

ABSTRACT

The Lucas-Washburn equation describes the capillary penetration process by liquids using cylinder radius, liquid surface tension, contact angle, and viscosity. This paper considers how fundamental formulation variables of phenol-formaldehyde resins influence these physical properties that control the paper saturation process. The concept of relative penetrating power of a resin derived with the Lucas-Washburn equation from measurable physical properties is a characteristic resin property.

Application:

Calculating the relative penetrating power of a resin uses a derivative of the Lucas-Washburn equation with measurable physical properties.

PAPER IS A CAPILLARY NETWORK OF cellulose fibers. Klein presented the Lucas-Washburn equation to characterize the capillary rise of a liquid in a cylinder (1):

$$h = [rt\gamma(\cos\theta)/2\mu]^{1/2} \quad (1)$$

where:

h = penetration distance

r = radius of the cylinder

γ = surface tension of the liquid

t = time for capillary rise

θ = contact angle of the liquid on the solid

μ = viscosity of the liquid.

This paper will demonstrate how formulation variables and fundamental properties of phenol-formaldehyde (PF) polymers influence the values in the Lucas-Washburn equation related to the liquid component. These values for surface tension, contact angle, and viscosity then control the paper saturation proper-

Relationship between phenol-formaldehyde resin chemistry and paper saturation

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ties of a resin. Most research presented here was originally part of an M.S. thesis (2).

Due to the chemical composition and porous nature of wood, its behavior is sometimes analogous to paper. The interaction of a resin with wood therefore provides a model for the paper saturation process.

EXPERIMENTAL

The experiment investigated resin and wood interactions for typical plywood resin formulations. A PF resin series in a 3 x 2 factorial design used varying molar ratios of formaldehyde to phenol and sodium hydroxide to phenol. To separate the effects of sodium hydroxide and molecular weight interactions on viscosity, samples taken during each synthesis showed a broad molecular weight range at representative viscosities of about 20, 100, 400, and 1000 mPa-s. Resin formulation characteristics were therefore comparable using plots of properties against molecular weight as an example. Surface tension, contact angle, and viscosity were measured. The effects of methanol on resin viscosity were also studied later.

Resin synthesis procedure 1

Twelve resins were synthesized including two replicates of the six variable combinations. The formaldehyde to phenol ratios were 1.70, 2.00, and 2.30. The sodium hydroxide to phenol ratios were 0.40 and 0.60. All formulations had 50% theoretical solids. The materials were 100% phenol, 43% formalin, and 50% sodium hydroxide. All reagents were a tech-

nical grade. The cooks used a round-bottom glass reactor equipped with a mechanical agitator, reflux condenser, thermometer, and sample port. Temperature control used an electric heating mantle and a cooling bath of ice water. Large samples of 200–500 mL were drawn by vacuum aspiration. Small samples of 10–20 mL were drawn by pipette.

The cooking procedure ensured that all samples from a cook had the same formaldehyde to phenol and sodium hydroxide to phenol ratios. The initial charge was all the phenol, sufficient sodium hydroxide for a sodium hydroxide to phenol ratio of 0.20, and 200 g of water. The temperature was 45°C–50°C. Formalin was charged over 30 min. with 150–200 g water. The reaction was allowed to exotherm to 60°C where it remained for 60 min elapsed cooking time. The remaining sodium hydroxide and water were added, and the temperature was increased to 85°C. Samples were taken to give viscosities covering three orders of magnitude ranging from approximately 20–1000 mPa-s (cP). At least three samples were drawn for each cook.

Resin synthesis procedure 2

Two resins were synthesized with two replicates of the same formula. The formaldehyde to phenol molar ratio was 2.00, and the sodium hydroxide to phenol molar ratio was 0.10. The theoretical initial non-volatiles were 50.0%. Total batch size was 5500.0 g. Phenol, formalin, and water were loaded in a kettle and cooled to 40°C. Sodium hydroxide

was added. The mix was allowed to react exothermically to 60°C where it was held for 30 min. After the exothermic reaction subsided, the temperature was increased to 75°C. The resin was condensed at 75°C to a viscosity of 50 mPa·s. After condensation to the target viscosity, 20% of the water was distilled off and the concentrate was cooled at 25°C. The concentrate was split into 800 g portions. Varying proportions of methanol and water were added to the split portions. Their water and methanol mixture weight was 200 g or 20% of the total batch weight of 1000 g. Methanol was added as 0%, 5%, 10%, 15%, and 20% of total batch weight. The splitting procedure ensured that the starting molecular weight distribution was identical for all blends.

Resin characterization

Four samples from each cook were characterized for viscosity, density, molecular weight, surface tension, and contact angle on wood. Each test used a randomized sample run order. Small test portions were removed, frozen to minimize polymerization during storage, and thawed before testing.

Molecular weight

Number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity (M_w/M_n) were determined by gel permeation chromatography on 103, 500, and 100 Å commercially available columns in series (10 Å is 1 nm). The columns were 30 cm long with 7 mm internal diameter. The mobile phase was tetrahydrofuran with a proprietary additive. Flow rate was 1.00 mL/min. The columns were calibrated with 34500, 5000, 1250, 446, and 162 molecular weight (MW) standards. The 34500, 5000, and 1250 MW standards were polystyrenes. The 446 MW standard was *n*-decyl phthalate, and the 162 MW standard was 1-phenyl hexane. A commercially available UV detector was set

at 254 nm. The pump and injector were commercially available units. Samples were diluted at 20 mg/mL in the mobile phase and filtered. 50 µL were injected. The resulting chromatograms were analyzed for M_w , M_n , and M_w/M_n .

Viscosity

Measurement of viscosity for resins prepared by procedure 1 used a commercially available viscometer with a small sample adapter equilibrated to 25.0°C using a commercially available constant temperature bath. Samples were equilibrated to constant temperature for 5.00 minutes before reading the viscosity. Low viscosities of less than 150 mPa·s used a number 5 spindle at 1.25 rad/s (12 rpm). High viscosities used a number 7 spindle at 1.25 rad/s (12 rpm). Samples were 8.0 and 10.0 mL, respectively.

Viscosity for resins prepared by procedure 2 used a commercially available viscometer equipped with a small sample adapter with an internal thermocouple for concurrent temperature monitoring. The small sample adapter connected to a commercially available constant temperature bath at 25.0°C. The spindle was a number 21, and the resin sample size was 8.0 mL. Samples were equilibrated to constant temperature before reading the viscosity.

Surface tension

Surface tension was determined by the pendant drop method using a computer image analysis technique and equipment outlined by Hansen and Rodsrud (3). A hanging resin drop of approximately 10–15 µL was suspended from a microsyringe. Its silhouette image was captured by video camera. The video image was bit-mapped on a computer for digital analysis of its dimensions. The interfacial surface tension of the resin was calculated from these dimensions, the resin density, and the ambient air density.

Density

Density in g/cm was measured with a commercially available digital density meter at 25/4°C and converted to 25/25°C density by multiplying with a conversion factor of 1.00294. Measurements were made after 4.00 min equilibration. Density was used in the calculation of surface tension.

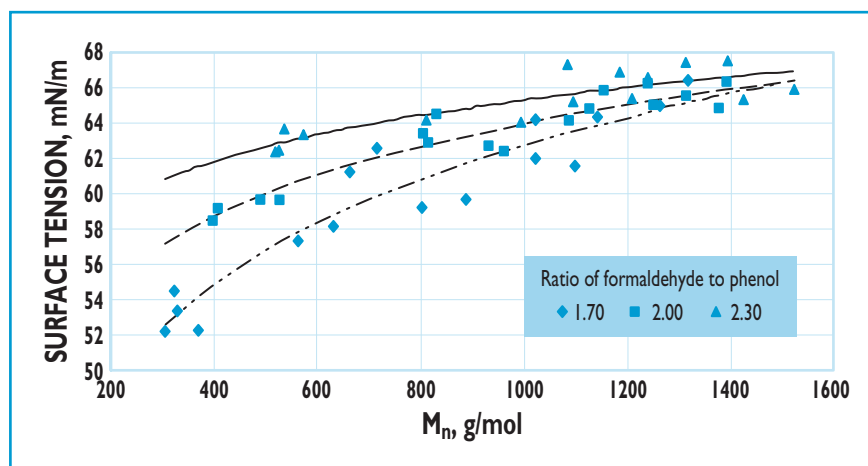
Contact angle

Contact angles were measured with the same equipment as surface tension by the method of Hansen and Rodsrud (3). Contact angle was taken on southern yellow pine wooden samples 1.6 cm high x 1.6 cm wide x 50 cm long. The wood was selected for maximum exposure to only springwood (early wood) or summerwood (late wood) of the resin droplet on the tangential face. The wood was conditioned at 23°C and 50% RH for more than one month before measurement. Moisture content was 7.45% on an o.d. basis. The wood was planed to expose a fresh surface before measurement and used within 5 h. Contact angles were taken 30 s after the droplet touched the wood. The reading was in the direction parallel to the grain. Contact angles were also measured on slabs of polymethylmethacrylate (PMMA). The 5.0 cm x 7.5 cm slabs were cleaned by immersing in hexanes and wiping with paper tissue.

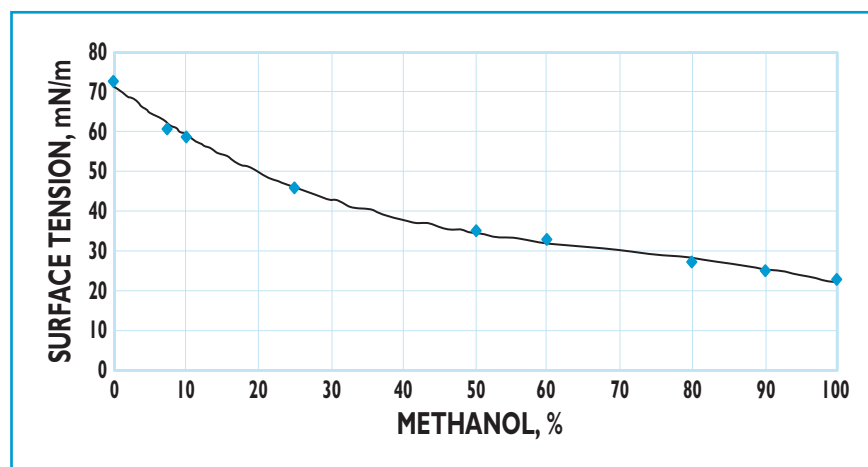
RESULTS AND DISCUSSION

Surface tension

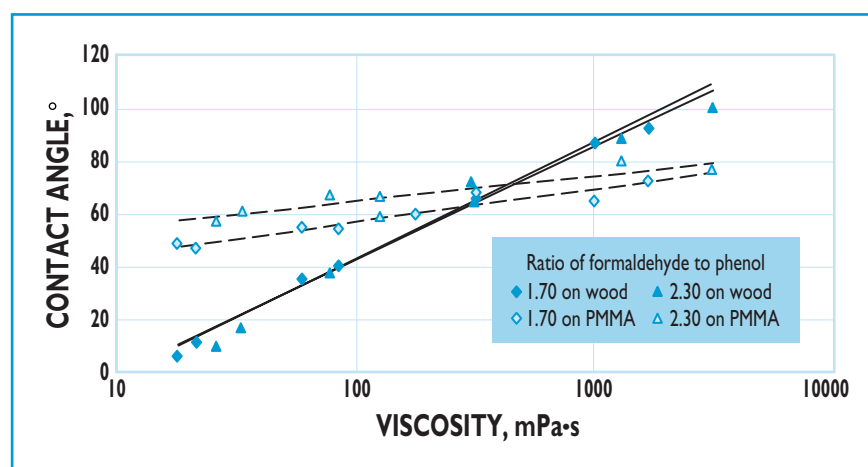
The graph in Fig. 1 illustrates that surface tensions increase with increasing M_n and formaldehyde to phenol molar ratio. Dependence of surface tension on these variables is a combination of intramolecular and intermolecular forces (2). Hydrogen bonds are the critical intermolecular forces that increase the surface tension. With increasing formaldehyde to phenol molar ratios, the methylol functionality of the polymer increases. This increases the potential



1. Effect of formaldehyde to phenol molar ratio and M_n on surface tension



2. Surface tension of methanol in water at 20°C (4)



3. Effect of capillarity and viscosity on contact angle

number of hydrogen bonds. The curvature of the graph at low M_n appears related to the degree of saturation by

methylol groups of available reactive sites on the condensing PF polymer.

Methanol is a common co-solvent

in paper saturation resins. Methanol present in the resin as a co-solvent alters the surface tension because it has a surface tension of 22.65 mN/m at 20°C (4). Water is 72.75 mN/m at 20°C. Figure 2 shows the surface tension of various methanol and water blends. The effect on resin surface tension depends on the ratio of water, methanol, and polymer in the resin. Methanol should reduce the surface tension component of the Lucas-Washburn equation.

Contact angle

Figure 3 shows how capillarity and viscosity impact the apparent contact angle of a phenolic resin on wood compared with PMMA. The regression trend lines should be parallel. Due to the capillary effect on the low viscosity, low molecular weight resins, the trend lines cross each other. The wood probably has higher surface energy than the PMMA, but the interactive effect of viscosity on capillary uptake obscures the effects of surface energy alone.

The wetting of the walls of a capillary is an interaction of the surface energy forces of the liquid and the solid being wetted. When a liquid droplet is placed on a surface, three interfacial forces are present. The Young equation describes the balance between these forces at equilibrium (5):

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos \theta \quad (2)$$

where

γ_{sv} = solid to vapor surface energy

γ_{sl} = solid to liquid surface energy

γ_{lv} = liquid to vapor surface energy

θ = contact angle of the liquid on the solid.

The three key components of the contact angle according to the Young equation are the solid to liquid, solid to vapor, and liquid to vapor surface energies. The surface energies are the results of their chemical composi-

tion. The liquid surface tension obviously has a significant impact on the liquid to solid and liquid to vapor surface energies. The surface energy of the solid being wetted has a significant contribution to the solid to vapor and solid to liquid surface energies. In the Young equation, the contribution of the liquid to solid interface is minor and usually considered negligible. A low surface energy liquid will spontaneously wet a higher energy solid (5). Due to their higher surface tension, aqueous resins are therefore not as likely to wet paper spontaneously as some methanol-modified resins. For liquids with higher surface energy than the solid phase, an additional driving force such as pressure is necessary to wet the surface.

Viscosity

Viscosity is a measure of the resistance to flow of a liquid. In a PF resin, nonvolatiles and temperature influence viscosity. The key fundamental polymer properties that affect viscosity are molecular weight distribution and sodium hydroxide to phenol molar ratio. Methanol substantially reduces the resin viscosity compared with water. According to the Lucas-Washburn equation, increasing viscosity will decrease the depth of penetration. The graphs in Figs. 4 and 5 illustrate the effects of weight average molecular weight, sodium hydroxide to phenol molar ratio, and methanol content on viscosity.

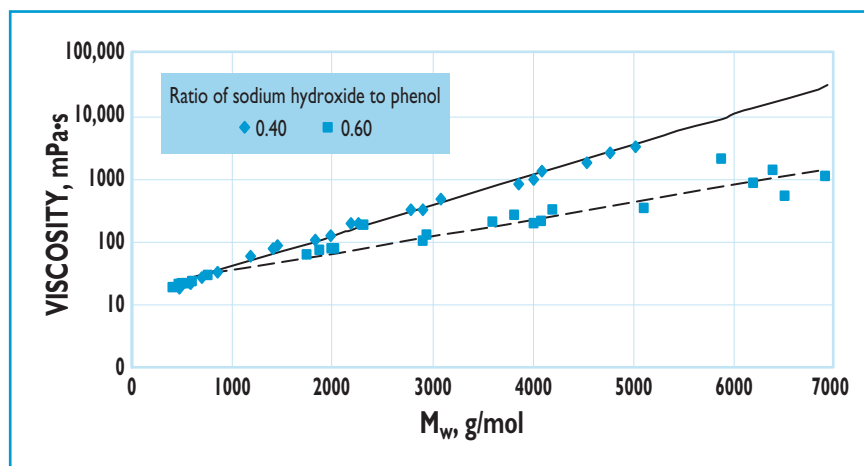
Relative penetrating power of a resin

Under conditions of constant capillary radius and time of penetration, the penetration distance depends on resin surface tension, viscosity, and contact angle. If r and t are constant, rearranging the Lucas-Washburn equation gives an equation that expresses the relative penetrating power of a resin using the measurable quantities of surface tension, contact angle, and viscosity:

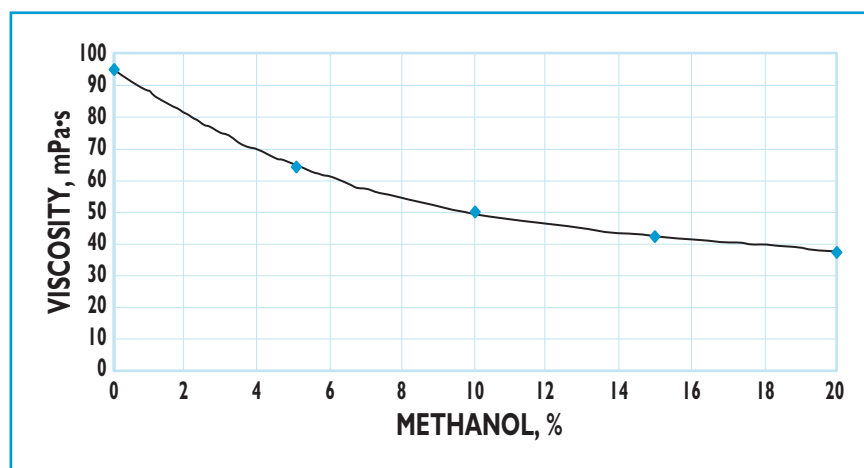
$$kh = [\gamma(\cos\theta)/2\mu]^{1/2} \quad (3)$$

where

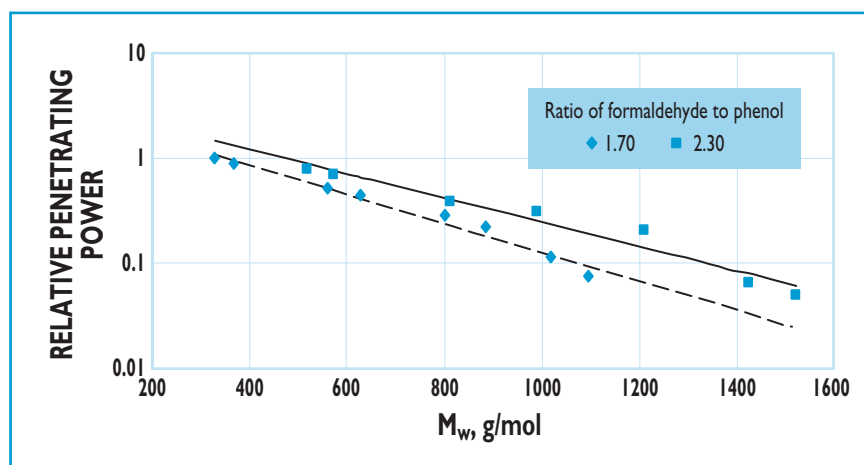
$$k = 1/(tr)^{1/2} \quad (4)$$



4. Effect of M_w and sodium hydroxide to phenol molar ratio on viscosity



5. Effect of methanol on resin viscosity using an average of two samples



6. Effect of M_n and formaldehyde to phenol molar ratio on relative penetrating power, $[\gamma(\cos\theta)/2\mu]^{1/2}$

The relative penetrating power of samples from resins formulated at formaldehyde to phenol ratios of 1.70 and 2.30 has been calculated. Contact angles against PMMA have been used. The graph in **Fig. 6** shows that the relative penetrating power of a resin decreases with lower formaldehyde to phenol molar ratios and higher molecular weights. Viscosity may increase by several orders of magnitude during condensation while surface tension and $\cos\theta$ increase incrementally within an order of magnitude. Changes in viscosity will therefore have the strongest impact on the relative penetration of any given phenolic resin.

Other considerations

The actual paper saturation process is dynamic. Since several variables are interrelated, the entire process becomes very complex. The paper may not have uniform capillary size or distribution within the paper. Changes may occur in the paper during saturation such as swelling that could alter the capillary radius. Water may also swell paper differently than methanol. As mentioned before, an environmental variable such as temperature that will also affect

the resin penetration can influence viscosity. Essentially, any factor that can alter any variable within the Lucas-Washburn equation will affect paper saturation properties.

CONCLUSIONS

The fundamental formulation parameters of PF resins and their degree of condensation determine the surface tension, contact angle, and viscosity of the resins. These physical properties affect the time necessary for and depth of penetration of paper during saturation. Rearrangement of the Lucas-Washburn equation using the resin related variables predicts the relative penetrating power of a resin using measurable quantities. **TJ**

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