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Curing behavior of soy flour with phenol-formaldehyde and isocyanate resins

William G. Hand[a], W. Robert Ashurst[a], Brian Via[b,*], Sujit Banerjee[c,*]

[a] Department of Chemical Engineering, Auburn University, Auburn, AL 36849, United States
[b] School of Forestry and Wildlife Sciences, Auburn University, Auburn, AL 36849, United States
[c] School of Chemical and Biomolecular Engineering, Georgia Tech, Atlanta, GA 30332, United States

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ABSTRACT

Cost savings are realized when phenol formaldehyde (PF) and polymeric methylene diphenyl diisocyanate (pMDI) resins are partially substituted with soy flour during the manufacture of engineered woods such as oriented strand board. The interaction of soy flour with the two resins was studied through thermogravimetric analysis, Fourier transform infrared spectroscopy, and mass spectroscopy. No significant differences in the results from all three analyses were observed between neat PF and PF resin partially (up to 30%) substituted with soy flour, suggesting that chemical bonding between soy flour and PF resin was minimal. In contrast, soy flour induced major changes in the thermogravimetric and spectroscopic properties when substituted in pMDI resin because of chemical cross-linking between the two species.

1. Introduction

Wood composites such as oriented strand board (OSB) and veneer are typically made with formaldehyde based resins such as phenol formaldehyde (PF) and urea formaldehyde (UF), or with polymeric methylene diphenyl diisocyanate (pMDI). The resin is applied to the wood, which is then hot-pressed to bond the structure. Concerns with formaldehyde release from products used indoors have prompted the development of soy-based adhesives, one of which is now in commercial use for making hardwood veneer. Formaldehyde exposure considerations do not apply to OSB for sheathing and other applications where off-gassing into an indoor environment is minimal. Nevertheless, formaldehyde is released during board manufacturing and a formaldehyde-free resin would be attractive if cost and performance standards could be maintained.

A drawback of resins that include soy products is their tendency to retain water. Although this is less of a factor for indoor applications, manufacturers are still leery of using soy-based resins where exposure to moisture is possible. It has been previously shown that 10% substitution of soy flour in PF resin offers cost advantages while meeting strength criteria [1]. In this study, the interaction of soy flour with PF and pMDI resin was examined so that the soy dosage and mode of application can be rationally determined, especially for OSB. The cost of soy flour is about a third of that of pMDI so there is economic advantage to partially substituting pMDI with soy flour.

2. Materials and methods

Soy protein isolate (SPI), ProCote 4200, was donated by Solae. Defatted soy flour (7B) was provided by Archer Daniels Midland. Soy protein constitutes about half of the mass of soy flour [2]. The liquid PF resin used was GP 240C11 RESI-STRAN (aqueous solution – 52% solids content), the powder resin was GP 190C80 Woodweld, both from Georgia-Pacific. The pMDI resin was MONDUR 541 from Covestro. Thermogravimetric data were collected using a TA Instruments Q5000 IR thermal analyzer. Mass spectra were obtained with a Micromass Q-Tof Premier Mass Spectrometer incorporating electrospray ionization and a time of flight mass analyzer. Fourier transform-infrared (FT-IR) spectra were collected using a Perkin Elmer Spectrum 400 Imaging System spectrometer. Spectral subtractions were made with the Dewiggle algorithm [3,4] from Thermo Fisher Scientific. Here, the spectrum of an individual component in a multi-component spectrum is progressively subtracted from the mixture spectrum and the first derivative taken at each stage. The derivative minimizes when the component is exactly stripped out. For the mass spectral work, the pMDI samples were cured at 180 °C for 60 minutes for the 3:7 soy flour:pMDI mixture and for 20 hours for the neat pMDI sample, ground in a mortar and pestle, and then soaked overnight in chloroform.

DTGA (the derivative of the thermogravimetric analysis profile) was performed on liquid PF with 0 and 30% soy flour substitution and on soy protein isolate (SPI). Each sample was heated under nitrogen up to

* Corresponding authors.
E-mail addresses: brianvia@auburn.edu (B. Via), sb@gatech.edu (S. Banerjee).

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700 °C at ramp rates of 2.5, 5.0, 10.0, 15.0, and 20.0 °C/min. Activation energies were calculated by the Kissinger method [5] from at least five replicates. The resin was vacuum-dried prior to the measurement.

3. Results and discussion

Most soy-based resins described in the literature are chemically modified soy isolates [6]. However, cost issues, especially in comparison to the relatively low price of hydrocarbon feedstocks, have prevented commercialization. Soy flour has been used for making hardwood veneer where the flour is applied along with kymene or poly (amidoamine epichlorohydrin), in an aqueous suspension [7,8]. An application to OSB has been proposed but not yet realized [9]. The principal target in this study was OSB, where the addition of water is detrimental because it can lead to board delamination as the pressure is relieved when the press opens. Hence, dry soy flour was added directly to the resin.

The question arises as to whether the soy flour releases protein when pressed commercially at a platen temperature of about 210 °C for about 2.5 minutes at a pressure of about 2 MPa. The heat is principally transferred to the interior of the board by the steam generated from the water present in the wood. Lee et al. [10] have reported the peak mat temperature in a continuous press to be 140 °C. Naithani et al. [11] have shown that soy flour releases soluble material in water at 50 °C pH 7.5 with a half-life of about 15 minutes. The activation energy for this release is not known, but if the rule of thumb that the rate doubles for every 10 °C rise in temperature [12] is followed, then the half-life drops to about 2 seconds at peak mat temperatures. Clearly, there is sufficient time for the soy flour to release soluble material under pressing conditions. This is consistent with practice where soy flour has been shown to augment bonding if sufficient moisture is available. [13].

3.1. DTGA analysis

DTGA results of soy flour, soy isolate, liquid PF resin, and liquid PF resin with 30% soy flour or isolate substitution are illustrated in Figs. 1 and 2. Corresponding plots with powdered PF were very similar to liquid PF and are not shown. The plots reflect the rate of change of weight loss with temperature. The temperature range of 120–200 °C is particularly relevant because it brackets industrial pressing temperatures.

The DTGA profiles for soy flour and soy isolate in Figs. 1 and 2 are similar, as are those for the 30% soy substituted resins, which demonstrates that the two soy products behave similarly. The soy flour more than likely breaks down during the earlier stages of the DTGA measurement and releases protein; it would then behave similarly to the isolate. The DTGA signals up to 200 °C for the 30% soy substituted resins appear to be a simple combination of the signals from PF and the soy alone, except for the central signal for the soy products at about 300 °C, which is attenuated in the PF mixture. It is proposed that this attenuation arises from more extensive degradation of the soy materials in the strongly alkaline environment of the resin formulation. It is less likely that soy components cross-link with the resin, because this reaction should lead to new signals from the cross-linked product, which are not observed. Furthermore, as discussed below, the activation energies of PF alone and of PF mixed with 30% soy flour (or isolate) in the curing zone are very similar, suggesting that soy components do not participate in the curing process.

Corresponding DTGA plots of pMDI with and without soy flour are illustrated in Fig. 3. The results for pMDI alone are broadly similar to those reported by Sato et al. [14] who found that exothermic processes

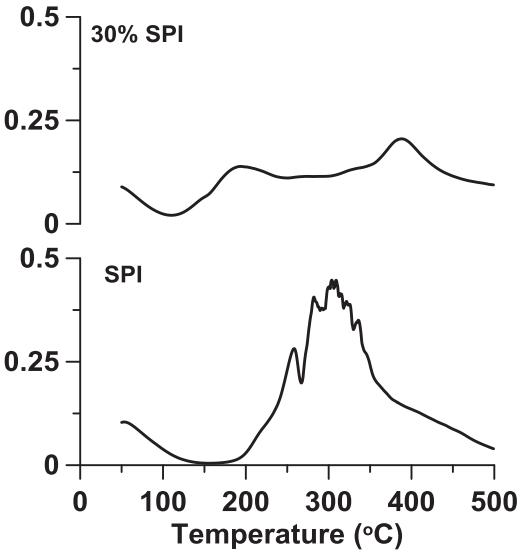

Fig. 2. DTGA data (5 °C/min) of soy flour isolate (SFI) and soy flour substituted with 30% SFI.

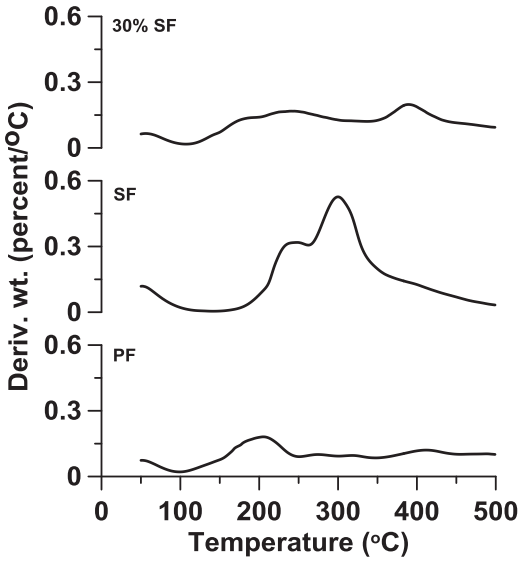

Fig. 1. DTGA data (5 °C/min) of soy flour (SF), liquid PF, and liquid PF substituted with 30% SF.

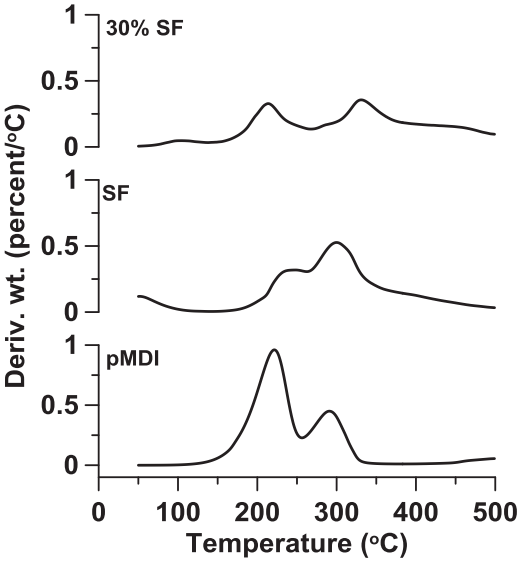

Fig. 3. DTGA data (5 °C/min) of soy flour (SF), pMDI, and pMDI substituted with 30% SF.

begin at about 200 °C. The signals at higher temperature reflect degradation and do not relate to curing. The peak signal at about 280 °C for soy flour moves to about 350 °C for the soy/pMDI mixture. This change is attributed to crosslinking between pMDI and soy, which is the expected outcome because pMDI aggressively reacts with hydroxyl groups.

The DTGA results support the cross-linking of pMDI resin with soy flour hydrolysate but offer no evidence for an analogous cross-linking with PF. This is unexpected because numerous studies have demonstrated interactions between PF and soy, *e.g.* studies on bond strength [15] and viscosity [16], and cross-linking has been assumed [15]. The GPC work of Lorenz et al. [17,18] showed that reacting soy flour hydrolysate with formaldehyde increased molecular weight, as was also expected from the work of Tome and Naulet [19] who demonstrated a reaction between the amino acid side chains of proteins contained in soy flour and formaldehyde. Lorenz et al. [17] showed that essentially no nitrogen was present in the hot water extract of the cured soy-PF resin. Because soy-derived materials are the only nitrogenous materials present it follows that soy-derived moieties were retained in the cured resin. However, as the authors recognize, this does not confirm cross-linking; the soy materials could equally be trapped in the resin matrix.

3.2. Mass spectral analysis

Mass spectra of chloroform extracts of heated soy flour, pMDI, and a 3:7 soy flour:pMDI mixture are shown in Fig. 4. The chloroform extracts contain unreacted and partially reacted material as well as degradation products, therefore a detailed spectral analysis is inappropriate. The spectrum of the mixture (top panel) is mostly comprised of fractions from the other two spectra. Certain small peaks appear; *e.g.* the high molecular weight peak in the soy spectrum is absent and the cluster of peaks at about 650 m/z in the pMDI spectrum is attenuated. These changes are quite small; the interaction of soy and pMDI do not appear to lead to major changes in molecular weight in the material analyzed. However, the sample introduced to the mass spectrometer does not contain the final polymeric product but only fragments present in the reaction mixture, so these conclusions are suggestive rather than definitive.

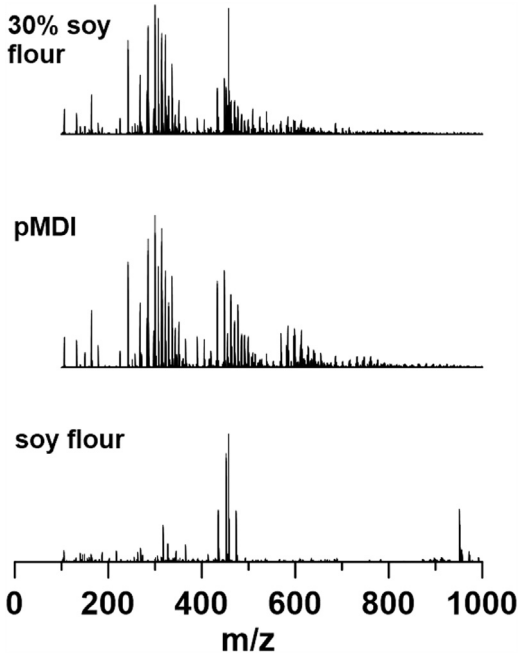

Fig. 4. Mass spectra of chloroform extracts from heated soy flour, pMDI, and a soy/pMDI mixture.

Table 1
Activation energies by DTGA of processes in the curing zone of 120–200 °C.

	Activation energy (kJ/mole)[a]
PF	142 ± 14
PF with 30% soy flour substitution	122 ± 5
PF with 30% soy isolate substitution	140 ± 8
pMDI	81 ± 4
pMDI with 30% soy flour substitution	115 ± 4
pMDI with 30% soy isolate substitution	107 ± 2

[a] The uncertainties are standard deviations

Further evidence for the absence of cross-linking between PF and soy comes from the activation energies of the curing reactions that lead to the peaks in the curing zone of 120–200 °C. These were calculated using the Kissinger method and provided in Table 1. Corresponding differential scanning calorimetry measurements gave similar results [20]. The PF activation energies compare well to literature values [21]. For PF, the substitution of soy does not change the activation energy, which is consistent with the DTGA traces above in that it does not support a separate mechanism of bonding between soy and PF.

3.3. Infrared spectral analysis

IR spectra of PF resin, soy flour, and a mixture of PF with 30% substitution of soy flour, were taken after heating at 130 °C for 30 minutes. Corresponding measurements were also made with pMDI resin. If there were no reaction between PF and soy flour, then the spectrum of the mixture would be a simple combination of the spectra of the PF and soy flour. In this case, the spectrum of the PF could be subtracted leaving behind the spectrum of the soy. The spectrum of the mixture after subtraction of the PF spectrum is compared to that of soy in Fig. 5. The two spectra are similar but not identical because spectral subtraction is difficult as noted by Myers et al. [22] and can lead to ghost peaks. Although we used an automated algorithm that eliminated any subjective bias, some differences remain. This is regarded as supportive (but not conclusive) evidence of the absence of significant interaction between soy flour and PF resin during curing.

Corresponding spectra using pMDI instead of PF are provided in Fig. 6. The two traces are much more different from each other than the analogous spectra in Fig. 4, because the pMDI and soy react to form a new species. The initial spectrum reflects contributions from soy flour, pMDI, and their reaction product. Subtracting out the pMDI spectrum leaves the spectra of both soy flour and of the new species, so the difference spectrum will be more complex than that of soy flour alone. This is the case in Fig. 6, which supports our proposal that there is reaction between soy flour and pMDI.

Overall, the DTGA data, activation energies, and the mass and IR spectra support the absence of chemical cross-linking between PF and soy flour but confirm a chemical interaction between pMDI and soy

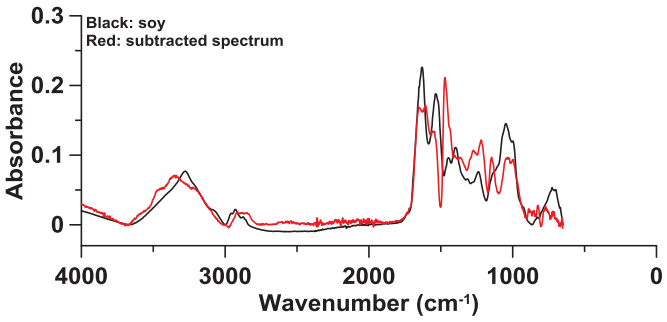

Fig. 5. FT-IR spectra of cured soy flour and of a cured mixture of 30:70 soy:PF with the cured PF component stripped out.

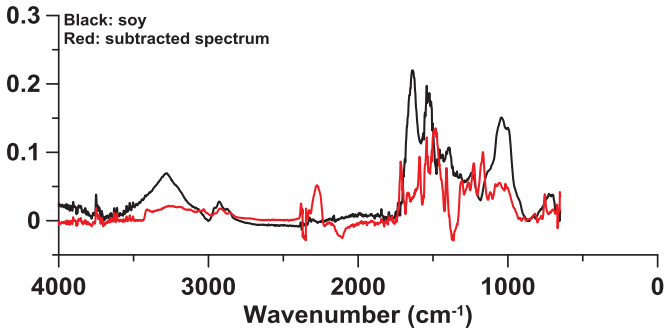

Fig. 6. FT-IR spectra of cured soy flour and of a cured mixture of 30:70 soy:pMDI with the cured pMDI component stripped out.

flour. Up to 10% of liquid PF can be replaced by soy flour without deteriorating board properties [1], and it was proposed that the soy interacted by changing the contact angle of the resin droplet on the wood surface. He and Riedl [23] demonstrated that almost no chemical reaction occurs between PF resin and wood although there are secondary interactions between hydroxyl groups of resin and wood. Yang et al. [15] showed through microscopy that increasing the soy content in mixtures of PF and soy hydrolysate decreased the level of penetration into southern pine plywood, thereby preventing over-penetration or "wash-in" [24] into the wood structure. This would lead to greater surface coverage of resin on the surface of wood and an increase in the relative bonded area of two flakes in contact. Sonnenschein et al. [25] have made similar arguments of resin coverage with pMDI.

Both PF and pMDI resins can be partially substituted with soy flour without significant loss of properties, but their interaction with soy is markedly different. Soy components chemically bond with pMDI but not with PF; their interaction with PF is only to change the geometry of the droplet on the wood surface. We emphasize that our conclusions only apply to conditions where soy flour and PF resin are mixed and heated. Chemical cross-linking may well occur in other situations, *e.g.* where the soy flour and resin are heated in water in the presence of depolymerizing agents such as sodium bisulfite [15].

4. Conclusions

Both PF and pMDI resins can be partially substituted with soy flour to bond wood during hot-pressing. Yet, their mechanisms of action are markedly different. pMDI cross-links with soy flour as expected; the formation of new chemical bonds is supported by analyses of DTGA data, changes in activation energy for curing, mass spectrometry data, and FT-IR data. The chemistry of some of these changes have been discussed by Vnučec et al. [6]. None of these analyses change significantly when PF is cured with and without soy flour substitution. It is concluded that partial substitution of PF resin by soy flour does not degrade board properties because the soy increases the viscosity of resin droplets by reducing over-penetration of the resin into the wood structure and increasing resin spread on the interfacial area between the two wood surfaces to be bonded.

Acknowledgements

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