

Investigations of the Molecular Interactions of Soy-Based Adhesives

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Abstract

Formaldehyde-free wood adhesives based on combinations of soy flour and polyamidoamine-epichlorohydrin (PAE) resins are being used commercially. This combination has been shown to provide enhanced strength and water resistance compared with traditional soy-based adhesives. This study was undertaken to better understand the molecular interactions between a PAE resin and the various components of soy flour. PAE resins are cationic, water-soluble, thermosetting resins that contain high levels of azetidinium functionality. The main components of soy flour are protein (~50%), polysaccharides (15% to 25%), and soluble sugars (10% to 15%). Solid-state nuclear magnetic resonance spectroscopy (SSNMR) was used to study the molecular interactions occurring between soy flour components and a PAE resin. In these initial studies the efficiency of spin diffusion was observed and related to morphological differences between formulations comprising different ratios of PAE resin and soy flour. The thermal transitions of these adhesive formulations were explored using differential scanning calorimetry (DSC).

Awareness has increased in recent years about green building practices and the use of green building products (Evertz 2006, Johnson 2007). Interest in these practices is driven by societal awareness and concerns about indoor air quality, health, and the environment. Inventive individuals and materials providers have responded to the concern with new building design practices and innovative products.

A recent green adhesive technology developed by Professor Kaichang Li of Oregon State University and commercialized by Columbia Forest Products and Hercules Incorporated has been receiving much attention from the wood composites industry. This technology uses soy flour with a proprietary polyamidoamine-epichlorohydrin (PAE) resin to form a water resistant, high strength adhesive for use in wood composites (Li et al. 2004, Li and Yuan 2006, Li 2007, Watt 2008). These soy/PAE adhesives are formaldehyde-free compositions and are being used in applications where formaldehyde emissions from wood products are an issue. In this article we discuss the nature of the soy flour and PAE resin interactions and the resultant polymer properties.

To investigate the molecular interactions, solid-state nuclear magnetic resonance (SSNMR) spectroscopy was used. SSNMR has been shown in previous studies to be a valuable means of characterizing molecular interactions of wood adhesives on substrates (Marcinko et al. 1994, Wendler and Frazier 1996). Using this spectroscopic

technique allows one to investigate the chemical bonding environment and the molecular dynamics of a polymer or composite in its functional state, i.e., its solid state. Since the molecular interactions and molecular motions of a solid polymer determine its physical performance, this technique is ideally suited to investigate adhesive structure–property relationships.

The acquisition and interpretation of SSNMR spectra is often more complex than that of solution NMR of polymers because of the broadening and overlap of resonances due to dipolar interactions and chemical shift anisotropy. In solution NMR, a large amount of molecular motion averages out chemical shift anisotropy and dipolar interactions. This results in spectra with highly resolved chemical shifts. In a solid sample, the molecules are fixed in space and limited in mobility. This leads to broadened, less

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resolved chemical shifts and more complicated spectra (or simpler spectra, depending on your perspective). Despite the lack of chemical shift resolution, much information can be derived from an SSNMR experiment related to chemical interactions between molecules, which reflect their actual chain conformation and molecular packing (via the γ -gauche effect; Bovey and Mirau 1992).

Using specific SSNMR techniques that are sensitive to the influence of spin diffusion on equilibrium magnetization, we are able to look at the organization of polymer chains on a scale of 20 to 200 Å. In these initial studies we chose to measure proton spin lattice relaxation in the rotating frame ($^1\text{HT}_{1\rho}$) to investigate whether there were any differences in spin diffusion efficiency that we could use to begin to elucidate how this unique type of adhesive polymerizes.

Differential scanning calorimetry (DSC) was also used as another means of investigating molecular mobility. Specifically, changes in thermal transitions were investigated to provide information about the compatibility of these PAE resin-soy flour blended adhesives.

Experimental Methods

Materials

Prolia 100/90 defatted soy flour having a protein dispersibility index (PDI) of 90 was obtained from Cargill Incorporated, Minneapolis, Minnesota, and used as received. ChemVisions CA1000 PAE resin was obtained from Hercules Incorporated, Wilmington, Delaware, and used as received. The ChemVisions CA1000 resin is an aqueous solution with a polymer solids content of 20 percent.

Sample preparation

Samples were prepared by combining soy flour with CA1000 at a mass ratio of 2:1 and soy flour with water at a mass ratio of 2:0.8. This was done to keep the ratio of water the same in the samples, since the CA1000 resin contains approximately 20 percent polymer solids. The samples were mixed in a 100-mL glass beaker using a spatula, and then the resulting dough-like material was mechanically kneaded to ensure good mixing. Samples were put into a 120°C oven for 1 hour to promote chemical cure and to mimic the exposure of these components to heat, as might be seen in a hot press. All samples were allowed to equilibrate for at least 24 hours on a laboratory benchtop prior to testing. The laboratory temperature was 23°C, and the relative humidity was recorded to be 50 percent.

NMR procedures

Solid-state ^{13}C NMR spectra were obtained at 4.7 tesla using a Varian Unity Inova 200-MHz (^1H frequency) spectrometer with a Doty Scientific supersonic magic angle spinning (MAS) probe. The ^{13}C NMR $^1\text{HT}_{1\rho}$ experiments were conducted using a variable ^1H spin lock time with ramped cross-polarization. Twenty-one delay times were arrayed varying in time between 0 and 26 milliseconds. The experiments were conducted with a MAS speed of 5 kHz, 2-second relaxation delay, 1-millisecond contact time, 5-microsecond 90° pulse width, and a 52-kHz decoupling field. Hexamethylbenzene ($\delta_{\text{CH}_3} = 17.3$ ppm) was used as an external reference to correct ^{13}C chemical shifts. The soy flour was a powder. The cured adhesive samples were ground to powder with a mortar and pestle. The respective

samples were packed into 7-mm silicon nitride rotors with Kel-F end caps.

The relaxation data were obtained by measuring the intensity of the defined resonances as a function of the spin lock time and then by fitting the data to either single or double exponential decay models using KaleidaGraph software from Synergy Software.

DSC procedures

The thermograms were generated using a TA Instruments DSC 2920 standard cell with a nitrogen purge. The DSC was calibrated, based on the procedures recommended by the instrument manufacturer, at +10°C/min and under a nitrogen purge to the cell at 50 mL/min. The calibration included the baseline slope and offset calibration, the cell constant calibration, and a temperature calibration, using indium as the standard material.

DSC was performed using cured (heat-treated) samples. Approximately 10 mg of cured sample was heated at 10°C/min to an upper temperature limit, cooled, and reheated. The glass transition data of the samples were determined from DSC reheat thermograms (second heat). Aluminum pans were used for all the thermal scans.

Results and Discussion

The interactions of a PAE resin with soy flour have been investigated using SSNMR and DSC techniques to better understand the cure mechanism of PAE/soy adhesives.

NMR experiments

The ratios of the components that define the samples were chosen to ensure sufficient molecular interaction while keeping the soy protein in great excess. This was also done to determine whether chemical shift differences could be resolved. Covalent and hydrogen bonding interactions can cause chemical shift differences, and hydrogen bonding can cause chemical shift broadening due to changes in the nuclear dipolar interactions.

Figure 1 represents a typical ^{13}C solution-state NMR spectrum of Prolia 100/90 soy flour. We can observe many well-resolved resonances associated with the water-soluble amino acids and carbohydrates in the chemical shift range between 60 and 105 ppm. The broadened peaks in the aromatic and carbonyl regions resulted in a wavy baseline due to the insoluble polymeric portion of the soy flour that are not efficiently decoupled under the conditions of the solution NMR experiment performed.

Figure 2 illustrates a typical cross-polarization SSNMR spectrum for neat soy flour collected under the conditions previously described in “NMR procedures.” As noted in that section, the resolution is not as good due to the broadening of the lines caused by chemical shift anisotropy and dipolar interactions; however, it is still possible to resolve peaks associated with amino acids and carbohydrates.

Figure 3 shows an SSNMR spectrum of the cured soy flour/water sample, and Figure 4 shows the SSNMR spectrum of the cured soy flour/PAE resin sample. These spectra are dominated by the resonances associated with the soy structure. Although the solid-state spectra appear to be similar, we are able to observe some distinct differences between the spectra.

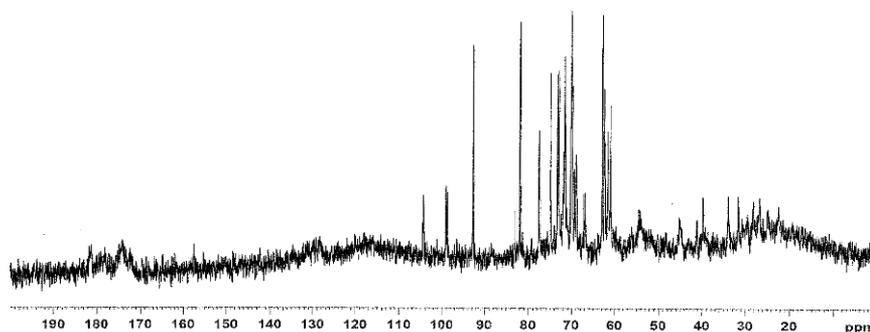


Figure 1.—Solution-state NMR spectrum of isolated soy protein.

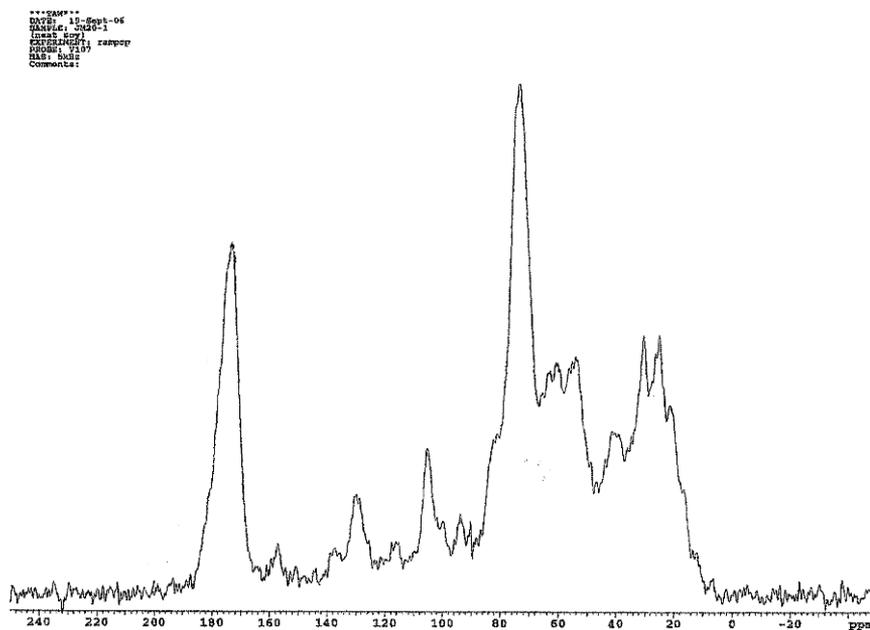


Figure 2.—SSNMR spectrum of neat soy flour.

A comparison of Figure 3 and Figure 4 shows little difference in chemical shift but does show considerable difference in the broadening, resolution, and dispersion of the resonances in the region between 10 and 70 ppm. A difference in resolution and dispersion is also observed for the carbonyl carbons in the region of 173 ppm. The greater resolution and dispersion of the soy resonances in these regions indicates that the cured PAE resin sample behaves differently under the conditions of the cross-polarization experiment used in this study. The differences can arise due to variations in the efficiency of spin diffusion associated with the intimacy of mixing of the hydrated soy polymers or the soy polymers with the PAE resin. The differences may also be due to variations in the mobility of the molecules.

Mixing efficiency and the length scale of spin diffusion can be measured via rotating frame spin lattice relaxation measurements ($T_{1\rho}$). To define the length scale of mixing of the soy flour and the PAE resin would require additional study; however, we can present a reasonable preliminary hypothesis about molecular order and molecular interactions with the data at hand.

The data presented in Table 1 compare the $^1\text{HT}_{1\rho}$ relaxation rates of several soy polymer peaks. The chemical

shifts given are based on those reported by Kakalis and Baianu (1990) for similar soy polymers. The peaks are assigned as follows: 173 ppm to the amino acid carbonyls, 105 ppm to the C-1 anomeric carbons of the carbohydrate, 73 ppm to the carbohydrate CHs having secondary hydroxyls, 60 ppm to the CH_2 s of the carbohydrate ring containing primary alcohol functionality, and 30 ppm to the CH carbons in the protein amino acids. The data compare neat soy flour with the cured soy flour/water samples and the cured soy flour/PAE resin samples. The data were fit to either single exponential or biexponential models to achieve the best correlation of the magnetization decay. Table 1 reports the fractional percentages of the relaxing components as well as the $^1\text{HT}_{1\rho}$ relaxation rates.

Based on these data one can observe that the cured samples differ from the neat soy flour in relaxation time and the fractional distribution of the relaxing components. As we analyzed the individual chemical shifts, we observed, for all the samples, that the carbonyl carbons at 173 ppm were fit best by a single exponential model and that the $^1\text{HT}_{1\rho}$ relaxation times differ greatly. The cured soy flour/water sample has a significantly shorter relaxation time compared with both the neat soy flour and the cured soy flour/PAE

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***FHM***
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SAMPLE: U22-3
(1:2 (marker:soy cured)
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PROB: Q107
PULP: S41
Comments:
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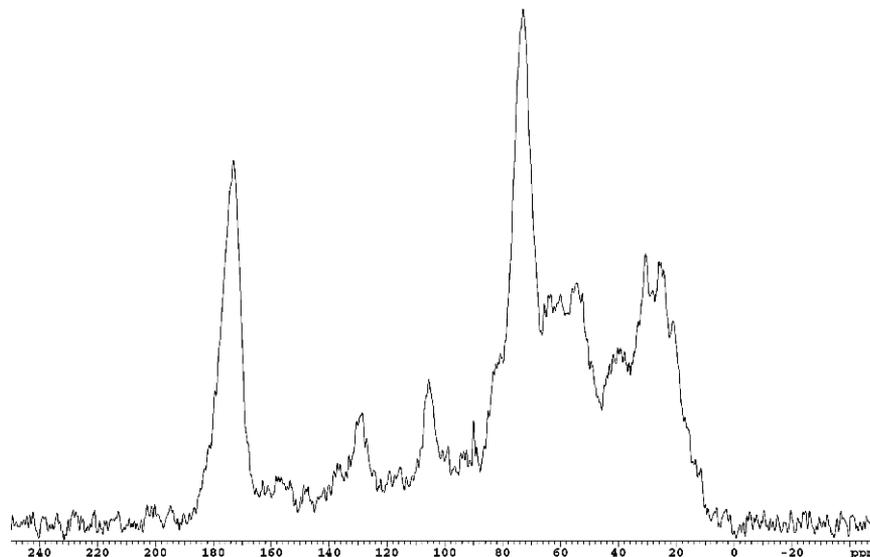


Figure 3.—SSNMR spectrum of a soy flour/water sample cured at 120°C for 1 hour.

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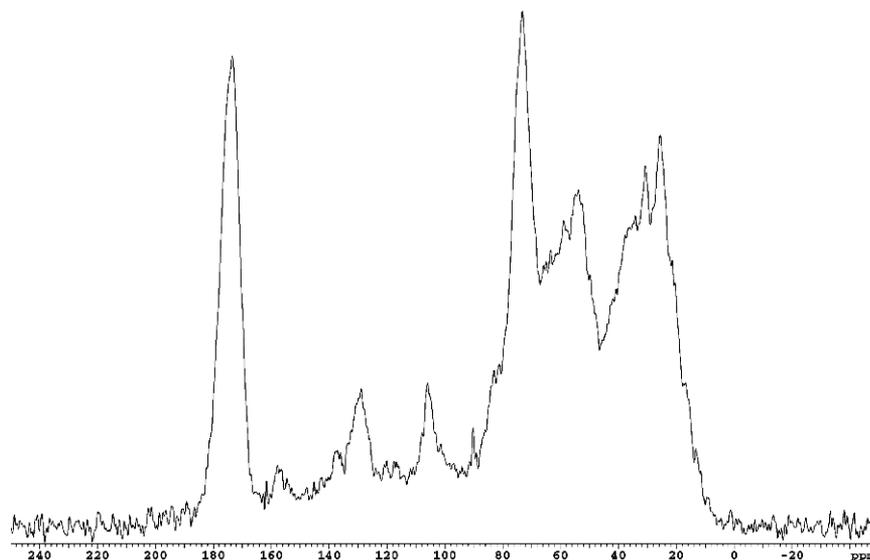


Figure 4.—SSNMR spectrum of a soy flour/PAE resin sample cured at 120°C for 1 hour.

resin sample. In addition, the cured soy flour/PAE resin sample has a significantly longer relaxation time. Carbonyl groups are very strong acceptor groups for hydrogen bonding. The fact that we do not observe significant broadening of these carbons but do see a resolution and dispersion enhancement of the carbonyl for the cured soy flour/PAE resin sample could mean that the efficiency of cross-polarization at a 1-millisecond contact time (as was used in these experiments) is selectively enhancing these signals in the cured soy flour/PAE resin sample.

A variable contact time experiment and measurement of cross-polarization rates (T_{CH}) would allow us to determine

whether this was the cause of the enhancement. In essence, to get such a resolution and dispersion enhancement indicates that we are selectively favoring certain carbonyl carbons by the association of these carbonyls with the PAE resin. Combining this with the rapid relaxation rate seen for the cured soy flour/water sample, which shows that spin diffusion is very efficient in this sample, the rapidly relaxing components may have diminished significantly relative to the slower relaxing components, thus providing the resolution and dispersion enhancements of the slower relaxing components.

Table 1.— $^1\text{HT}_{1\rho}$ relaxation data for neat soy flour, the cured soy flour/water (2:0.8) sample, and the cured soy flour/PAE resin (2:1) sample.

Chemical shift (ppm)	Fractional % A	$^1\text{HT}_{1\rho}$ A (ms)	Fractional % B	$^1\text{HT}_{1\rho}$ B (ms)	Correlation coefficient (<i>R</i>)
Neat soy flour					
173	100	1.3	—	—	0.999
105	62	2.8	38	14.2	0.996
73	100	8.1	—	—	0.999
60	27	1.8	73	5.9	0.998
30	34	9.4	66	3.1	0.999
Cured soy flour/water					
173	100	0.1	—	—	0.999
105	18	0.1	82	8.3	0.995
73	37	3.5	63	9.6	0.999
60	7	1.4	93	6.2	0.997
30	41	10.6	59	3.6	0.998
Cured soy flour/PAE resin					
173	100	3.9	—	—	0.999
105	87	6.6	13	2.8	0.997
73	20	2.1	80	6.9	0.999
60	17	1.6	83	6.0	0.998
30	100	4.2	—	—	0.999

Comparing the 105-ppm carbons (C-1 anomeric carbons of the carbohydrates), we see that the relaxation data were best fit by a biexponential model for all the samples. $T_{1\rho}^A$ is the faster relaxing component, and $T_{1\rho}^B$ is the slower relaxing component. The cured soy flour/water sample has a smaller fractional percentage of rapidly relaxing carbons as compared with the neat soy flour and also has much faster relaxation times for both fractional components. In contrast, the cured soy flour/PAE resin sample has a significant increase in the fractional percentage of rapidly relaxing carbons, but the relaxation times of those carbons are longer. Since the rate of spin diffusion is strongly dependent on the spatial mixing of the polymer chains and since the carbon resonances follow the protons they are coupled to, multiple relaxing components tells us that we have 105-ppm carbons in multiple environments. The presence of the PAE resin seems to greatly influence the relaxation of the anomeric carbon, thereby yielding more of those species and longer relaxation times for the rapidly relaxing components.

As we continued to analyze the carbon resonances, we observed that the 73-ppm carbons from the carbohydrate CHs were best fit by a single exponential model for the neat soy flour and a biexponential model for the cured soy flour/water sample and the cured soy flour/PAE resin sample. The differences in the fractional percentages and the relaxation times illustrate significantly different distributions of relaxing components as a result of differences in spin diffusion efficiency.

The 60-ppm carbons, assigned as the pendent CH_2 s of the carbohydrate ring, were best fit by a biexponential model for all the samples. For these carbons the fractional distributions changed for each, but the relaxation times were similar for all the samples.

The 30-ppm carbons from the CH carbons in the protein amino acids were best fit by a biexponential model for the neat soy flour and the cured soy flour/water sample, and the relaxation times were similar for those samples. In contrast, the cured soy flour/PAE resin sample was best fit by a single exponential, which had a significantly shorter relaxation time. This indicates that, for this sample, all the carbons are

intimately and homogeneously mixed over the length scale of spin diffusion.

Without further study of $^1\text{HT}_{1\rho}$ in combination with other SSNMR techniques that are more sensitive to molecular structure at different regimes of molecular mobility and distances of magnetization transfer, it is difficult to definitively state the cause of the differences described by the fitting of the relaxation data presented in this article. However, we can say that we have observed in these samples a mixed system in which the intimacy of mixing of the polymer species must be great in order to affect the transfer of magnetization (via spin diffusion) in relaxation times of approximately 10 milliseconds or less. In other words, the molecules are very close together, and this affects how energy is transferred between them. As discussed by Bovey and Mirau (1992), if the polymer molecules are closer than the length scale of spin diffusion, the magnetization transfer from the slower to the more rapidly relaxing molecules will be a very effective relaxation mechanism; if the molecules are farther apart than the length scale of spin diffusion, then we would not observe a change in $^1\text{HT}_{1\rho}$. Since some of the relaxation rates we measured for the cured soy flour/PAE resin sample are shorter than the neat soy flour and the cured soy flour/water sample, we can say that the proximity of the PAE resin molecules affects the efficiency of energy transfer of the soy molecules. Since we observe changes in the distribution but similar relaxation rates for one of the carbon chemical shifts measured, the 60-ppm chemical shift, it is also possible that we are observing partial mixing of the soy molecules and the PAE resin molecules.

When interpreting the data, we must also keep in mind that soy proteins are macromolecules containing various amino acids that can pack in varying conformations depending on the chemical, physical, or enzymatic treatment of those macromolecules. In addition, we must keep in mind that we are looking not at an isolated soy protein but at a combination of soy proteins with soluble and insoluble polysaccharides, low-molecular-weight carbohydrates (saccharides), as well as a small amount of inorganic (salt)

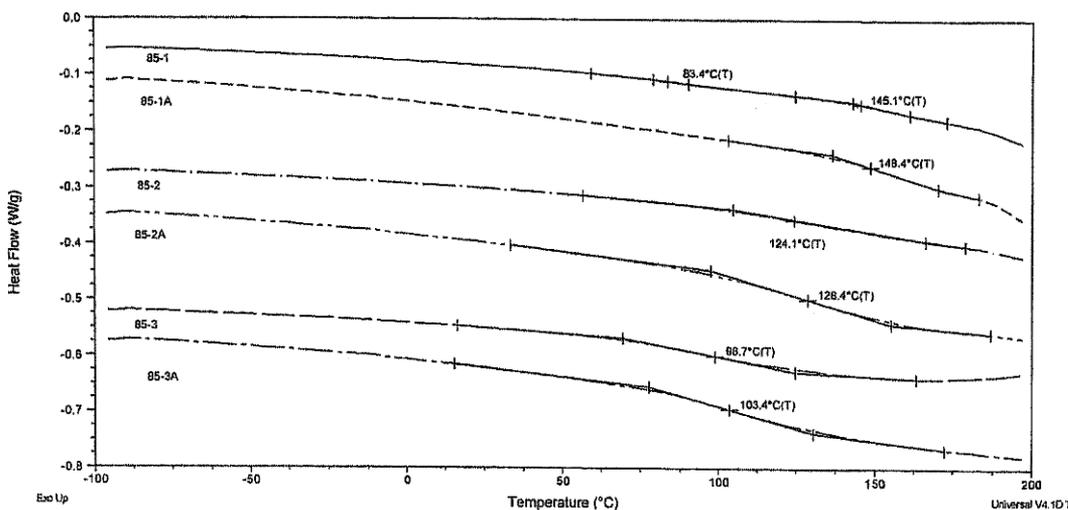


Figure 5.—DSC runs of the cured H₂O/soy and cured soy/PAE resin samples at different ratios.

components. The amount of soy protein in the soy flour used is approximately 52 percent. As such, the morphological possibilities are quite large, making the interpretation complicated without additional spectroscopic and physical data. Also, considering the nature of the chemistry of the PAE resin (an amino functional polymer) and that the relaxation rates of the carbonyl carbons at 173 ppm and the carbohydrate anomeric carbon at 105 ppm are significantly increased, it is reasonable to assume that the PAE resin is interacting with these soy flour components, most likely via secondary interactions.

DSC experiments

From a physical perspective, another possible explanation of the differences in ¹HT_{1ρ} relaxation rates is a change in the motion of the molecules. Therefore, we decided to measure the glass transition temperature (T_g) of cured soy/PAE samples. A series of samples was prepared and run via DSC using ratios of 2:1 soy flour/PAE resin, 7:1 soy flour/PAE resin, and 2:0.8 soy flour/water. These samples were prepared and cured at two different temperatures, 120°C and 150°C, for 1 hour. These data are presented in Figure 5 and Table 2. Figure 5 shows the DSC traces of the cured soy flour/water and cured soy flour/PAE resin samples. The thermograms shown in Figure 5 are all from the second heat, and the corresponding values in Table 2 are for these second heat thermograms.

Interestingly, these samples all showed only a single glass transition temperature despite the fact that there are a number of polymer species in these mixtures (soy protein, PAE resin, and various carbohydrates). From the data in

Table 2 and Figure 5 we observe that the samples containing PAE resin have lower T_g values than the soy flour/water samples at both cure temperatures, and the T_g decreases with higher levels of PAE resin in the mixture. This further supports the hypothesis that PAE resin plasticizes the soy protein by creating free volume (most likely by associating with the electron-rich portions of the protein molecules). This is also consistent with the changes in relaxation data observed using NMR techniques. The samples cured at 150°C show slightly higher T_g values than the samples cured at 120°C, indicating that cross-linking reactions have occurred to a greater extent at the higher temperature, as would be expected.

Summary and Conclusions

We observed changes in the relaxation behavior of soy-based adhesives via ¹HT_{1ρ} in SSNMR experiments. These experiments showed that soy flour combined with a PAE resin affects spin diffusion efficiency. Therefore, the PAE resin is intimately mixed with the soy polymer and interacts, most likely through hydrogen bonding, with soy proteins and carbohydrates. Further NMR analysis is needed to better define the nature of the interaction between PAE resins and soy protein. We further observed by DSC that the presence of the PAE resin results in a homogeneous polymer blend, which lowers the T_g of the soy protein. This depression of T_g by the PAE resin may be due to secondary molecular interactions that affect the morphology and packing of the soy polymer chains, thereby resulting in an apparent plasticization. This is consistent with the NMR studies, which showed changes in the distribution and rates of relaxation for different portions of the soy polymers.

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Table 2.—Glass transition temperatures for cured samples.

Sample	Description	Cure temperature (°C)	T _g (°C)
85-1	0.8:2 (H ₂ O/soy)	120	145
85-1A	0.8:2 (H ₂ O/soy)	150	148
85-2	1:7 (PAE resin/soy)	120	124
85-2A	1:7 (PAE resin/soy)	150	128
85-3	1:2 (PAE resin/soy)	120	99
85-3A	1:2 (PAE resin/soy)	150	103

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