this respect has studied the potential use of pyrolysis oils (bio-oils), a portion of which comprises of phenolic compounds, for replacing part of the phenol needed in the formulation of a phenol-formaldehyde resin. Phenol-formaldehyde resins were produced by substituting up to 50% of the phenol needed in the formulation with bio-oils and by modifying the synthesis procedure. The resins were successfully used in the production of OSB and plywood. This difference in the field of application required an adaptation of the resin production sequence. The use of bio-oils provided in both cases phenolic adhesives with reactivity and performance equal to the non-modified resins. Further increase in the substitution level is envisaged, with the aim to achieve a higher reduction of the resin cost. The lower toxicity of bio-oils as compared to pure phenol would facilitate resin manufacture. The conformity with the EU directive for sustainable development makes them attractive for further investigation.

## 1. Introduction

In view of the environmental strain caused by fossil fuels and chemicals, and their inherent vulnerable and limited supply, industry efforts were focused on identifying adhesive raw materials based on renewable resources. To this direction, the oil obtained by the pyrolysis of renewable biomass was seen as an attractive substitute for petroleum phenol in the production of phenolic type adhesives.

Phenol-Formaldehyde (PF) resins are extensively employed as exterior-grade panel adhesives. They are mainly the products of the reaction between phenol and formaldehyde, which is catalyzed by alkali to provide a thermosetting polymer called resole. Other phenolic compounds (e.g. resorcinol) can also react with formaldehyde to provide polymers of the same type with differences in adhesive cost and reactivity. Phenolic resins represent the second important type of wood adhesives following amino resins in terms of consumption volume. In North America, they account for approx. 32% of the total resin solids used compared to 59% for amino resins and the rest 9% for a variety of binders like isocyanates [1]. In Europe, this statement is equally true, the percentage of PF resin solids applied, however, is estimated to be lower with a higher use of amino resin types.

Although much attention has been paid to biomass pyrolysis for the production of fuels, the research on its use for the production of wood adhesives is limited and relatively new. The oils obtained from fast pyrolysis processes consist of depolymerized biomass and contain compounds, which are derived from both the carbohydrates and the lignin [2, 3]. The chemical compounds in the pyrolysis oils include those of phenols, acids, alcohols, hydroxyls, esters, aldehydes, and unsaturated hydrocarbons. Waste resources, such as bark and sawdust from various kinds of wood, and kraft lignins (produced in papermills) represent main biomass feedstocks investigated and pyrolysis temperatures are in the range of 450-600°C. The phenolic compounds represent a fraction of about 12-17 wt % of the pyrolysis oils, hence it has been found that they may account for up to one-third of the pyrolytic oil [4, 5].

Analysis of the phenolic fraction of the bio-oil revealed the presence of a number of phenolic compounds apart from phenol: *o,m,p*-cresol, guaiacol, catechols, isomers of mono-, di- and tri-substituted phenol with methyl and ethyl groups, isomers of substituted guaiacol with methyl, ethyl, vinyl, allyl and propenyl groups [4-6]. In addition, a few carbohydrate-derived components are also present in this fraction such as furfuryl alcohol and other furfural derivatives. Although the phenolic fraction is a mixture, all compounds are derivatives of phenol and would have the same type of chemical properties. Therefore, efforts have been made to utilize the pyrolytic oil or its phenolic fraction as a phenol source for thermosetting PF resins. The potential for partial replacement of the formaldehyde resin component by the aldehyde fraction of the oil was also another important research task.

First attempts in this area were based on the complete fractionation of the pyrolysis oil to recover its phenolic fraction together with separate fractions of neutrals and organic acids [7]. It was found later that obtaining a combined fraction of phenolic and neutral compounds is more economically promising and the yield of PF resin attainable is increased [2, 3, 6, 8]. The process becomes more economically attractive if the carbohydrate and acid by-products can be utilized commercially. Catalytic upgrading of the fractionation by-products helps to obtain useful chemicals [9]. Furthermore, it was found that the phenolic/neutral fraction can be used to replace not only phenol, but also part of the formaldehyde in the formulation of a PF resin [2].

Phenol-formaldehyde resol resins have been produced by substituting 50% of the phenol with the phenolic fraction of the bio-oil in order to compare their performance in the production of plywood with that of commercial PF resins obtained from petroleum derived phenol [3, 6-8]. Results of these studies indicated that the two adhesives are comparable and the performance obtained with the bio-oil route is even better. Higher substitution levels of the petroleum-derived phenol were considered possible, when a fraction richer in phenolics is used and that is the case for bark as a pyrolysis starting material. Substitution levels of up to 75% have been reported [7]. Another important result found was that about two-thirds of the usual amount of formaldehyde employed in conventional phenolic adhesives is necessary in producing adhesives wherein 50% of the phenol is substituted with the phenol/neutral fraction of pyrolysis oil [8]. However, the complexity of the lengthy solvent extraction/fractionation methods associated with relatively low phenolic fraction yields influence negatively the process economics.

In an attempt to better utilize pyrolysis oils for PF resin production, various pyrolysis routes were investigated. The aim was to appropriately modulate pyrolysis process to obtain bio-oil suitable for phenol replacement in the making of PF. Parameters such as source material, pyrolysis conditions, reactor configuration and biomass moisture content influence the yield and composition of pyrolysis oils [10]. Two trends are identified in recent pyrolysis procedures: a) increase of the phenolic fraction yield by modifying pyrolysis conditions and/or feedstock (e.g. catalytic pyrolysis, bark as a raw material for pyrolysis[11, 12]) and b) production of phenol-rich but lower yield bio-oil by carefully selected pyrolysis reaction conditions. The latter can be used directly in the synthesis of PF resins without the need for fractionation [12-15].

The economics of producing PF resins with the use of bio-oils have been evaluated on a preliminary basis and found to be very competitive with the current cost of petroleum derived phenol [2, 3, 6, 14].

In this framework, the A.C.M. Wood Chemicals research group has investigated the use of pyrolysis oils as a phenol and/or formaldehyde replacement in the synthesis of phenol-formaldehyde (PF) resins for the production of wood-based panels of superior water resistance with the aims to:

- identify resin raw materials that are less toxic than petroleum-derived phenol
- reduce the demand on fossil fuels and promote sustainable development by using alternative resin feedstocks derived from renewable resources
- reduce resin production cost by introducing raw materials of lower cost than phenol
- obtain resins with the same or enhanced quality than the ones conventionally synthesized.

The first two requirements are fulfilled by bio-oil. The scope of this work was to evaluate, whether the two remaining requirements can also be fulfilled by pyrolysis oil. Various bio-oil samples were tested and a common problem encountered is bio-oil instability and heterogeneity as compared with petrochemical phenol. Preliminary results [16, 17] have shown that the phenol replacement by bio-oil is feasible, however to achieve high substitution levels, i.e. above 15% by weight, fractionated bio-oil should be employed (due to the low phenolic content of total bio-oil) and several modifications in the resin synthetic route should be made. These results were considered promising and worthy of further investigation, of which results are presented herebelow.

## **2. Methodology and results**

Phenol-formaldehyde resins were successfully produced by substituting up to 50% of the phenol needed in the formulation with bio-oil, using slight modification of the commercial synthesis Know How. The resins were intended for use in two different applications: production of either Oriented Strandboard (OSB) or plywood (PW) panels. This difference in resin application requires a different approach in resin production sequence.

## Materials

A commercial phenol sample was purchased and diluted to 91% w/w concentration. Formaldehyde solution 37% w/w was employed. The pyrolysis oil samples used to substitute the phenol in the resin formulation had been obtained from different biomass feed stocks – pure wood or bark.

## PF resin synthesis & testing

PF resins were synthesised using various reaction routes and depending on their application, T1 synthetic route for plywood and T2 or T3 for OSB. The main differences between these techniques lie in the number of polycondensation stages as well as in the percentage of the caustic used to catalyse the condensation. The final resin specifications were similarly different (Table 1).

**Table 1: Specifications of PF resins synthesized.**

	T1	T2 and T3
Solids, %	42±1	50±1
Viscosity, cp	400-500	100-130
NaOH, %	6.0	2-3

When bio oils were used to substitute part of the phenol required, some modifications in the cooking of the resin were necessary, e.g. increase of caustic level, change of the order of raw materials loading. Depending on the case, urea was added at various production stages, at levels up to 20% w/w, based on resin solids.

Viscosity measurements were performed with a Brookfield viscometer, at 25°C using a small sample adaptor. The amounts of solid content were determined by weighing resin samples before and after drying in an oven at 120°C and for 2 hours. The alkalinity was determined by titration with HCl.

GPC measurements were effected using a Shimadzu LC-9A liquid chromatograph with a Rheodyne injection loop. Two Plgel columns (Polymer Labs) with pore diameters 100 and 500 Å respectively were used. DMF containing 0.5% LiCl was used as an eluent. Detection was effected by a Shimadzu RID-6A differential refractometer. Resin samples were dissolved in DMSO and the solutions (ca. 0.5 %) were introduced in the injection loop of the liquid chromatograph after filtration through a 0.45µ filter. The temperature of the columns was kept at 70°C and the flow rate was 1 mL/min.

Resin cure was determined by means of a Shimadzu DSC-50 Differential Scanning Calorimeter. For the measurements, a resin sample of approximately 10 mg was placed in a special aluminium cell, which was then sealed. Measurements were done under a nitrogen atmosphere. The

samples were kept at 30°C for 5 min and then heated up to 220°C at a rate of 10°C/min. This particular cell can withstand pressures up to 30 bar. Since the sample is placed in a closed cell, water evaporation is suppressed and therefore the endotherm peak in the DSC scan is absent.

### **OSB, plywood preparation & testing**

For OSB pilot scale production, standard aspen strands (*populus tremuloides*) with a nominal thickness of 0.7mm and a length of 142mm containing 4-5% moisture were used. Panel target density and thickness were 640kg/m<sup>3</sup> and 11 or 12.5mm respectively. For the core, MDI binder was used at 2 or 3% level and for the face, 3 or 5% of various PF resin samples was applied. 1% slack wax or emulsion was applied in the face and core. Panel dimensions were 76 x 76cm with face to core ratio 55/45 and random orientation. Platen temperature was 210°C and the press cycle applied was 220s. In some cases, only PF resins were used to produce one-layer boards. The cure behaviour was examined by pressing boards at various press cycles.

Two different types of wood veneers were employed for industrial or lab scale plywood production: poplar (hardwood) and okoume (tropical) veneers with 5-6% moisture. Glue mixture with hardeners and fillers was spread on the veneers at a quantity of 130g/m<sup>2</sup>. In industrial scale production, 9-layer panels were formed with 18 or 20mm thickness. After 10-15 min assembling time, panels were pressed at 120°C and press time corresponding to their thickness. At lab scale, 3-layer boards were formed and pressed at 130°C for 3.5min.

For OSB panels the IB (internal bond), MOR (modulus of rupture) and MOE (modulus of elasticity) were measured with the use of a tensiometer. Samples of the OSB boards were subjected to 2h boiling and then the IB, MOR and MOE were measured. In some cases, the moisture cycling test APA-D4 according to the Canadian standard CSA 0437 was carried out: test specimens were placed in a vacuum-pressure vessel with water at 66°C, a vacuum of 34 millibars was applied for 30 min and after the vacuum release the samples were allowed to soak for another 30 min. After drying for 15 hours at 82°C, IB or MOR/MOE were tested. The panels swelling behaviour was determined by measuring the thickness of specimens (15 x 15cm) before and after immersion in water (20°C) for 24 or 48 hours. For some specimens the water absorption was also determined.

For plywood boards, the bond quality WBP (Weather and Boil Proof) according to the British standard 6566 was determined after 72 hours boiling and using a special knife.

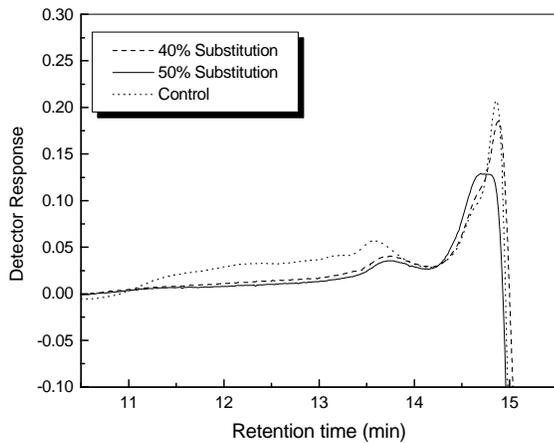
### **Results**

Representative samples of the 40 and 50% substituted resins of the T2 and T3 types were subjected to GPC (Gel Permeation Chromatography) measurements, to determine their molecular weight distribution. An increase of the Mn, Mw and especially Mz was noted, when bio-oils were used to substitute part of the phenol in the formulation (Table 2). There was an increase in dispersion as well, especially when 50% phenol substitution was tried. This increase in molecular weights is more pronounced in T3 type resins and for pure wood pyrolysis oils. The GPC graphs (Figures 1-4) show, that in 50% substituted resins, a broad peak appears at lower

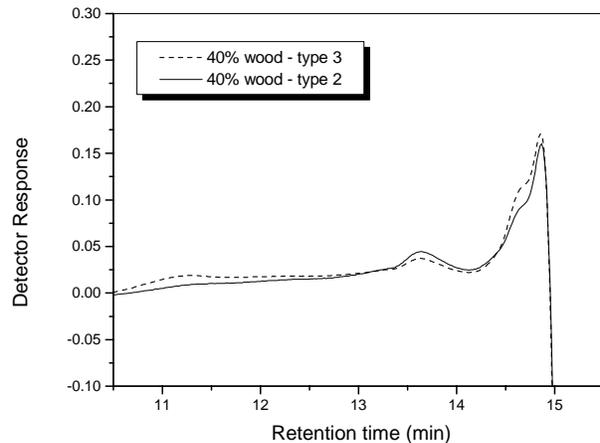
molecular weights, which could be due to the more complex composition of the bio-oils as compared to petroleum phenol, that produces a wider range of low molecular weight products.

**Table 2: PF resins molecular weight distribution obtained from GPC measurements.**

Resins	Solids, %	Viscosity, cp	$M_n$	$M_w$	$M_z$	PDI
T2 control	51.0	140	156	454	977	2.899
T2 40% wood	51.0	145	198	455	1320	2.291
T2 40% bark	50.6	130	167	415	1442	2.483
T2 50% bark	51.1	125	182	416	1191	2.293
T2 50% wood	51.1	130	196	870	7917	4.444
T3 50% bark	50.1	195	173	583	3241	3.362
T3 40% wood	50.0	145	150	772	6717	5.157
T2 40% wood	50.6	130	142	448	1533	3.160
T3 control	48.7	130	142	416	787	2.936

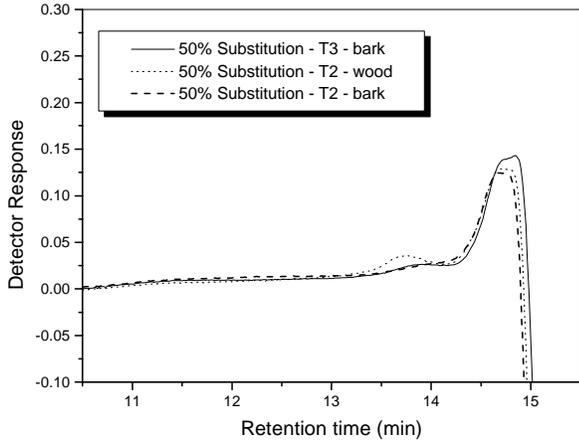


**Figure 1: GPC graphs of 40 and 50% modified resins.**

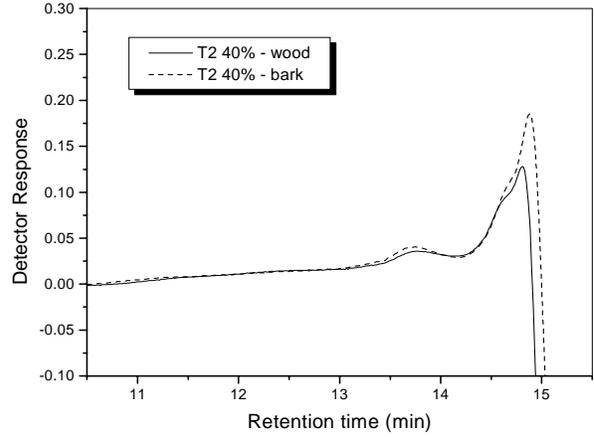


**Figure 2: GPC graphs of T2 and T3 resin types with 40% substitution.**

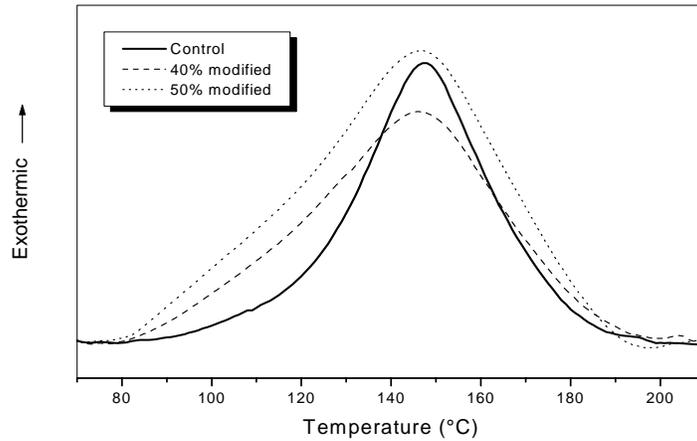
Furthermore, the DSC scans of bio-oil modified versus control phenolic resins are shown in Figure 5. All resins were of the T2 type. Both modified-PF scans show a large positive (exothermic) peak, which is due to the polymerization reaction of the resins. The DSC peak characteristics are given in Table 2.



**Figure 3: GPC graphs of T2 and T3 resins - 50% substitution with bark and wood bio-oil.**



**Figure 4: GPC graphs of T2 resins - 40% substitution with bark and wood bio-oil.**

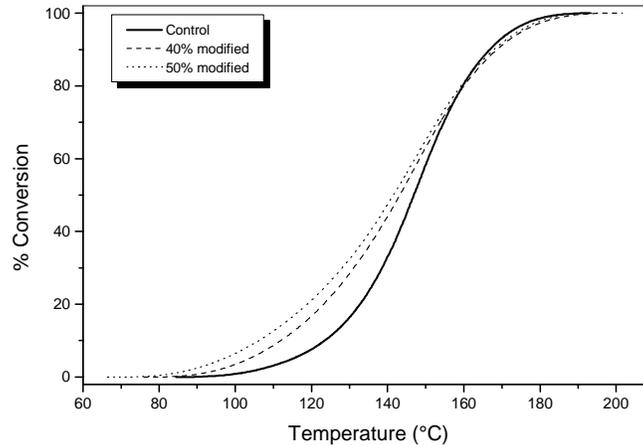


**Figure 5: DSC scans of bio oil modified vs. control PF resin.**

**Table 2: DSC results.**

Resin	Onset, °C	Peak maximum, °C	Endset, °C	Heat of reaction (J/g)
Control	85	147	195	95.2
40% modified	79	146	206	110.0
50% modified	75	146	196	151.0

The DSC thermograms show that the modified PF resins cure faster than the control one, since all peak characteristics (onset, maximum, endset) are shifted to lower temperatures. The higher heat of reaction of the modified PF resins suggests that the crosslinking density is higher compared to the control PF resin. This result is further substantiated by the % conversion versus temperature graph (Figure 6).



**Figure 6: % conversion as a function of temperature.**

The % conversion (C), which can be regarded as a measure of the extent of crosslinking, is defined as:

$$C(T) = 100 \times (A_T/A_0)$$

where  $A_T$  is the peak area up to a temperature T and  $A_0$  is the total peak area (i.e. total heat of reaction).

In pilot scale OSB production, 40% substituted resins synthesised according to T2 and T3 techniques were employed. By the results of these tests, the more suitable resin synthesis technique was identified. Boards with 12.5 mm thickness were prepared, using 3% MDI in the core and 5% PF in the face. The corresponding board properties are presented in Table 3.

The results show that the resin produced according to T2 technique has a better overall performance than the one synthesized according to T3 – higher IB values in both dry and moisture cycling test conditions, higher cycling test MOR and lower swelling and water absorption values. Thus, T2 technique was retained for further evaluation.

**Table 3: Properties of OSB produced with T2 and T3 40% substituted resins.**

<b>Property</b>	<b>T2</b>	<b>T3</b>
Density, kg/m <sup>3</sup>	649	659
IB, N/mm <sup>2</sup>	0.70	0.51
IB, APA-D4, N/mm <sup>2</sup>	0.51	0.39
MOR, N/mm <sup>2</sup>	34.56	37.46
MOR, APA-D4, N/mm <sup>2</sup>	36.27	29.86
MOE	4322	4753
MOE, APA-D4	4487	4422
24h swelling, %	12.2	11.9
24h edge swelling, %	18.8	19.0
48h swelling, %	15.0	16.0
Water absorption, 24h, %	22.4	23.6
Water absorption, 48h, %	31.4	33.7

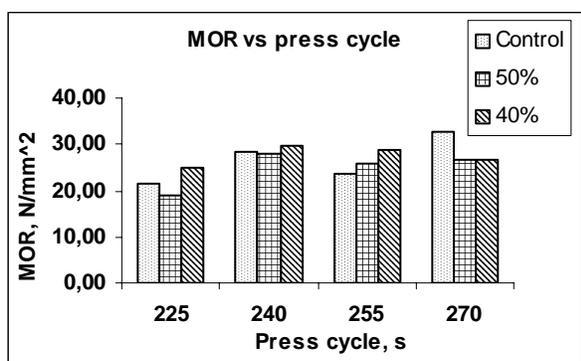
Further trials were carried out comparing two different bio-oils from wood (W) and bark (B) at two substitution levels: 40 and 50%. The board production conditions were the same as previously reported. It was proven that all substituted resins have equivalent or even better performance than the control resin (Table 4). A decrease in the performance of 50% substituted resins as compared to 40% ones was observed, however still superior than the performance of the control resin. Both bio-oils seem equally efficient, with the bark-derived slightly better.

**Table 4: Properties of OSB produced with T2 substituted resins (40 and 50% substitution with bark and wood bio oil.**

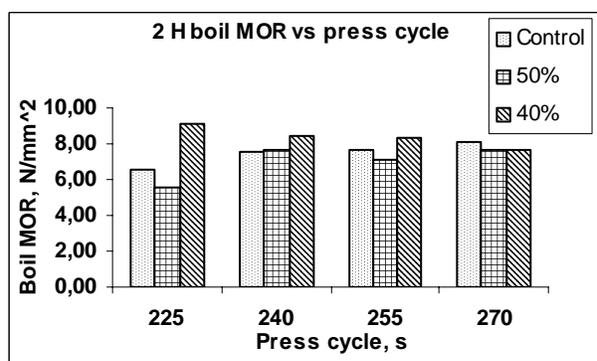
<b>Property</b>	<b>Control</b>	<b>40%</b>	<b>50%</b>	<b>40%</b>	<b>50%</b>
		<b>W</b>	<b>W</b>	<b>B</b>	<b>B</b>
Oil type					
Density, kg/m <sup>3</sup>	647	650	652	649	646
IB, N/mm <sup>2</sup>	0.57	0.74	0.66	0.70	0.54
IB, APA-D4, N/mm <sup>2</sup>	0.31	0.51	0.48	0.51	0.38
MOR, N/mm <sup>2</sup>	33.79	34.61	35.13	34.56	37.97
MOR, APA-D4, N/mm <sup>2</sup>	30.82	33.21	34.58	36.27	34.09
MOE	4572	4381	4666	4322	4501
MOE, APA-D4	4405	4278	4413	4487	4664
24h swelling, %	13.9	12.9	12.6	12.2	11.2
24h edge swelling, %	20.6	18.5	18.8	18.8	18.0
48h swelling, %	19.3	15.7	16.1	15.0	14.5
Water absorption, 24h, %	22.8	24.6	25.3	22.4	21.6

Water absorption, 48h, %	32.3	34.5	34.8	31.4	30.1
--------------------------	------	------	------	------	------

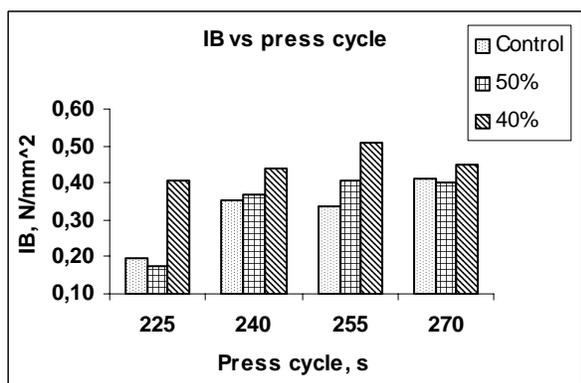
The curing behaviour of substituted resins was evaluated by producing 11mm one-layer boards, formed with only 3% phenolic resin at various press cycles: 225, 240, 255 and 270s. Representative results from the testing of board properties are depicted in Figures 7-10, which show that the 40% substituted resin is more reactive than the control, while the 50% substituted resin is less reactive than both of them. It should be noted that, at shorter press time, the 40% substituted resin had better IB and MOR at dry conditions, better MOR after boiling (bonding durability, BD), and lower swelling values. The overall performance of the 50% substituted resin was, however, comparable to the control and quite satisfactory.



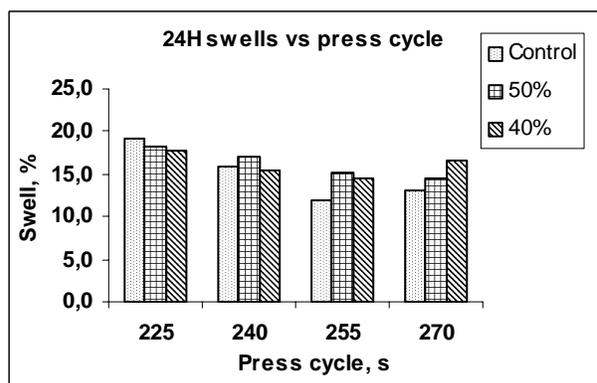
**Figure 7: MOR as a function of press cycle.**



**Figure 8: 2 h boil MOR as a function of press cycle.**



**Figure 9: IB as a function of press cycle.**



**Figure 10: 24 h swell as a function of press cycle.**

The resins curing behaviour was further tested, using more conservative glue factors: 2% MDI in the core and 3% PF in the face. However, these conditions are much closer to industrial practice. In this case, the press cycles were shorter: 115, 125, 135 and 145s (Figures 11-14). The board testing results indicate more or less the same trend as in the previous experiment. The 40% substituted resin is the best followed by control resin. The 50% substituted resin comes last, however, behaves very closely to the control.

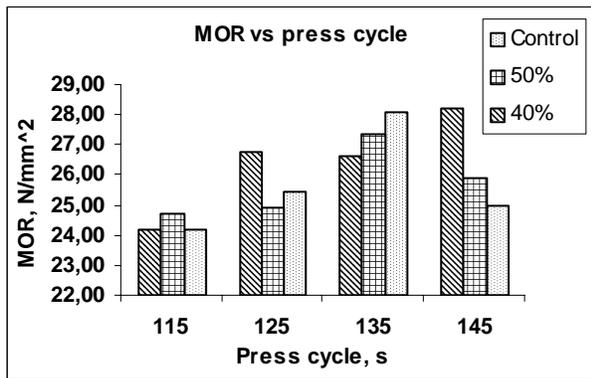


Figure 11: MOR as a function of press cycle.

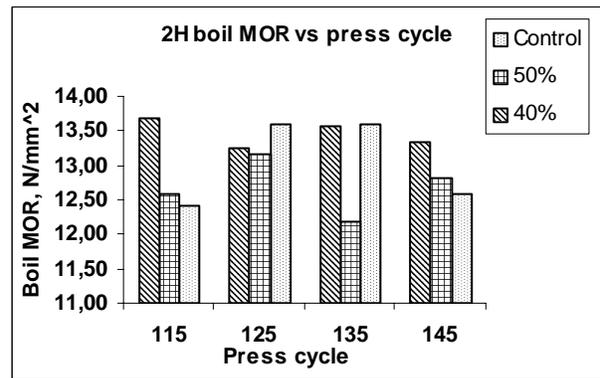


Figure 12: 2 h boil MOR as a function of press cycle.

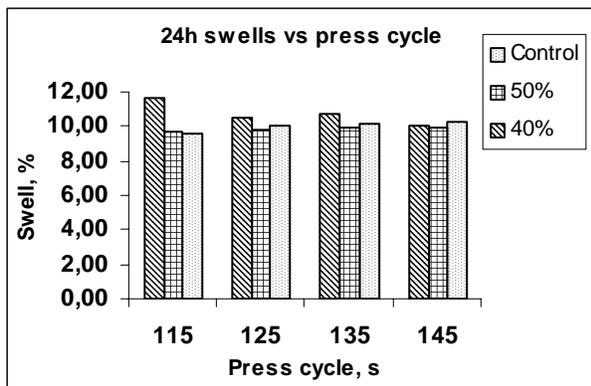


Figure 13: 24 h swell as a function of press cycle.

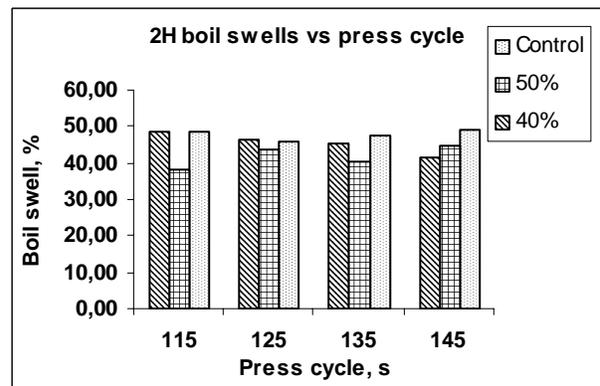
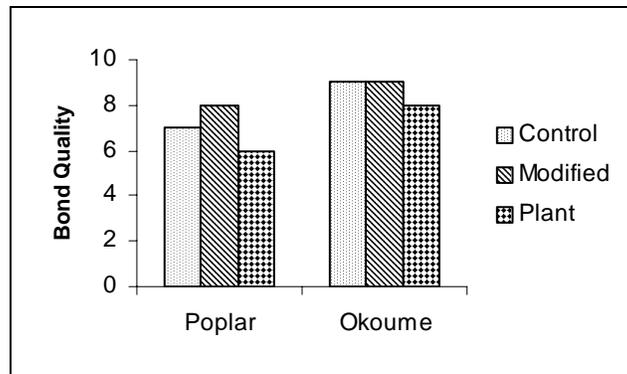


Figure 14: 2 h boil swell as a function of press cycle.

Industrial scale production of plywood was realized by employing T1 type phenolic resin, modified with wood bio-oil at 40% substitution level. Representative results from testing of the board properties are given in Figure 15. The board samples were tested according to the

requirements of bond type WBP (Weather and Boil Proof) of British Standard 6566, using the knife test for assessing the bond quality. The bond quality of the modified resin was compared with that of the conventional resin (control) and the value of plant control. The panel bond performance, however, is highly dependent not only on the resin type but also on the type of wood veneers. The results show that the bond quality of the bio-oil modified resin is equal or even better than that of the conventional resin and higher than the plant control value.



**Figure 15: Bond quality of industrial plywood produced with bio-oil modified PF resin.**

### 3. Conclusions

The pyrolysis oil can be used in the manufacture of phenolic resins for various panel types with positive results. An up to 50% phenol substitution was realized already and further increase in the substitution level is envisaged. To provide significant savings for the resin manufacturer the phenol substitution level should be above 40% and the price of the pyrolysis oil should be maximum 50% of the phenol price. Its lower toxicity as compared to phenol and its conformity with the EU directive for sustainable development (it is produced from renewable resources) make it attractive for further investigation.

### 4. References

1. Sellers, T. Jr., 2001. "Wood Adhesive Innovations and Applications in North America", *Forest Prod. J.*, Vol. 51, No. 6, p.12-22.
2. Diebold, J., Power, A., 1988. "Engineering Aspects of the Vortex Pyrolysis Reactor to Produce Primary Pyrolysis Oil Vapors for Use in Resins and Adhesives", *Research in Thermochemical Biomass Conversion*, Bridgwater, A.V., Kuester, J.L., Elsevier Applied Science, London, p.609-628.
3. Chum, H.L., et al., 1991. "Inexpensive Phenol Replacements from Biomass", *Energy from Biomass and Wastes XV*, Eds. Klass, D.L., p.531-540.

4. Elder, T.J., Soltes, E.J., 1980. "Pyrolysis of Lignocellulosic Materials. Phenolic Constituents of a Wood Pyrolytic Oil", *Wood and Fiber*, Vol. 12, No. 4, p.217-226.
5. Achladas, G.E., 1991. "Analysis of biomass pyrolysis liquids: separation and characterization of phenols", *J. of Chromatography*, Vol. 542, p.263-275.
6. Chum, H.L., Diebold, J.P., Scahill, J.W., Johnson, D.K., Black, S., Schroeder, H.A., Kreibich, R.E., 1989. "Biomass Pyrolysis Oil Feedstocks for Phenolic Adhesives", *Adhesives from Renewable Resources*, R. Hemingway and A. Conner, Eds., ACS Symp. Series, No 385, p.135-151.
7. Gallivan, R.M., Matschei, P.K., 1980. "Fractionation of Oil obtained by Pyrolysis of Lignocellulosic Materials to recover a Phenolic Fraction for use in making Phenol-Formaldehyde Resins", *US Pat.* No. 4 209 647.
8. Chum, H.L., Black, S.K., 1990. "Process for Fractionating Fast-Pyrolysis Oils, and Products derived therefrom", *US Pat.* No. 4 942 269.
9. Sharma, R.K., Bakhshi, N.N., 1993. "Catalytic Upgrading of Pyrolysis Oil", *Energy & Fuels*, Vol. 7, p.306-314.
10. Pakdel, H., Roy, C. and Lu, X., 1997. "Effect of Various Pyrolysis Parameters on the Production of Phenols from Biomass", *Developments in Thermochemical Biomass Conversion*, Bridgwater, A.V., Boocock, D.G.B., Blackie Academic & Professional, London, Vol. 1.
11. Samolada, M.C., Papafotica, A. and Vasalos, I.A., 2000. "Catalyst Evaluation for Catalytic Biomass Pyrolysis", *Energy & Fuels*, Vol. 14, p.1161-1167.
12. Roy, C., Calve, L., Lu, X., Pakdel, H., and Amen-Chen, C., 2000. "Wood Composite Adhesives from Softwood Bark-Derived Vacuum Pyrolysis Oils", *Proceedings of Wood Adhesives 2000*, USA, in press.
13. Lu, X., Roy, C., and Pakdel, H., 2000. "Process for the Production of Phenolic-rich Pyrolysis Oils for Use in Making Phenol-Formaldehyde Resole Resins", *US Pat.* No. 6 143 856.
14. Himmelblau, D.A., 1995. "Phenol-Formaldehyde Resin Substitutes from Biomass Tars", *Proceedings of Wood Adhesives 1995*, Forest Products Society, Madison, WI, p.155-162.
15. Himmelblau, D.A., Grozdits, G.A. and Gibson, M.D., 2000. "Performance of Wood Composite Adhesives Made With Biomass Pyrolysis Oil", *Proceedings of Wood Adhesives 2000*, Forest Products Society, Madison, WI, in press.
16. Nakos, P., 1998. "Binders for the Wood Industry made with Pyrolysis Oil", *PyNe Newsletter*, Aston University, issue 6, p. 6-7.
17. Tsiantzi, S., Athanassiadou, E., 2000. "Wood Adhesives Made with Pyrolysis Oil", *PyNe Newsletter*, Aston University, issue 10, p. 10-11.
18. Goldstein, I.S., 1981. "Chemicals from biomass: present status", *Forest Prod. J.*, Vol. 31 No. 10, p.63-68.

19. Kelley, S.S., Wang, X-M., Myers, M.D., Johnson, D.K. and Scahill, J.W., 1997. "Use of Biomass Pyrolysis Oils for Preparation of Modified Phenol Formaldehyde Resins", *Developments in Thermochemical Biomass Conversion*, Bridgwater, A.V., Boocock, D.G.B., Blackie Academic & Professional, London, Vol. 1.
20. Knop, A., Pilato, L.A., 1985. "Phenolic Resins. Chemistry, Applications and Performance. Future Directions", Springer-Verlag, Berlin.