

Phenol–Formaldehyde–Pyrolytic Oil Resins for Wood Preservation: A Rheological Study

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ABSTRACT: The rheological properties of a phenol–formaldehyde resin containing various ratios of softwood pyrolytic oil as phenol substitute were investigated using the simple Bingham rheological model for viscoplastic fluids. Flow activation energy was determined for the various resin blends and the pyrolytic oil between room temperature and 50°C and correlations relating the flow activation energy to the weight fraction of pyrolytic oil in the resin are proposed. Apparent crosslinking activation energy with and without copper chloride used as an activator was

also evaluated based on two gel time measurements between 75 and 105°C. A significant decrease in activation energy was observed for the phenol–formaldehyde resin cured with copper chloride, while the effect was less important for resins containing pyrolytic oil even when gel times were much shorter for PF-resins. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1087–1094, 2007

Key words: pyrolytic oil; phenol–formaldehyde resin; rheology; copper chloride; activation energy

INTRODUCTION

In 2004, withdrawal of chromated copper arsenate (CCA)-treated wood for domestic use created a void to be filled in the treated wood market. The demand for safer wood preservatives for both the public and the environment is the principal drive behind this withdrawal, since many of the proposed substitutes are more costly, leachable or less efficient than CCA. Many paths have been explored to come up with a better solution for wood preservation respecting the environment while ensuring good qualities of the end product.

In a series of experiments with phenol–formaldehyde (PF) resins modified with the addition of pyrolytic oil obtained from the pyrolysis of softwood bark and used in conjunction with a copper chloride solution, Mourant et al.^{1–4} obtained promising results with regard to leaching reduction, weight losses attributed to fungal decay, and the effect of this treatment on some mechanical properties (elasticity and rupture moduli) of treated wood. However, resin penetration into wood cells was not very extensive;

i.e. most of the resin penetrating at most 100 µm in the transversal plan of white pine and American Beech. Deeper penetration was observed in maple samples, mostly due to the vessel elements of this wood species. Since penetration of the resin in wood is affected partly by the viscosity of the treating solution, it is important to better understand the flow dynamics of the various resin formulations to obtain more effective wood preservation.

Pyrolytic oil is obtained from the thermal degradation of biomass in absence of oxygen and is one of three products obtained from this process, the other two being charcoal and gases. The most popular pyrolysis system used today is flash pyrolysis; while other systems are being tested, namely vacuum pyrolysis, which is used in this study. It is known that the kind of process will have an impact on the yields and quality of the products obtained.^{5,6} The nature and size of the feedstock, humidity, and residence time of the gases in the reactor also have an impact on the resulting pyrolytic oil.⁷ Pyrolytic oils obtained from bark residues are quite complex, containing organic acids, phenols and their derivatives, furans, aldehydes, and ketones of various sizes.^{5,8,9} These compounds are either volatilized from the feedstock, as is the case for some wood extractives, or obtained from the cracking of the wood constituents, namely cellulose, hemicelluloses, and lignin.⁹

On the other hand, PF resins are one of the most used polycondensation resins available, because they are easily produced and relatively inexpensive. They

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are found as two main types depending on the conditions under which they are produced. Novolac resins are produced by the reaction, under acidic conditions, of an excess of phenol with formaldehyde; while resoles are prepared by the addition of an excess of formaldehyde to phenol under basic conditions. Resoles are created by the formation of an addition compound followed by the condensation reaction of a methylol group in either the ortho or para position, producing methylene bridges.^{10–12}

Previous studies made on the inclusion of pyrolytic oil in resins were directed toward the panel industry and showed promising results. Amen-Chen et al.^{13,14} studied the formation of resoles consisting of a PF-pyrolytic oil blend for the fabrication of oriented strand-board (OSB) panels, work further enriched by Chan et al.,¹⁵ who also investigated the impact of such resins on mould growth and decay resistance. It was observed that inclusion of pyrolytic oils in resins formulation greatly decreased fungal growth on OSB samples.¹⁶ Gagnon et al.¹⁷ studied the rheological properties of a polymethylene diphenyl diisocyanate (pMDI)–pyrolytic oil blend used in the fabrication of OSB panels.

The inclusion of copper in the formulation of the antifungal system is justified by its role as a proven fungal growth inhibitor and as a curing accelerator. Even though copper would be impregnated in wood as a first treatment independent of the resin impregnation, interactions between copper ions and resin constituents will occur. It is important to better understand the impact of copper on the resin's viscosity to ensure good wood penetration by the second treating solution. Interactions between cations and phenolic compounds are known to exist and have been widely studied.^{11,18,19} Bivalent metallic salts are also known to promote phenol–formaldehyde condensation.¹⁹

Even though studies on the impact of metallic ions on the rheology and curing kinetics of resins exist, the recent use of phenol substitutes like lignin or pyrolytic oil in resin formulation requires more research as these systems behave differently than neat PF resins. It is thus the objective of this study to better understand the impact of temperature, pyrolytic oil concentration, and presence of copper on the rheology of modified PF-resins. This information will help in designing an impregnation scheme to optimize wood treatment. Steady shear viscosity will provide useful information for wood impregnation, while dynamic complex viscosity will help understanding curing rates and treatment limitations.

MATERIALS AND METHODS

Pyrolysis of softwood bark

A mixture of softwood barks was obtained from a large pulp and paper plant in Quebec City (Papiers

Stadacona). The mixture composed of 70% (v/v) balsam fir (*Abies balsamea*) bark, 28% (v/v) white spruce (*Picea glauca*) bark, and 2% (v/v) larch (*Larix laricina*) bark was air-dried to a moisture content of $\sim 16\%$ and the feedstock was shredded to a mesh size less than 25 mm. The pyrolysis process and experimental equipment used have been described elsewhere.^{20,21} The H69 pyrolysis run was performed at 450°C and a total pressure of 20 kPa in a vacuum pyrolysis process development unit at a throughput capacity of 34 kg/h. A total of 206 kg of feedstock was converted into pyrolytic oil, pyrolytic charcoal, and gases. This pyrolytic oil was kept at 4°C to minimize chemical reactions during storage.

Resin synthesis procedure

Aqueous formaldehyde at a concentration of 37% by weight and phenol were loaded at a molar ratio of 1 : 2.5 (P : F) in a kettle equipped with a mechanical stirrer. After homogenization, a 50% by wt. NaOH solution was added dropwise to obtain a phenol : NaOH molar ratio of 1 : 0.15. The mixture was heated up to 65°C in 15–20 min and kept at this temperature for 100 min. The mixture was then cooled to 30–40°C and a predetermined amount of formaldehyde scavenger (NH₄OH at 28% by wt.) was added. The final viscosity of the PF-resin was of 20 ± 1 mPa s at 25°C. Resins of various compositions were obtained by mixing the PF-resin with pyrolytic oil at different ratios of substituted phenol: 50, 75, and 85% on a weight basis. Hereafter, the treated resins will be named R350, R375, and R385 according to the pyrolytic oil content. The resins were stored at 4°C until used.

Apparent viscosity and flow activation energy

The plastic zone apparent viscosity of the resins was measured between 25 and 50°C, with 5°C increments, using a Brookfield LVDV III+ digital viscometer mounted with a no. 18 spindle. Samples studied included the PF resin alone (R3), the resin mixed with 50, 75, and 85% of phenol substitution by weight with pyrolytic oil, and the pyrolytic oil alone (H69). No catalyst (copper chloride) was included for these tests. Averages of five observations are reported for each condition tested.

A Rheometric Scientific ARES rheometer was used to investigate the yield stress zone under steady shear, from 0.05 to 150 s⁻¹, with a delay of 120 s between each measurement. The gap between two 40-mm circular plates was set at 1 mm to obtain shear stress–shear rates curves.

Gel time and activation energy

The evolution of viscosity with time at different temperatures and for various resin formulations was

studied with a Rheometric Scientific ARES rheometer. The samples were placed between two disposable aluminum plates of 40 mm diameter and the gap between the plates programmed at 0.90 mm. Measurements were made in the dynamic mode (small amplitude oscillatory motion) to study the sample under "no flow" conditions. The selected frequency of oscillation was 0.5 Hz and the strain amplitude was set at 0.25 to remain within the linear deformation domain (linear viscoelastic region). The complex viscosity (η^*), storage modulus (G'), loss modulus (G''), and loss tangent ($\tan \delta$) were monitored as a function of time. All samples were allowed to stop foaming and the excess of resin was cleaned from the side of the plates before starting the measurements. The test sequence was then initiated when the temperature reached the desired values of 75, 85, 95, and 105°C. Samples containing copper were also prepared by manually mixing 5% wt. copper chloride to the resin no more than 5 min before being placed on the plates to minimize reaction time at room temperature.

RESULTS AND DISCUSSION

Two separate steps can be seen during the cure of thermosetting resins. The first step involves growth and branching of the resin constituents in larger polymer chains while remaining in a free flowing liquid state. The second step occurs at the gel time where an infinite network of polymer chains appears and develops. The reactive system then loses its solubility and fusability. The gel time is an important parameter, since it determines when the resin becomes physically unprocessable and depends on various conditions like temperature, pH, presence of an accelerator, etc.

Impregnation of the resins in wood is obviously conducted under conditions well before reaching gel time; i.e. the resin is still liquid. It is thus possible to lower viscosity and improve penetration into wood cells by increasing temperature. A lower viscosity would increase the flow rate, Q , according to Poiseuille equation²²:

$$Q = \frac{\pi d^3 f \cos \alpha}{32\nu} \quad (1)$$

where d is the pore diameter, f is the surface tension, α is the contact angle between the resin and the cell wall, and ν is the kinematic viscosity. However, one must be careful since higher temperatures also mean faster polymerization, leading eventually to higher viscosity values and reduced working time.

At low temperatures and in the early stages of curing, all the blends have a thermoplastic-like behavior.²³ The pyrolytic oil content has a significant impact on viscosity. Comparison made at 25 and 50°C

shows that the pyrolytic oil viscosity is more affected by temperature variations than resin blends. High viscosity values obtained with pyrolytic oil for temperatures below 30°C is attributed to the three-dimensional structured state of the molecules it contains.¹⁷ Increased temperature induces relaxation of the various hydrogen bonds and van der Waals forces existing in the pyrolytic oil resulting in a partial destruction of these three-dimensional structures and a lower viscosity. However, it should be noted that prolonged heating of pyrolytic oil, especially at temperatures exceeding 80°C, was shown to increase viscosity through etherification and/or esterification reactions between hydroxyl, carbonyl, and carboxyl groups of the components.^{24,25}

Apparent flow activation energy

As presented in Figure 1, plotting shear stress as a function of shear rate for the various blends of resins, two separate zones are observed, indicative of a Bingham fluid. At low rates of deformation, the yield zone is obtained as the minimum shear stress needed to induce flow. As the shear rate increases, a transition occurs to the plastic behavior zone. Similar non-Newtonian behaviors have been observed for pyrolytic oils obtained from softwood bark in the past.^{9,24,26} The Bingham rheological model relates shear stress (τ) to shear rate ($\dot{\gamma}$) via²⁷:

$$\tau = \tau_0 + \eta_p \dot{\gamma} \quad (2)$$

where τ_0 is the yield stress and η_p is the apparent plastic viscosity. It is known that increasing temperature leads to lower τ_0 values because of reduced internal structures strength in the resins, which is responsible for the yield stress. As the pyrolytic oil content in the resins increases, higher yield stress values are obtained. In experiments conducted by Garcia-Perez,⁹

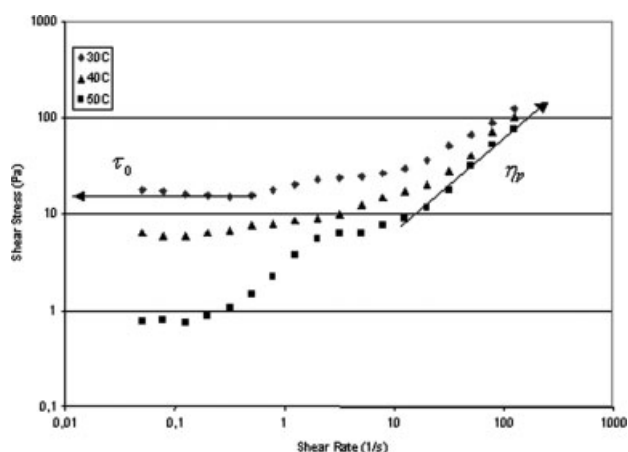


Figure 1 Typical rheological curves for the effect of temperature and shear rate for the resin R385.

TABLE I
Apparent Flow Activation Energies, for the Plastic and Yield Zones of Resins
Containing Various Content of Pyrolytic Oil

Pyrolytic oil content ^a (%)	E_{η_p} (kJ/mol)	A_{η_p} (s ⁻¹)	E_{τ_0} (kJ/mol)	A_{τ_0} (s ⁻¹)
0	32.3	5.4×10^{-6}	4.4	4.1×10^{-1}
50	38.1	8.2×10^{-7}	31.7	2.5×10^{-5}
75	48.9	2.6×10^{-8}	35.1	1.8×10^{-5}
85	53.4	8.7×10^{-9}	38.3	4.7×10^{-6}
100	77.0	6.7×10^{-12}	54.4	5.5×10^{-9}

^a Based on total phenol substitution ratio.

softwood bark pyrolytic oil was fractionated by heating at 50°C followed by rapid cooling where a phase separation occurred. The upper layer has been described as a Bingham liquid at temperatures lower than 45°C and this behavior has been attributed to the melting of waxy materials in the oil and their condensation in smaller crystals when rapidly cooled.

The flow activation energy of the plastic flow part of the rheological curve (E_{η_p}) can be determined by assuming an Arrhenius-like phenomenological law as:

$$\ln(\eta_p) = \ln(A_{\eta_p}) - \frac{E_{\eta_p}}{RT} \quad (3)$$

where R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), T is the absolute temperature (K), and A_{η_p} is the pre-exponential factor. The apparent flow activation energies and pre-exponential factors of the different blends of resins and the pyrolytic oil are presented in Table I. The activation energy increased with pyrolytic oil content, from 32.3 kJ/mol for the PF resin to 77.0 kJ/mol for the pyrolytic oil. The value obtained here for the pyrolytic oil is similar to the reported value of 85.3 kJ/mol by Garcia-Perez⁹ from a similar source of biomass and produced using the same pyrolysis process. Using the data presented in Table I, correlations are proposed here to relate both E_{η_p} and A_{η_p} with concentration of pyrolytic oil in the resin, using the weight fraction (ω) as reference instead of the phenolic substitution percentage. Plotting the logarithm of each parameter as a function of ω , linear behaviors were obtained and can be represented by:

$$\ln(E_{\eta_p}) = 0.87\omega - 3.45 \quad (4)$$

$$\ln(A_{\eta_p}) = -13.50\omega - 11.28 \quad (5)$$

An Arrhenius-like equation can also be used to obtain a relation between the yield stress (τ_0) and temperature. Substitution of E_{η_p} by E_{τ_0} and A_{η_p} by A_{τ_0} in Eq. (3) can provide information on the energy required for flow initiation and resin flow through

wood cells. However, since many of the values measured above 45°C and at low deformation rate were obtained at the lower detection limit of the rheometer, this may partially explain some noise in the data (especially at higher temperature). It is safe to assume a minimum of 20% error margin on the data. Nevertheless, a clear trend can be seen from the results as presented in Table I. Once again, correlations for E_{τ_0} and A_{τ_0} are proposed as:

$$\ln(E_{\tau_0}) = 0.71\omega - 3.25 \quad (6)$$

$$\ln(A_{\tau_0}) = -0.16\omega - 3.31 \quad (7)$$

Microscopic observations of the R385 resin at room temperature, after 1 h at 50°C, and after 1 h at 50°C at a shear rate of 150 s⁻¹ show internal modifications. Aqueous droplets can be observed in Figure 2, especially after a cooling period. This phenomenon resulted in modifications of the matrix. These modifications induced more complex viscous behavior due to the dispersion of aggregated material, as was observed in the pyrolytic oil alone, and polymerization, as was observed in the phenolic resin. However, the exact nature of this behavior was beyond the scope of the present study and should be investigated more carefully in the future. Nevertheless, previous studies showed that some modifications of the pyrolytic oil can be attributed to the presence of waxy materials and the degradation of certain oligomers.^{9,28} It is possible that these elements, at higher temperatures and under the effect of shear, were degraded and dispersed in the matrix, allowing for interspaced water droplets to aggregate and form larger aqueous droplets after cooling, visible under microscope. These observations indicate that the thermal history of the pyrolytic oil could have an impact on the rheological properties of the resin through matrix modification.

Gel time determination

This property characteristic of a reactive resin is somewhat difficult to define, but can be obtained

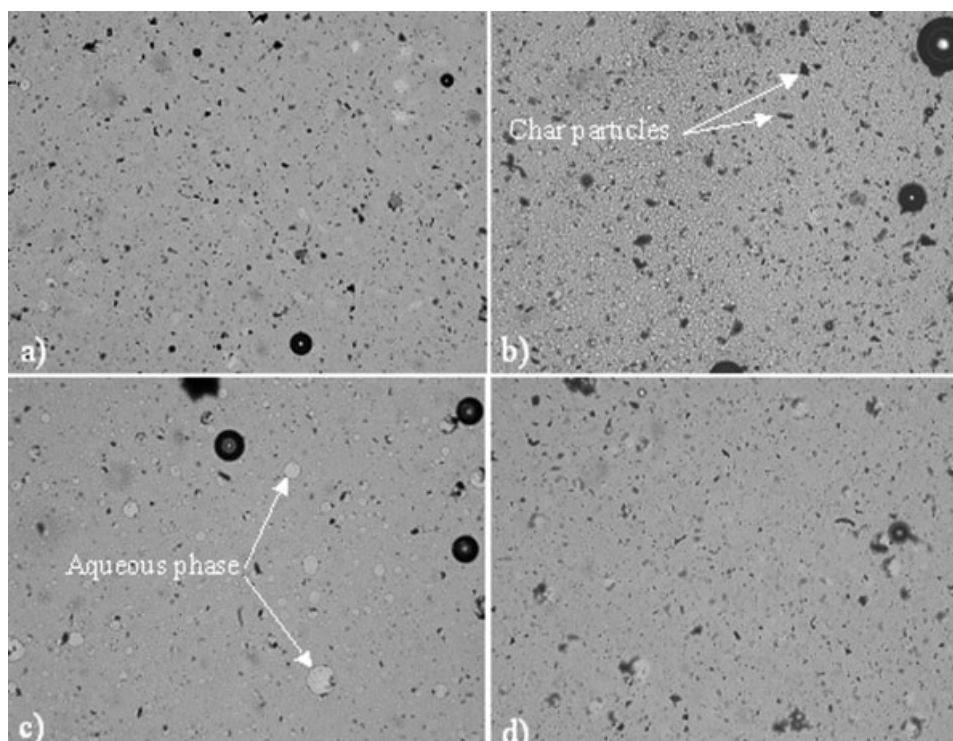


Figure 2 Typical evolution of some structures and various phases in a PF-pyrolytic oil resin (R385) at (a) 25°C, (b) 50°C, (c) cooled after being heated at 50°C, and (d) after having been submitted to a shear rate of 150 s^{-1} for 1 h at 50°C.

through various measurements, each yielding different values. Laza et al.¹⁰ selected several separate measures of gel times that they averaged to obtain more information on the crosslinking of a PF resin. Various preselected values of viscosity (1000, 2000, and 5000 Pa s), the maximum peak in $\tan \delta$ (the point where G' and G'' are the farthest from one another), the crossover between G' and G'' curves and the tangent line to the G' curve when G'' reached a value close to 100 kPa were all used in the determination of gel time.¹⁰ Since gel time is often described as the point where the resin becomes unprocessable, the selection of arbitrary viscosity values by Laza et al. is certainly not universal. The crossover of $\tan \delta$ curves

obtained at different frequencies was also used to determine the gel times.^{29,30} Here, gel time determination will be based on the $G'-G''$ crossover (denoted hereafter G_c) and the maximum in the $\tan \delta$ curve (peak). Table II shows that both methods yield somewhat different values and were not averaged for the lack of meaning of such an average.

Measures of the gel time, especially for samples containing copper chloride, were hampered by the initial foaming behavior of the resin. The time required to clean the overflowing resins was not included in the measured time, even though polymerization reactions were taking place. Temperature fluctuations before the instrument stabilized at the

TABLE II
Gel Times (min) of the Various Resin Blends with and without the Addition of Copper Chloride and Determined from the Peak of $\tan \delta$ and the Crossover of G' and G'' (G_c)

Resins	Peak $\tan \delta$				G_c			
	75°C	85°C	95°C	105°C	75°C	85°C	95°C	105°C
R3	175	75	33	10	267	125	50	17
R350	300	133	50	20	683	275	83	42
R375	417	167	58	33	1450	567	200	100
R385	533	275	117	67	1650	650	283	133
R3Cu	127	74	41	18	282	169	88	44
R350Cu	46	23	13	5	138	79	38	14
R375Cu	32	16	6	2	78	39	13	7
R385Cu	24	13	4	2	63	32	13	5

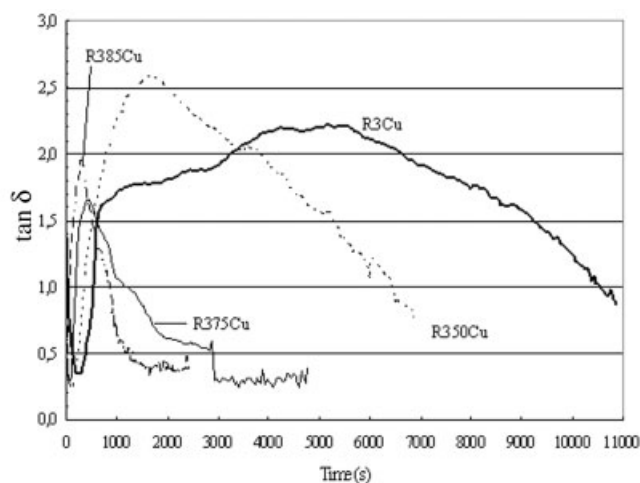


Figure 3 Typical $\tan \delta$ evolution curves obtained for various resin blends with 5% (w/w) copper chloride at 85°C.

selected temperature might also have influenced the results. However, this period of time was relatively similar for all samples tested; i.e. around 1–2 min and considered negligible with respect to experimental measurement time, since gel time values of more than 24 h at 70°C have been reported for PF resins in absence of accelerator.¹⁰

The addition of pyrolytic oil in the resin modified gel times by slowing down the curing reaction. Since the concentration of pyrolytic oil in the resin is presented as total phenol substitution, a resin containing 85% of pyrolytic oil actually contained more oil than PF resin. Many of the components of the pyrolytic oil are related to phenol and aldehydes and can react with the PF resin.^{7,8,31,32} However, some of these constituents will also dilute the blend and interfere with the reacting molecules, thus increasing gel time.¹⁴ This dilution effect and reaction competition could explain slower gelling process. It is also known that pH has an impact on the reaction rate of PF resins.¹¹ Wood, which is slightly acidic, can actually slow down curing.³³ The addition of pyrolytic oil, being acidic, can decrease pH to values between 4.3 and 6.8, a region where slower gel time of PF resins has been reported.^{4,11}

Copper chloride addition had an important impact on the viscosity and reaction speed of the various resin formulations tested (Table II). Gel times obtained with copper were lower for resins containing pyrolytic oil and higher for neat PF resin than obtained without copper. The addition of copper resulted in faster curing for resins containing higher amounts of pyrolytic oil (Fig. 3). This complete inversion of curing behavior can be attributed to interactions between copper ions and hydroxyl groups present in the resin, which promoted earlier crosslinking of the polymer chains (Fig. 4). Raising the concentration of pyrolytic oil in the resin however decreased

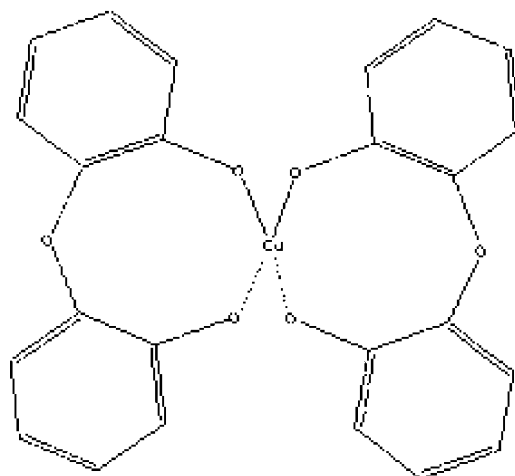


Figure 4 Interactions between copper ions and hydroxyl groups of the PF-pyrolytic oil resins. Adapted from Laks et al.¹⁹

the obtained viscosity peak values (Fig. 5). The decrease in viscosity is attributed to the physical fracture of the cured resin, possibly caused by the weaker links in presence of copper and a lesser degree of crosslinking.

Pyrolytic oil contains many groups that can interact with copper ions, even though phenol–formaldehyde resins have hydroxyl groups able to interact with copper, those groups are more abundant in the pyrolytic oil. In fact, phenolic resins do not have any catechol-type rings, which are numerous in tannins, and present in wood pyrolysis oils, giving rise to copper chelates such as in Figure 4. The addition of pyrolytic oil to PF resins increases possible condensation sites where copper ions could react, thus increasing polymerization rate. These reactions were faster at pH = 4.7, pH values similar to those of the PF-pyrolytic oil resins.⁴ Pizzi¹⁸ found that divalent metallic salts

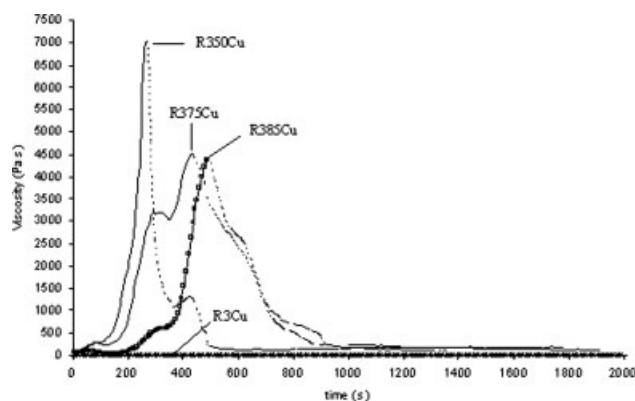


Figure 5 Typical viscosity evolution curves for PF resins containing different ratios of phenol substitution with pyrolytic oil in presence of 5% (w/w) copper chloride at 85°C. The maximum corresponds to the mechanical break-up of the thermoset resin, followed by its degradation (---).

TABLE III
Impact of Copper Chloride (5% w/w) on the Crosslinking Activation Energy (E_a) and on the Pre-Exponential Factor (A) of the Various Tested Resins

Resins	E_a (kJ/mol)		A (s^{-1})	
	Peak $\tan \delta$	G_c	Peak $\tan \delta$	G_c
R3	102	101	4.7×10^{-12}	1.3×10^{-11}
R350	99	105	2.2×10^{-11}	7.4×10^{-12}
R375	94	99	1.6×10^{-10}	1.1×10^{-10}
R385	78	92	7.3×10^{-8}	1.7×10^{-9}
R3Cu	70	68	2.8×10^{-7}	1.1×10^{-6}
R350Cu	77	84	7.2×10^{-9}	2.6×10^{-9}
R375Cu	95	91	1.2×10^{-11}	1.1×10^{-10}
R385Cu	102	91	7.5×10^{-13}	8.8×10^{-11}

could bond two resorcinol units. This reaction could be reproduced in pyrolytic oil, where numerous diphenols are known to exist, adding another reaction mechanism to the resin cure. The acidification of the more basic PF resin slowed curing, while the more acidic resins containing pyrolytic oil cured faster possibly due to a change in cure reactions, more similar to novolacs, which reacts at low pH values.

Apparent curing activation energy

The apparent polymerization activation energy (E_a) can be determined using an equation similar to Eq. (3), which is often determined through DSC analysis. The value is related to the energy required to initiate crosslinking of the polymer chains that develop until gel time is attained. Addition of pyrolytic oil to the blend reduced E_a values for the blends (Table III). This was more important for resins containing higher quantities of pyrolytic oil. It should be remembered that the activation energy, in our case, is based on the gel time, which can be obtained from different types of observations. In this case, activation energy values presented here must be considered as approximations based on both methods presented earlier ($\tan \delta$ peak and G_c).

Previous studies conducted on resins containing pyrolytic oil yielded E_a ranging between 119 and 149 kJ/mol for various formulations of PF-pyrolytic oil resins containing 50% of phenol substitution.¹⁴ These values were obtained through differential scanning calorimetry (DSC), and both the pyrolytic oil and PF-resins were different from those used here. E_a values of the PF-resins obtained by Amen-Chen et al.¹⁴ varied from 129 to 140 kJ/mol. Apparent activation energy of PF resins was found to be in the vicinity of 90 kJ/mol by Laza et al.¹⁰ with and without the presence of a catalyst. Results obtained here are more closely related to those of Laza et al. probably due to the use of similar ways of calculating the gel time; i.e. through rheological measurements. It is documented that activation energy may differ slightly with various measuring

techniques, DSC yielding higher values than rheological measurements.^{10,34} These differences can be explained by the dynamic measures of the rheometer, where convection would accelerate the reaction rate. DSC analysis, on the other hand, is static, resulting in a higher need of energy to obtain similar results.

The addition of copper chloride reduced the apparent activation energy of the resin cure. The impact of copper chloride on activation energy was more important for the PF-resin, with a reduction of 30%, than for resins containing pyrolytic oil, where the opposite trend was observed. Since E_a of a resin blend was obtained through a linear regression technique, differences between the various slopes for resins containing pyrolytic oil were not very important. This effect is probably caused by a shift in pH by the addition of the copper salt.

Significant translations of the curves to lower values in the presence of copper indicate that the pre-exponential factor A , indicative of the size of the molecules in presence, is affected by the metallic ion (Table III). The chelating effect of the copper ions is certainly responsible for these important differences. Without copper addition, pyrolytic oil substitution into the resin has a detrimental effect on the amount of branching, limiting the growth of the three-dimensional network. Chemical bonds or interactions between copper and the various compounds with catechol-like structures of the pyrolytic oil improved greatly the reticulation potential for resin containing large proportions of pyrolytic oil. It can be observed that the pre-exponential factor (A) obtained by G_c for the PF resin is higher than the one of the resin containing 50% phenol substitution, in absence of copper. This can be explained by the relatively small amount of data on which the slopes are based and the difference may not be statistically significant.

CONCLUSION

It was shown that addition of softwood bark pyrolytic oil to a PF-resin increased its viscosity. This parameter grew in importance for higher concentrations of pyrolytic oil in the blend. Blends of resins were found to behave as Bingham fluids below 45°C, and showed some phase modifications through a combined effect of temperature and shear. Flow activation energy varied in accordance to pyrolytic oil concentration in the resin, ranging from 38.1 to 53.4 kJ/mol for resin containing 50 and 85% pyrolytic oil, based on phenol substitution ratio. It is suggested to use weight fraction of pyrolytic oil in the resin in the proposed regressions since better fits were obtained. Deeper investigation is needed to better understand the effect of time on the viscosity and the various processes involved in either phase separation or polymeriza-

tion. A better model could then be developed to suit this particular polymer. Previous studies where the PF-pyrolytic oil resins were impregnated in wood were performed at room temperature.²⁻⁴ Wood impregnation results would certainly benefit from lower viscosity values obtained at temperatures in the range of 50–60°C, although no tests have been made yet for confirmation.

The addition of copper chloride decreased gel time of the blends, but had the opposite effect on the neat PF resin. The addition of pyrolytic oil increased gel times to values significantly higher than those obtained with the neat PF resin. Copper chloride lowered crosslinking activation energy in resins where the PF resin was still dominant in terms of absolute weight, and increased it slightly for the ones containing more pyrolytic oil (R385). Nevertheless, further investigations are needed to better assess the role of copper on blends increased reactivity and the nature of the polymerization reaction.

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