

## CHAPTER 7

### **Fiber Modification by Steam-Explosion. IV. Morphological Changes in Co-Refined Wood and Polyolefins.**

#### **Abstract**

Material from co-refined wood and polypropylene (iPP) by steam-explosion processing was investigated to elucidate chemical and morphological changes, as well as association between polypropylene and wood bio-polymer components. Four samples, which included steam-exploded wood mixed with neat iPP, co-steam-exploded wood and iPP, compression molded steam-exploded wood and neat iPP, and compression molded co-steam-exploded wood and iPP was investigated by solid state NMR. Chemistry of the material changed for both co-steam-exploded wood and iPP and compression molded co-steam-exploded wood and iPP samples. Additionally, crystalline morphology of the cellulose component was seen to increase because of steam-explosion processing. The relaxation parameter  $T_{1\rho}$  for the crystalline cellulose component of the co-steam-exploded material was found to be higher than  $T_{1\rho}$  of amorphous cellulose and lignin. In contrast,  $T_{1\rho}$  values for steam-exploded wood of lignin was higher than the amorphous and crystalline cellulose. After compression molding, the relaxation values of the co-steam-exploded were similar to that of the control. Dynamic mechanical analysis demonstrated a reinforcing effect by the steam-exploded wood fiber during the glass transition of polypropylene for the co-steam-exploded wood and iPP. However, no shift in the location of the glass transition of polypropylene was apparent. The paper concludes by describing a hypothetical scheme for a meta-stable interaction of wood bio-polymer and polypropylene.

## Introduction

Chemistry at the molecular level dictates the macroscopic properties of the material. This simple phenomenon is evident in biological materials that may be considered performance-engineered by Nature. Furthermore, substitution of a certain chemical group can alter the assembly and order of the components and change the interactions among them. A number of methods are sensitive to probing spatial arrangement at the nanoscale, however, only a select few can differentiate interactions between components at the molecular level. Both solid state nuclear magnetic resonance and dynamic mechanical thermal analysis can be used to investigate the nanoscale interactions of components of a system. These tools are applied to probe the interaction among wood components and polypropylene that underwent co-refining with steam-explosion processing. This processing technique was shown to modify the sorption properties of wood fibers [1] as well as cause chemical changes in both wood and polypropylene [2]. However, it is not known if the modification of individual components has changed the intimate interaction among the wood and polypropylene as well as the hierarchical ordering of the components. In addition, limited research has been performed on wood fiber thermoplastic composites using solid state NMR, consequently, compression molded specimens were tested to determine the possibility of enhanced interfacial interactions for the co-steam-exploded composite material.

## NMR Background

In addition to spectroscopic information, solid state NMR can provide information on a material's mobility and ultrastructure through cross polarization experiments [3]. This type of experiment measures the exchange of energy for coupled spin systems between  $^1\text{H}$  and  $^{13}\text{C}$  nuclei. The result is a competing system where the increase in  $^{13}\text{C}$  magnetization decreases the polarization from the  $^1\text{H}$  reservoir. Explicitly, four steps are involved that begin with the polarization of  $^1\text{H}$ , followed by a spin locking step that reduces the decay of the magnetization relative to the ordinary spin-spin magnetization, with an almost simultaneous energy exchange for a controlled contact time between the abundant  $^1\text{H}$  nuclei and the rare  $^{13}\text{C}$  nuclei, and ending with the measurement of the free induction decay signal [3]. Furthermore, the Angstrom environment is investigated by the static transfer of polarization under spin locking conditions by the cross polarization transfer rate constant  $T_{\text{CH}}$ . Transfer of polarization occurs rapidly for

carbon atoms that are directly bonded to hydrogen, such as methylene and methine carbons. The resulting  $T_{CH}$  values of these molecules are less than  $50\mu s$  [3]. These values increase for molecules such as aromatic carbons and further increase dramatically for non-protonated carbons such as phenolic carbons. In addition to the C-H intermolecular distance, the degree of mobility of the molecule influences the  $T_{CH}$ . A highly mobile molecule reduces the cross polarization rate and therefore lengthens  $T_{CH}$  [3].

Monitoring the decay of the polarization signal,  $T_{1\rho}$ , conveys the polymer's mobility (through relaxation rates), but is complicated by the interaction with neighboring species if blended on the nanoscale (less than 30 nanometers). The latter effect is seen through spin diffusion of materials that are homogenous at the nanoscale. This arises from the transfer of polarization by neighboring molecules to create spin equilibrium. The method is powerful in that it can help determine the interaction of components blended on the nanoscale (if they have distinct independent relaxations).

Solid state NMR has been used to examine the effect of steam-explosion processing on the bio-polymers of wood [4-10]. These studies looked at the chemistry of the material [4,5], extracted material [7], as well as interactions between components [6,9-10]. It was confirmed that steam-explosion causes rearrangement of wood biopolymers by examining  $T_{1\rho}$  relaxation parameters before and after steam-explosion [5]. With steam-explosion treatment the  $T_{1\rho}$  relaxation parameter for lignin and cellulose became independent indicating separation of components on the nanoscale.

Other studies have explored the morphology of cellulose by solid state  $^{13}C$  NMR spectroscopy [11]. Degree of crystallinity along with cellulose polymorphs, cellulose I $\alpha$ , cellulose I $\beta$ , cellulose II have been described by deconvolution of the C4 cellulose signal occurring in the region 92-79 ppm by curve fitting procedures [12]. This technique has been applied to the study of cellulose within fiber walls and fines after kraft pulping [13-16]. Further studies on solid state NMR studies of wood and lignocellulosics are reviewed by Gil and Neto in detail [17].

## **DMA Background**

The nanoscale interaction of components can also be measured by the dynamic thermal mechanical response of the material. In this case, both the elastic and viscous response is

monitored as a result of a sinusoidal stress that is within the linear viscoelastic region of the material. As a polymer moves from the glassy state to a rubbery state (as a function of temperature or stress frequency) the response of the material changes with a decrease in the storage modulus and a maximum in damping occurring at the transition between two states (the glass transition,  $T_g$ ).

A number of investigators have used DMA to study wood in order to characterize the interaction among the biopolymers of wood [17], adhesion within wood-based composites[18], and the modification through derivitization of wood [19,20]. However, these studies are complicated with issues related to moisture [17], anisotropy of wood [21] , species dependence (related to chemical composition) [17,22], and thermal history that influence the response of wood [23]. Yet, from these studies general trends have been described relating to the constitutive polymers of wood, such as moisture dependence of the response of *in situ* wood components and response of extracted components. In the dry state wood has a single wide-ranging transition [24]. When the moisture content of wood is increased, the hemicellulose and lignin transitions become apparent.

## **Methods and Materials**

### **Steam-explosion**

Red oak wood chips and polypropylene were co-refined in a converted 1-gallon Parr reaction vessel by steam-explosion. The wood chips were sorted to a size that could fit through a screen of 5/8" diameter opening, but retained by the 3/8" diameter opening. The steam temperature was 230° C with a pressure of 400 psi. After 5 minutes of residence time the pressure was reduced to atmospheric pressure by opening a ball valve. The ejected material was separated from the steam by a cyclone into a collection container. The resulting material was placed in hot water in an Erlenmeyer flask and stirred with a magnetic stir bar for two hours. The material was then recovered by vacuum filtration across Whatman filter paper and subsequently rinsed with twice the original volume of water. The material was then dried and stored in a desiccator until further testing.

## NMR

Dried steam-exploded material that had a moisture content lower than 4% was gently dry mixed with polypropylene powder on a 1:1 dry weight basis and placed into a zirconium oxide rotor and closed with a Kel-f cap. The rotor was placed in a Bruker MSL-300 MHz spectrometer and rotated at 5,000 Hz. A standard variable contact time CP pulse was employed. Thirteen contact times ranging from 0.2ms to 20ms were used for the experiment. 1800 scans were accumulated at each contact time. Each treatment was duplicated. The same procedure was used to test the co-steam-exploded fiber polypropylene and the compression molded composites. The composites were made from pressing the samples (steam-exploded wood fiber and virgin iPP and co-steam-exploded wood and iPP) at 170°C with 300 psi. The samples were annealed by letting the platens cool to room temperature. The resulting sample had a calculated thickness of 0.5 mm.

Relative intensity  $I^*$  and relaxation parameters  $T_{CH}$  and  $T_{1\rho}$  were calculated by fitting the intensity vs. contact time with Equation 1 [25].

$$I(T) = I^* \left[ \frac{{}^H T_{1\rho}}{{}^H T_{1\rho} - T_{CH}} \right] \left( \exp\left(-\frac{t}{{}^H T_{1\rho}}\right) - \exp\left(-\frac{t}{T_{CH}}\right) \right) \quad \text{Equation 1}$$

Where  $I(t)$  is the function for the intensity ( $I$ ) at a given contact time ( $t$ ) of a specific chemical shift. Assuming resolution of peak intensity for a given chemical shift, the relaxation of individual components may be determined. For wood, the relaxation parameters were fitted for two peaks related to lignin, two peaks relating to cellulose, and one peak relating to general carbohydrate (C1). Additional relaxation parameters were found for the methylene, methine, and methyl groups for polypropylene.

## DMA

### Composite manufacture

Steam-exploded wood, co-steam-exploded wood and polypropylene, and neat polypropylene panels were compression molded following the same press schedule in a Carver press. This included heating the material in a stainless steel press box with a 1" thick plunger to 170°C, applying a force of 13 metric tons, and cooling the platens with water. Total press time from loading the material to unloading the panel is estimated at 35 minutes. The 3.5 mm thick panels

were cut into specimens with a width of 12.5 mm and a length of 22 mm. The specimens were then dried in a vacuum oven for 30 hours at 40°C. Subsequently the materials were stored in a desiccator that contained Dri-rite and silica gel until testing.

### DMA Testing

Dynamic mechanical analysis tests were performed with a TA Instruments 2910 DMA. Linear viscoelastic regions were determined for each panel using a strain sweep experiment at the extreme testing temperatures (-150°C and 150°C). A single cantilever test set-up was used for the linear viscoelastic region determination and the temperature ramp tests. All temperature ramp experiments were recorded with 0.04% strain at a frequency of 1 Hz.

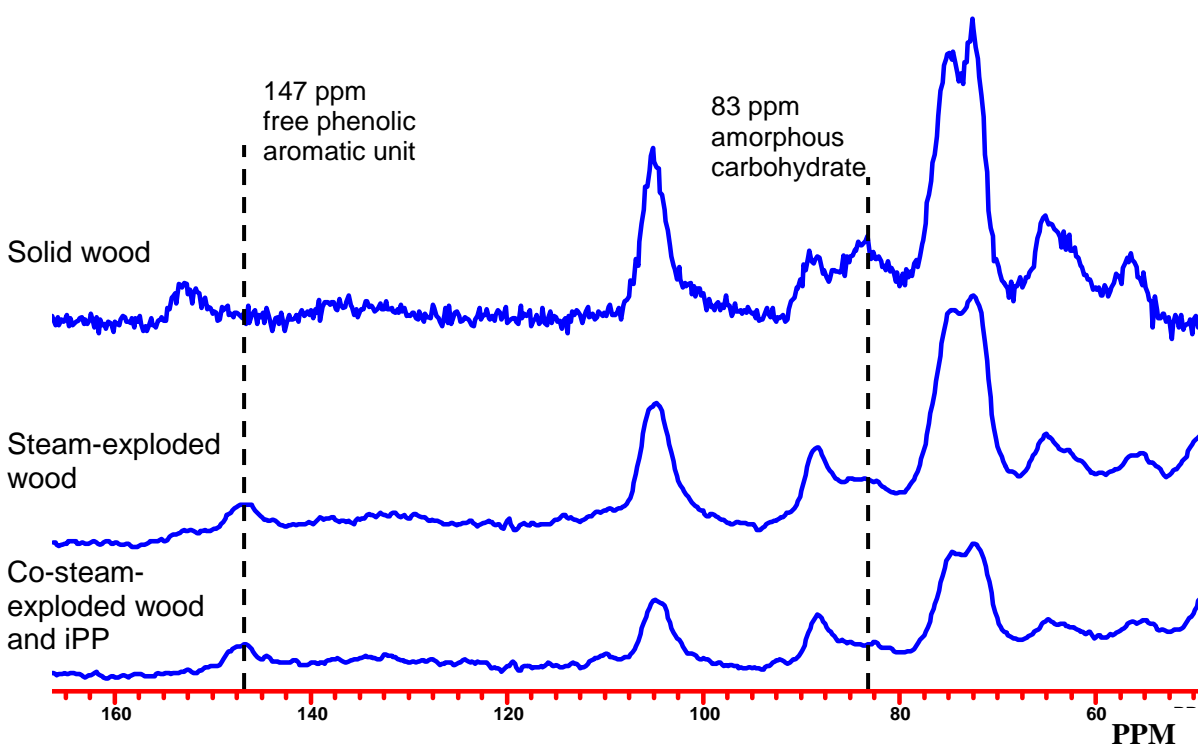
## **Results**

### NMR Spectra

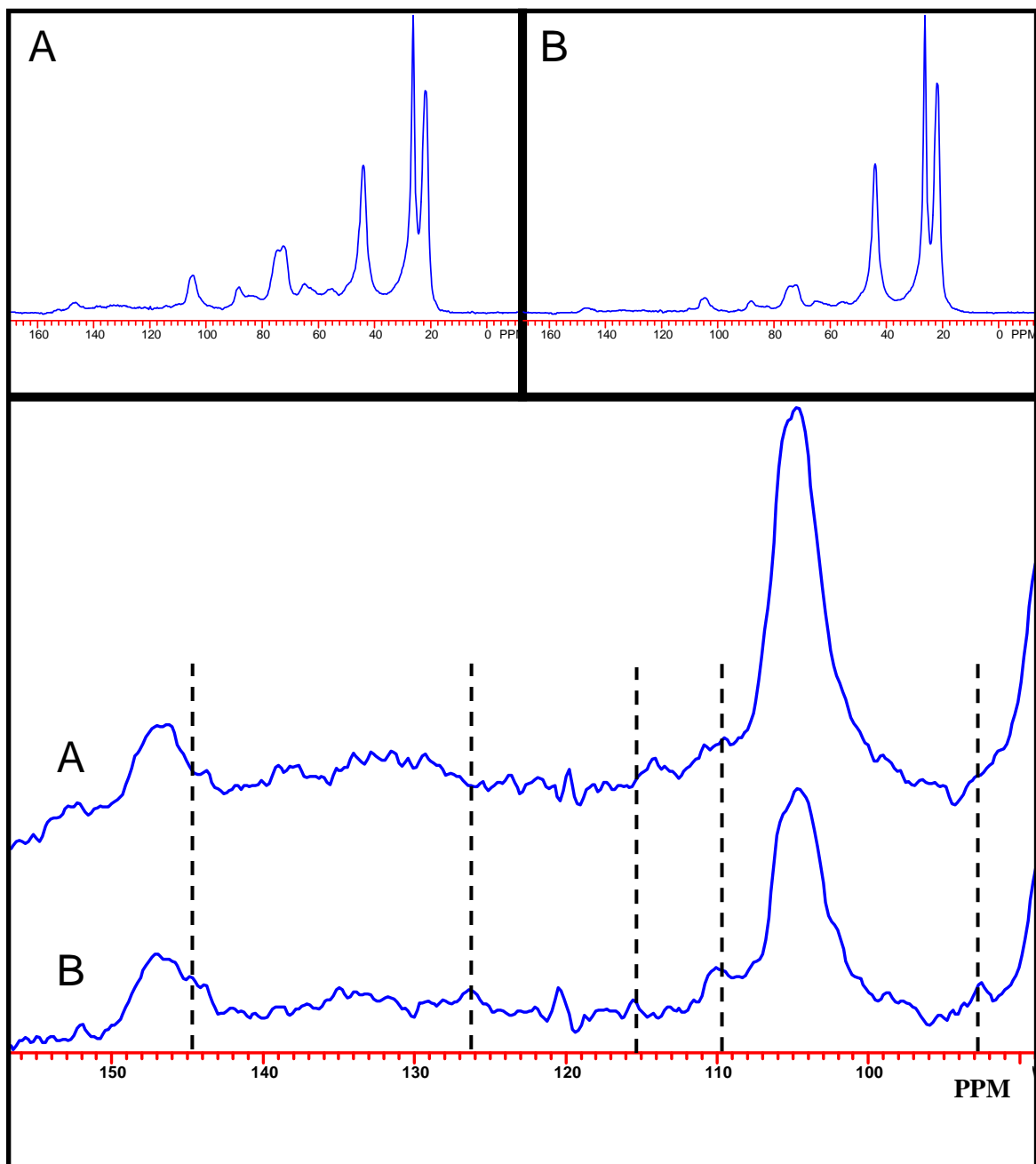
<sup>13</sup>C CP/MAS NMR spectra of steam-exploded wood fiber collected at contact times between 0.4 to 0.8ms gave the best signal to noise ratio for the cellulose-based signals, while contact times of 0.8 to 2ms gave the best signal to noise ratio for the lignin-based signals. Figure 7.1 contains spectra for solid wood flakes, steam-exploded wood and co-steam-exploded wood and polypropylene at a contact time of 0.8ms. The spectra for the steam-exploded samples are similar to the spectrum for solid wood demonstrating the main carbohydrate resonances at 105 ppm (C1 carbohydrate), 89 ppm (C4 crystalline cellulose), 83 ppm (C4 amorphous cellulose), 75-72 ppm (C2,3,5 cellulose), 65 ppm (C6 crystalline cellulose), 62 ppm (C6 amorphous cellulose), and 56 ppm (methoxy lignin). However, the most prominent lignin peak is located at 147 ppm for steam-exploded wood instead of 153 ppm for solid wood. Also apparent is a reduction at the 83 ppm resonance peak for the steam-exploded samples relative to the solid wood sample. The change in the lignin related shift signifies conversion from etherified to free phenolic aromatic units of lignin via homolytic cleavage at the βO4 linkages of lignin. The difference for the amorphous carbohydrate peak arises from the hydrolysis of the amorphous component and/or conversion of it to a crystalline state under high temperature and humidity.

New resonance peaks predominately located above the C1 resonance are distinguished for the co-steam-exploded wood and polypropylene compared to steam-exploded wood (Figure 7.2). These peaks are located at 93,110,115.5, 126.2, and 144.5 ppm (see dashed lines in Figure

7.2). Most of these peaks occur in the aromatic carbon region (115-145ppm) except for two peaks that fall in the region where acetals occur (93 and 110 ppm). The aromatic region may arise from differences in lignin structure, while it is speculated that oxidation of the iPP may contribute to the difference in the peaks at 93ppm and 110ppm. A general acetal bond is shown with its chemical shift in Figure 7.3A. Overall, comparison of the spectra demonstrates important change arising within the co-steam-explosion; chemically, additional species are found, however, the bulk of the material is not changing with all of the major components still resolved.

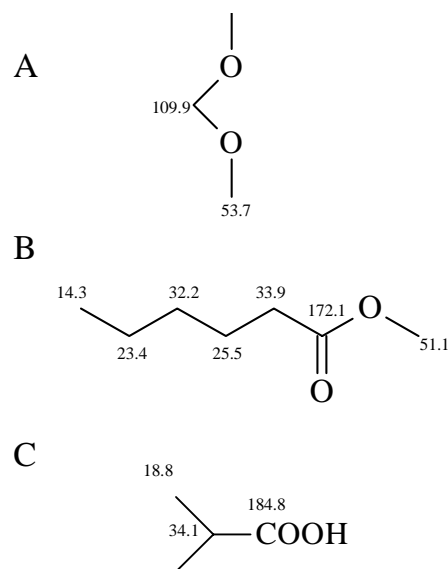


**Figure 7.1.**  $^{13}\text{C}$  NMR spectra for solid wood, steam-exploded wood and co-steam-exploded wood and iPP (air). Note shifts arising from the conversion of etherified lignin to free phenolic lignin (153 to 147) and reduction of amorphous carbohydrate portion (83 ppm).



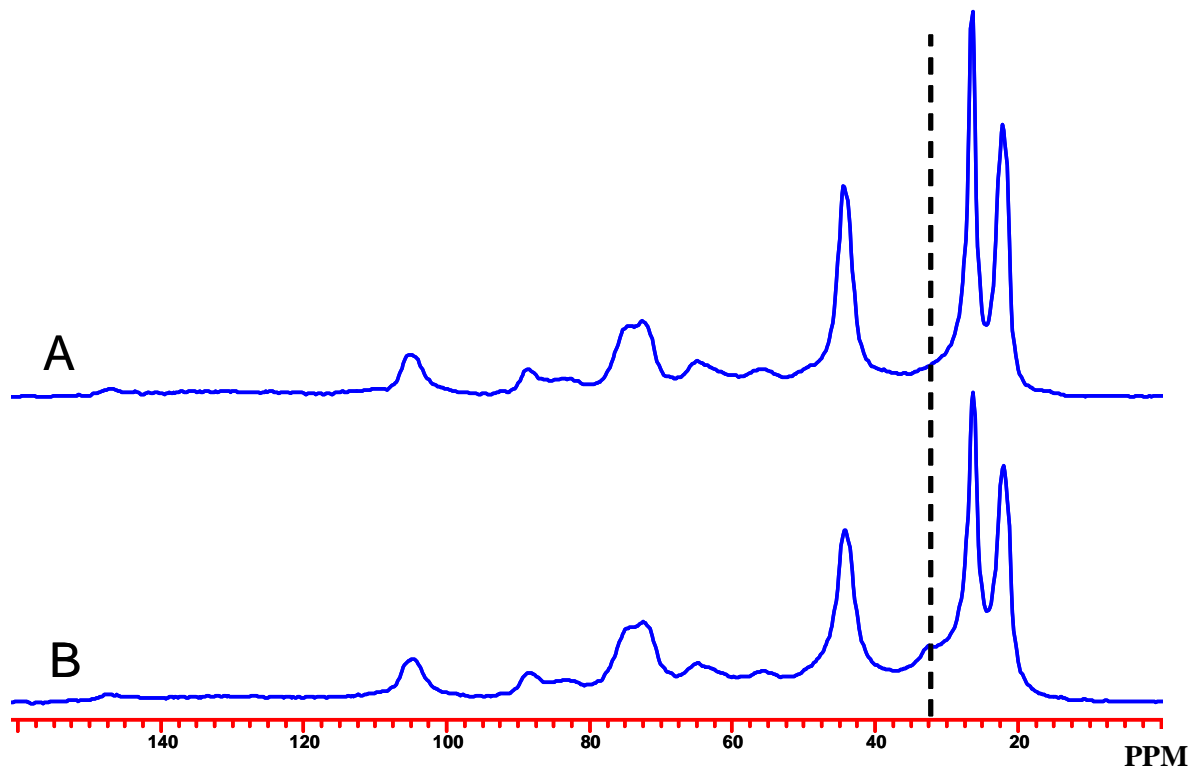
**Figure 7.2.**  $^{13}\text{C}$  NMR spectra for A) steam-exploded wood dry-mixed with neat iPP and B) co-steam-exploded wood and iPP.





**Figure 7.3.** Specific chemical shifts that may coincide with peaks in the co-steam-exploded wood and iPP sample from Silverstein and Webster [26]. A) General acetal group, B) Alkyl ester (for pressed sample), and C) Carboxylic acid (for pressed sample).

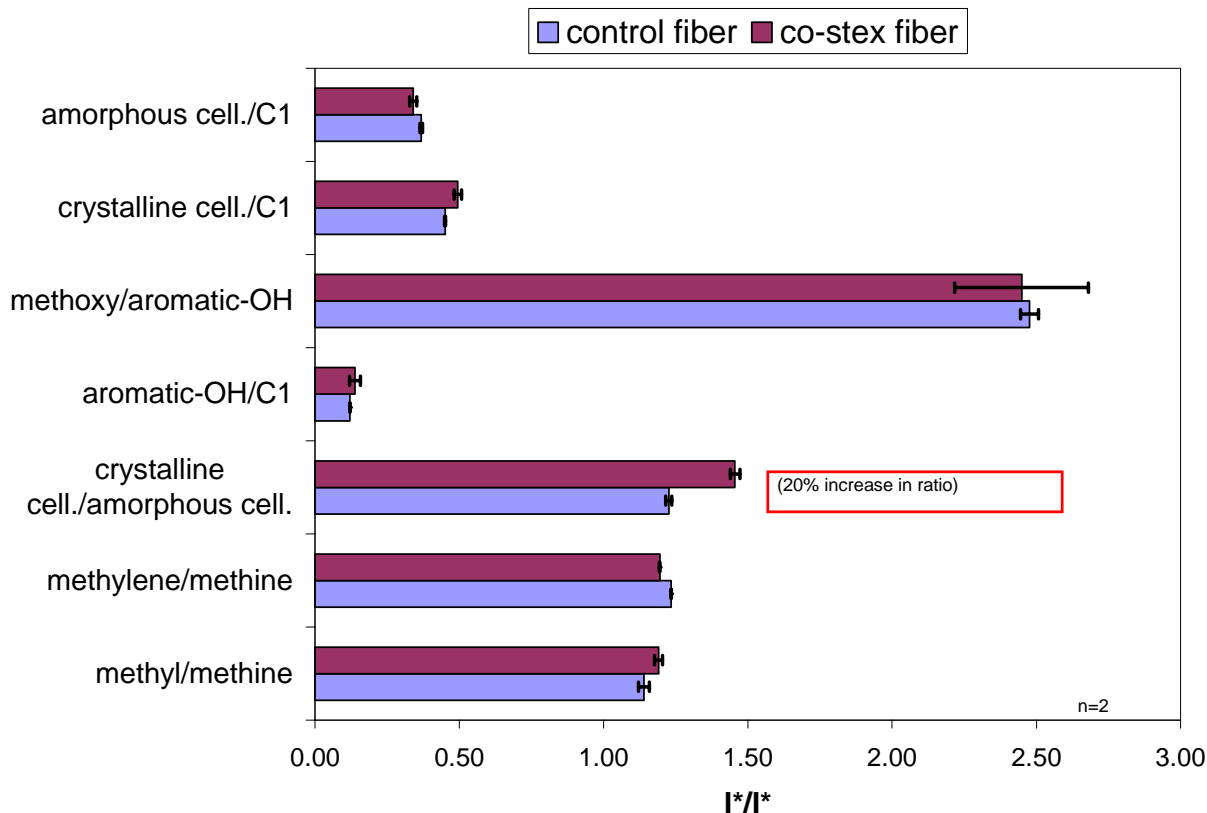
Composite materials were formed by compression molding at  $170^\circ\text{C}$  from steam-exploded wood fiber dry mixed with neat iPP and co-steam-exploded wood and iPP.  $^{13}\text{C}$  NMR spectra indicate a distinction in the polypropylene resonance regions (44 ppm for methylene, 27 ppm for methine, and 22 ppm for methyl) for the two samples (Figure 7.4). Namely, upon pressing the co-steam-exploded wood and polypropylene, a shoulder develops for the methine peak at 33 ppm that is significant in size relative to the wood related peaks (C1 105 ppm). Furthermore, the shoulder is not apparent in either the unpressed co-steam-exploded material (Figure 7.2) or the pressed “control” sample (Figure 7.4). Therefore, it is suggested that co-steam-explosion provides the precursor chemical species, labile oxygen containing bonds, for this shoulder to develop upon application of heat and pressure during the press cycle. Carbons adjacent to carbonyl carbons have chemical shifts close to the 33 ppm peak (Figure 7.3B,C). The other chemical shifts (carbonyl carbon 172.1 and 184.8) are in an indistinguishable region of the spectrum where there is poor signal to noise.



**Figure 7.4.**  $^{13}\text{C}$  NMR spectra for 1) compression molded steam-exploded wood and neat iPP at  $170^\circ\text{C}$  and 2) compression molded co-steam-exploded wood and iPP (air) compression molded at  $170^\circ\text{C}$ . Note co-steam-exploded sample has shoulder at 33 ppm, previously not seen non-compression molded sample.

## **NMR I\***

I\* values, relative peak intensity, relate the concentration of components within the sample. Although these values are typically not absolute they provide for a qualitative compositional analysis among treatments. I\* values were determined for peaks relating to polypropylene, amorphous cellulose, crystalline cellulose, carbohydrate (C1), aromatic lignin, and methoxy lignin. Specific ratios were calculated for the control and co-steam-exploded wood samples (Figure 7.5). Not much change is found in the ratios except for the ratio of crystalline cellulose to amorphous cellulose, which increases by 20% as a result of co-steam-explosion. Re-crystallization is known to occur during steam-explosion processing [27]. However, an additional enhancement by the presence of iPP has not been observed previously. This provides evidence for the presence of polypropylene interacting with wood-based polymers during co-refining by steam-explosion processing. By changing the degree of crystallinity of the cellulose component within wood it is apparent that the co-refining process has a dramatic influence on the constitutive polymers that make up the cell wall. Furthermore, this increase in crystallinity ratio may result from reorganization of the mobile amorphous cellulose during steam-explosion conditions or additional hydrolysis of the amorphous component. The factor can be elucidated if the I\* ratio is investigated for the amorphous and crystalline content in relation to the C1 carbohydrate content. The C1 peak includes all forms of polysaccharides and as a result gives an internal reference for the amount of cellulose present. The C4(crystalline)/C1 ratio increases, while the C4(amorphous)/C1 ratio decreases (Figure 7.5). If the change in the C4(crystalline)/C4(amorphous) was only due to hydrolysis of the amorphous component, then the ratio for C4(crystalline)/C1 would remain constant, while the C4(amorphous)/C1 decreased. Based upon the observation of an increase in C4(crystalline)/C1 ratio it is suggested that the increase in the cellulose ratio reflects both an increase in crystalline cellulose and decrease in the amorphous cellulose.



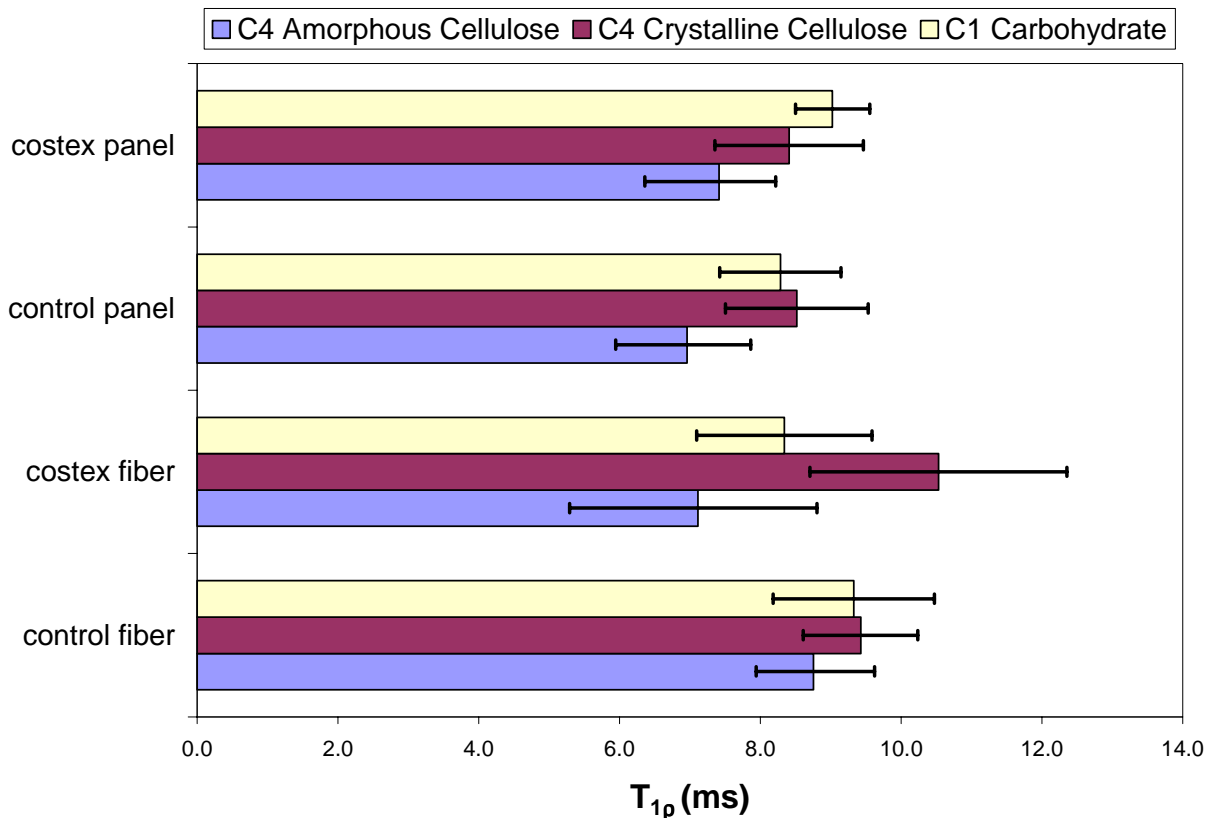
**Figure 7.5.** I\* ratios for relative concentration of components.

The lignin aromatic-OH to carbohydrate (C1) ratio remains unchanged by co-steam-explosion when compared to the control fiber (Figure 7.5). Additionally, no significant difference is detected in the ratio of the methoxy group to lignin phenolic group. These ratios indicate two important factors concerning co-refining with steam-explosion: 1) the lignin concentration relative to the carbohydrate concentration is not changing to a detectable degree and 2) the lignin is not undergoing increased demethylation. These factors are important in analyzing the interaction of iPP with the lignin component. In contrast, modification of the lignin may be occurring in ways not detectable in this experiment. A previous study showed an increase in methylene content for the lignin by co-steam-explosion with polyethylene [2].

Ratios for the polypropylene have minimal change (less than 5% increase/decrease), but are reproducible (Figure 7.5). An increase in the methyl concentration relative to the methine content for the co-steam-exploded material is apparent. Additionally, the methine content is increasing relative to the methylene content (Figure 7.5). From this data it can be seen that co-steam-explosion also affects the chemistry of the polypropylene component.

### **NMR Relaxation $T_{1\rho}$**

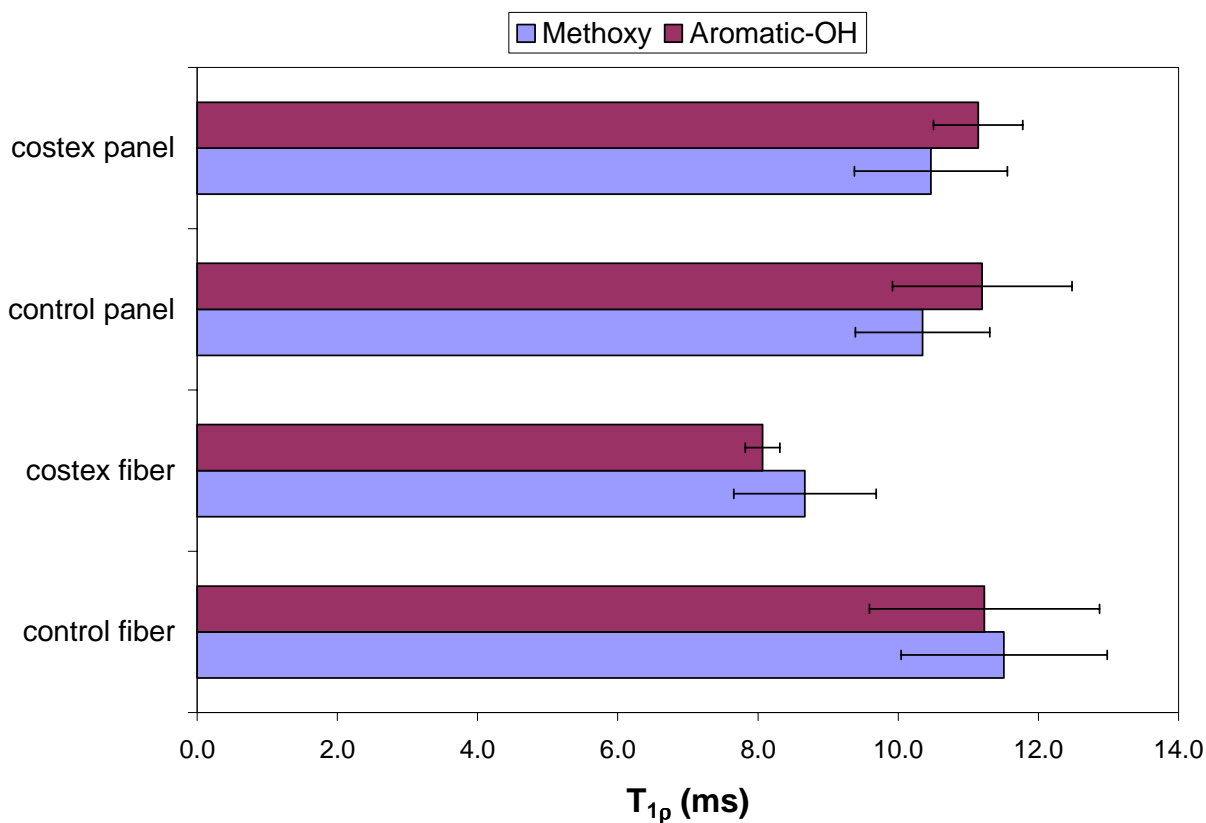
Many cell wall models of cellulose portray crystalline and amorphous regions in close association. This may arise from an individual cellulose chain passing through a number of crystalline and amorphous regions or an internal crystalline region encased by an amorphous component. Regardless of the true arrangement, both models should result in the cellulose components (amorphous and crystalline) with  $T_{1\rho}$  relaxation times that have similar values due to spin diffusivity between the materials. In fact this is seen in the literature for wood and is evident for the control steam-exploded wood sample (Figure 7.6). However, the relaxation parameters for the amorphous and crystalline cellulose components are different for the co-steam-exploded wood and polypropylene material (Figure 7.6). The relaxation time for the crystalline cellulose is greater than the amorphous component. Furthermore, the relaxation time changes for the co-steam-exploded wood and polypropylene after the material is pressed into a composite (Figure 7.6). The two C4 cellulose morphologies no longer have independent relaxation times after the addition of heat and pressure. Relaxation of the C1 carbohydrate is intermediate between the amorphous and crystalline components for the co-steam-exploded material (Figure 7.6). This carbohydrate includes signals from both the amorphous and crystalline cellulose regions and possibly from other hemicellulose fractions.



**Figure 7.6.**  $T_{1\rho}$  of cellulose related peaks.

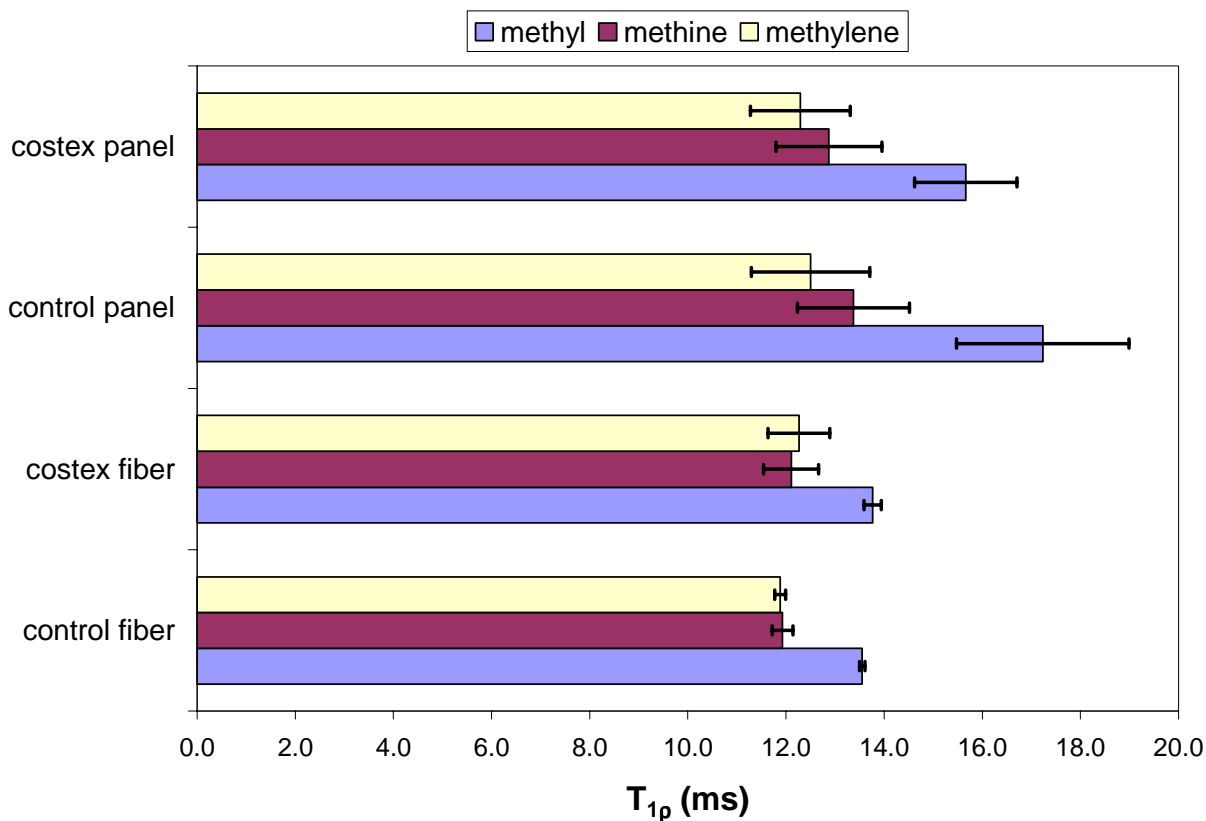
Two signals attributed to lignin, methoxy and C4-phenolic were used to investigate the relaxation of this wood-polymer within the steam-exploded sample. Initial observation of the  $T_{1\rho}$  relaxation times indicates both signals to be similar in magnitude (Figure 7.7). While this observation may appear trivial it indicates, 1) that the relaxation of the pendant methoxy group is representative of the relaxation of the lignin backbone and 2) there is reproducibility in the lignin relaxation through two different peaks. By calculating the  $T_{1\rho}$  relaxation times for these two peaks it is shown that co-steam-explosion decreases the relaxation time for lignin compared to the control (Figure 7.7). Upon pressing the material into a composite, the lignin relaxation time increases to a value that is identical to that of the control. Based on the change in relaxation times it appears that lignin adopts an arrangement with the cell components during co-steam-explosion processing that is transient and unstable, after raising the lignin to a temperature above its softening point it is able to flow into an arrangement similar to that of the control value. In

other words, when wood and polypropylene are co-steam-exploded the lignin is held in a temporary non-equilibrium state that can be reset by heat. This phenomenon was observed with shear-deformed (under high pressure processing conditions) polypropylene and polyethylene (27). After the two components were processed under 0.1GPa of pressure the incompatible blend had a single glass transition temperature. Upon heating the blend above the melting temperature the two materials phase separated demonstrating individual responses for their glass transitions. From comparison of the lignin relaxation to the polypropylene relaxation times (see next section) it is not expected that the lignin and polypropylene are in close association. However, the presence of polypropylene during co-steam-explosion does result in a faster  $T_{1\rho}$  relaxation time for the lignin component.



**Figure 7.7.**  $T_{1\rho}$  of lignin related peaks.

Peaks related to polypropylene for the two fiber samples, either dry mixed for the control fiber or co-steam-exploded, do not show any difference in  $T_{1\rho}$  relaxation times (Figure 7.8). In fact it is surprising because the two thermal histories are vastly different with one being exposed to high temperatures in the steam-explosion reactor. The two samples after being pressed and allowed to anneal also have similar  $T_{1\rho}$  relaxation values. While no measurable difference is apparent for the relaxation of the carbons within the backbone of the iPP (methylene and methine) the methyl relaxation time is increasing upon pressing the material. Because of the pendant nature of the methyl group the increase in relaxation time is not further discussed.

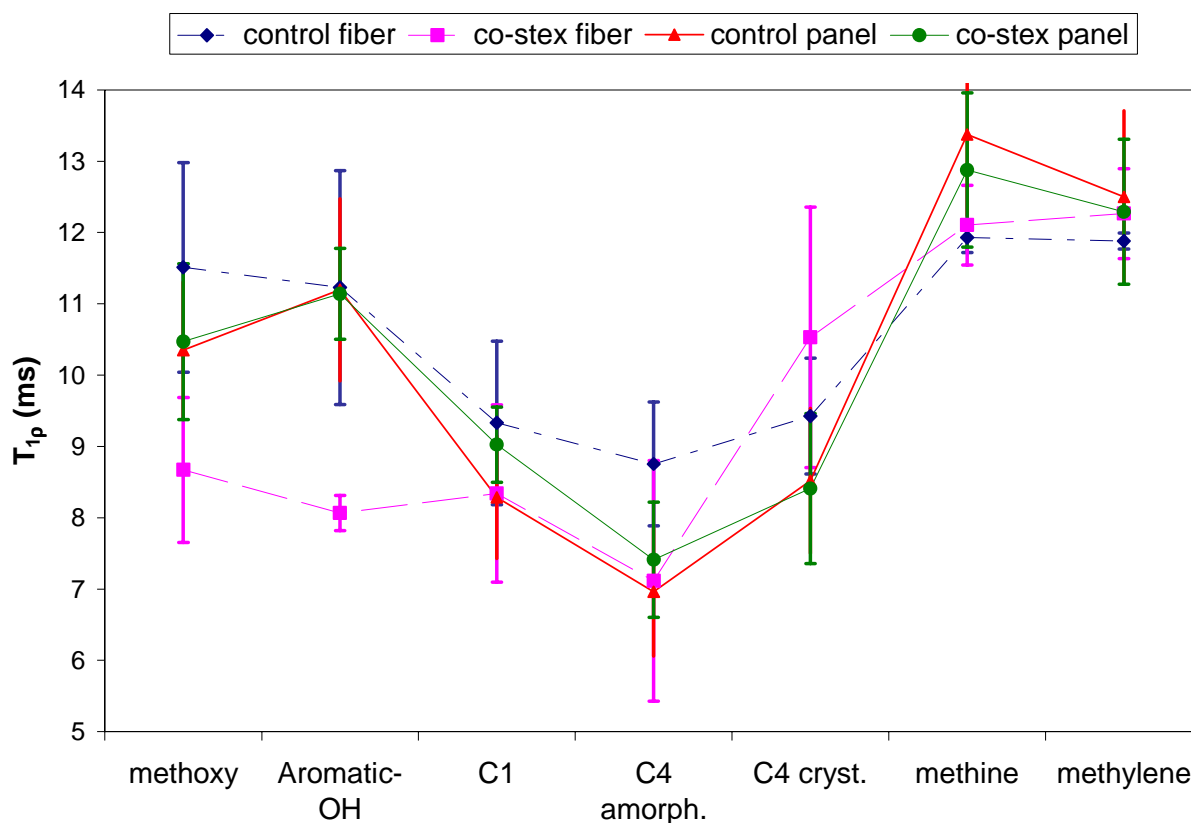


**Figure 7.8.**  $T_{1\rho}$  of iPP related peaks.



## **Spin Diffusion**

For components of a blend that are in close association containing independent domains in the nanometer range (2-30nm) the  $T_{1\rho}$  values should share a common relaxation time. In the case of solid wood  $T_{1\rho}$  relaxation values do not vary demonstrating the close association of the polymers. Upon steam-explosion of wood chips, lignin is liberated by hydrolysis of the lignin carbohydrate complex allowing for it to cluster and coalesce. Hence, lignin is no longer distributed on the nanoscale with cellulose and is reflected in the  $T_{1\rho}$  relaxation times, both experimental (Fig. 7.9) and reported [9]. For the control steam-exploded fiber the lignin relaxation is greater than what is seen for the carbohydrate components (Fig. 7.9). However, the lignin  $T_{1\rho}$  relaxation is suppressed for the co-steam-explosion of wood and polypropylene with relaxation times similar to the non-crystalline cellulose component (Figure 7.9). Upon applying heat and pressure the relaxation value of the lignin increases to a value similar to both the control fiber and control composite (Figure 7.9). It is not explained why the crystalline cellulose region has an independent relaxation time from that of the amorphous wood component in the co-steam-exploded fiber. However, like the change in lignin  $T_{1\rho}$  after heat molding, the crystalline cellulose  $T_{1\rho}$  relaxation value also changes. Both lignin and polypropylene are mobile at these higher temperatures and may contribute to the resulting change in the cellulose relaxation. In addition to the peaks mentioned, the new shoulder at 33 ppm for the co-steam-exploded wood and iPP compression molded panel has a relaxation time lower than the other iPP peaks. The relaxation time for this shoulder is 7.2 ms. This value is similar to the  $T_{1\rho}$  value for the amorphous cellulose of this sample.



**Figure 7.9.** Plot of  $T_{1\rho}$  vs. component of composite

### NMR $T_{CH}$

Methine carbons and methyl carbons have  $T_{CH}$  values in the range of 15 to 50 $\mu$ s [3]. The  $T_{CH}$  is faster than the minimal contact time (200  $\mu$ s) achievable with the available experimental protocol. As a result the  $T_{CH}$  values for methylene and methine peaks of iPP are over two times greater than the reported value (Table 7.1). Furthermore, the  $T_{CH}$  values for the phenolic lignin group are near 0.7 to 1 ms, arising from the aromatic backbone structure and the presence of oxygen. There is minimal difference in the average  $T_{CH}$  value and the variance for the control fiber, control pressed composite, and co-steam-exploded composite. However, the  $T_{CH}$  value for the co-steam-exploded fiber is higher, but the increased variance prohibits conclusive assessment

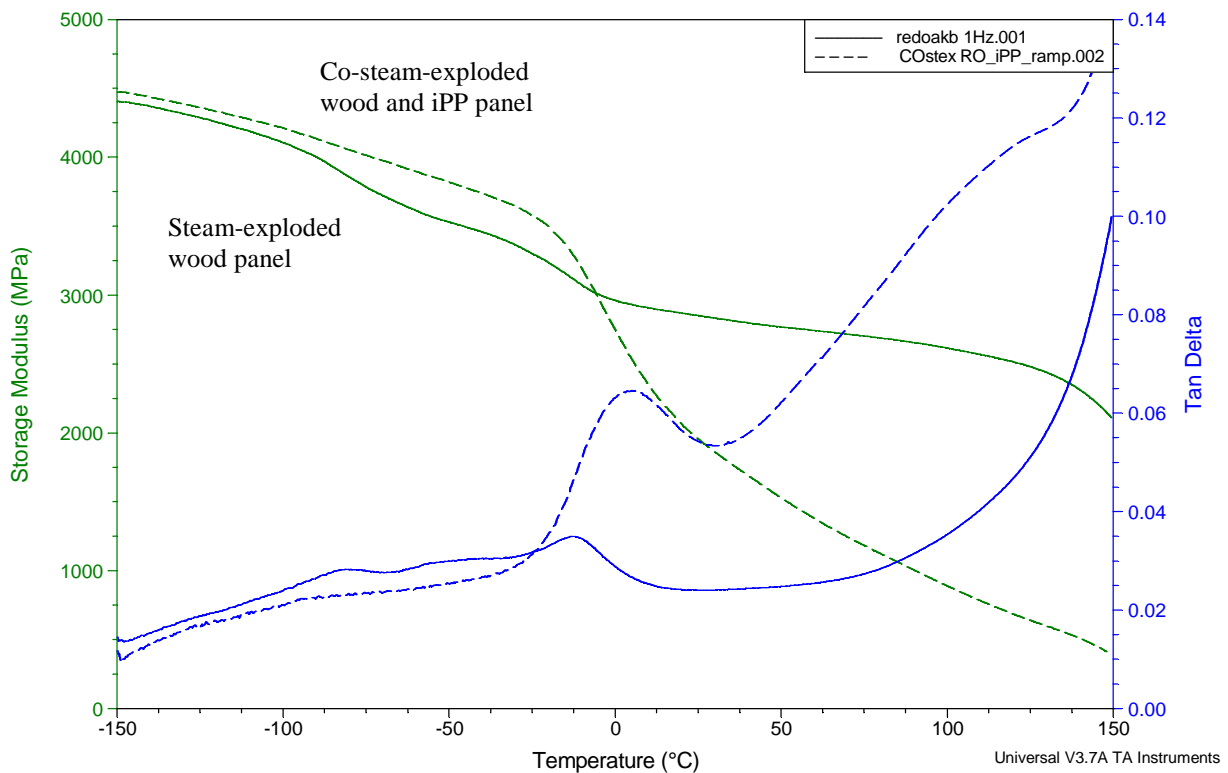
about the change. If this higher value is not an artifact then the increase in time may result from a mobile phenolic group of the lignin. This would occur by reduced hydrogen bonding.

**Table 7.1**  $T_{CH}$  values for steam-exploded materials (ms).

Chemical Group	control fiber		control panel		costex fiber		costex panel	
	average	std. dev.	average	std. dev.	average	std. dev.	average	std. dev.
Methyl	0.17	0.01	0.13	0.04	0.18	0.01	0.19	0.04
Methine	0.11	0.00	0.08	0.04	0.12	0.01	0.13	0.05
Methylene	0.08	0.01	0.05	0.05	0.10	0.01	0.10	0.06
Methoxy	0.14	0.04	0.08	0.07	0.18	0.07	0.14	0.06
C4 amorph.	0.13	0.04	0.09	0.07	0.18	0.04	0.13	0.06
C4 cryst.	0.13	0.04	0.11	0.05	0.19	0.03	0.14	0.06
C1	0.13	0.02	0.12	0.04	0.17	0.03	0.15	0.05
Aromatic-OH	0.72	0.08	0.71	0.10	1.01	0.30	0.69	0.07

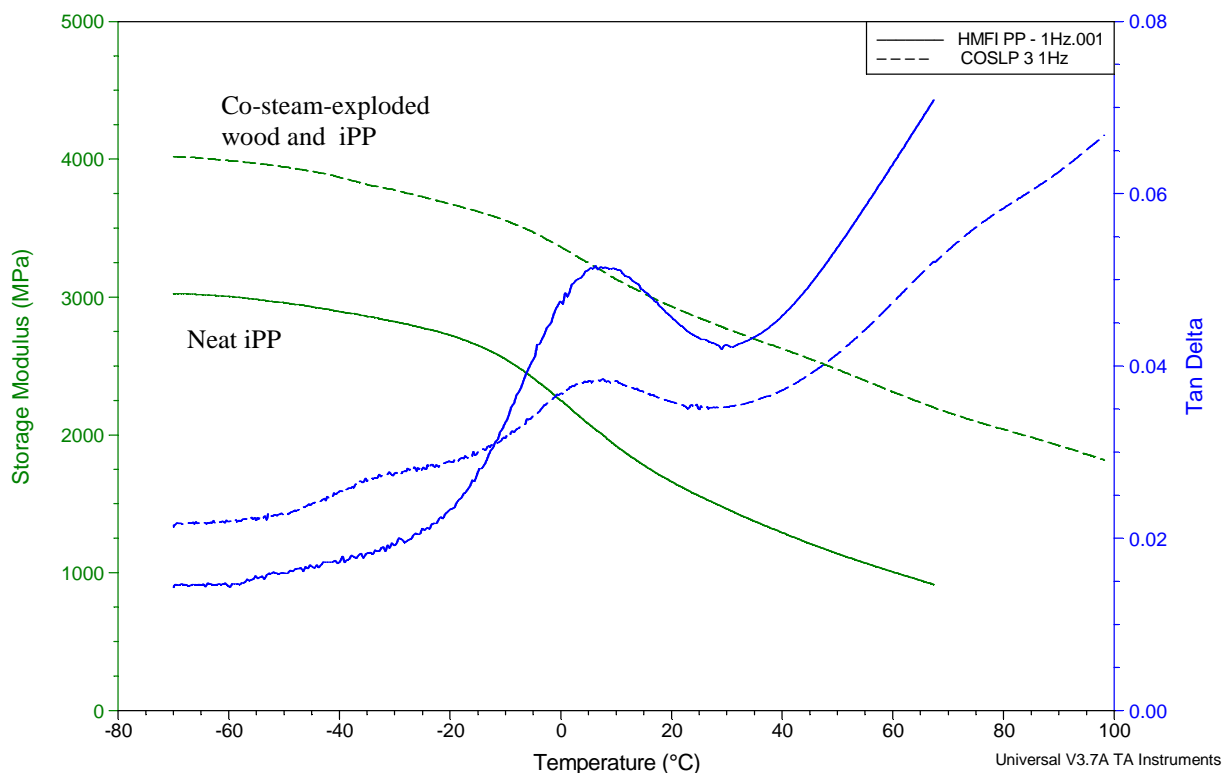
## DMA

The dynamic storage moduli for the pressed steam-exploded wood fiber and a pressed co-steam-exploded wood fiber and polypropylene, in their dry state, have similar storage modulus values at low temperatures (Figure 7.10). At temperatures above the glass transition ( $T_g$ ) of polypropylene the dynamic storage modulus of the steam-exploded wood panel is significantly higher. A number of low temperature secondary relaxations are evident in the steam-exploded wood panel (Figure 7.10). These transitions are not seen in the co-steam-exploded wood and polypropylene sample. It is not known if the presence of polypropylene is suppressing the events through interaction of the components or if the events are masked by the polypropylene transition. The percentage of polypropylene compared to the percentage of wood components should be taken into consideration. Polypropylene makes up 50% of the material by weight, while cellulose and lignin approximately make up the remaining 33% and 17% of the weight of the sample, respectively.



**Figure 7.10.** DMA of panels from steam-exploded wood and co-steam-exploded wood and iPP.

If two components of a blend are partially miscible the  $T_g$  of each component will shift accordingly towards the other component. It should be pointed out that the  $T_g$  of polypropylene (as seen in Fig-7.10) is in the range between -2 and 5°C. Further analysis of the  $T_g$  was performed with neat polypropylene and another co-steam-exploded wood and polypropylene composite that contained 10% lyocell fiber (Figure 7.11). The resulting material shows no shift in temperature in the  $T_g$  (observed by the peak of the loss modulus) of neat polypropylene and the polypropylene located in the composite. However, the tan delta peak is broadened and attenuated in the co-steam-exploded composite material showing a change in behavior for polypropylene's  $T_g$ . Overall, the lack of shift indicates minimal interaction of wood and cellulose components with polypropylene, while the broadening of the transition points to general reinforcement of the iPP by the wood and regenerated cellulose fiber.



**Figure 7.11.** DMA of co-steam-exploded wood and iPP panel (with 10% lyocell) and neat iPP panel.

## Discussion

It is clear that steam-explosion co-processing of wood with iPP changes both morphology and chemistry of the polymeric materials. The influence of this change has been previously documented in sorption [1], microscopy [30], and fractionation [2] studies on the material. Specifically, the initial diffusion coefficient for co-steam-exploded wood and iPP was shown to increase relative to steam-exploded wood [1]. This increase may now be attributed, in part, to differences in cellulose crystallinity content. Increase crystallinity would cause formation of capillaries within the wall, while reducing amorphous cellulose content. Furthermore, confocal laser scanning microscopy demonstrated that lignin on the co-steam-exploded wood and iPP material had an alternate arrangement compared to the steam-exploded wood [30]. Lignin did not appear coalesced in clusters on the fiber surface like it did for the steam-exploded wood,

instead, there was uniform appearance. The  $T_{1\rho}$  lignin relaxation supports the difference in lignin morphology. Additionally, the spin diffusion data suggests that lignin still has small domains on the nanometer scale with the amorphous cellulose component. Also, there is reduced water extractable yield for co-steam-exploded wood and iPP material [2]. This may indicate reduced cleavage of lignin and carbohydrate complexes which help maintain uniform lignin distribution. In other words, iPP may act as a scavenger of free radicals.

It is not fully understood why co-processing of wood and iPP increases the crystallinity of the cellulose component. However, two factors influence classical crystallization process for a given temperature-- molecular weight of the species and the number of nucleating sites. Under the assumption that the degree of polymerization of the cellulose is only affected by the severity factor, the molecular weight of the cellulose should remain constant in relation to the presence of iPP. This leaves the second factor that iPP may influence amorphous cellulose crystallization, directly or indirectly, by causing nucleation or limiting crystal growth. Polypropylene, polypropylene degradation products or polypropylene limiting the rearrangement of lignin during steam-explosion, may be the source of increased nucleating sites. If this occurs the cellulose crystals should be smaller in diameter with either polypropylene (or polypropylene degradation products) in direct contact with cellulose crystals. If the iPP is causing nucleation of the cellulose amorphous component then the newly formed cellulose crystals would be in close association with the polypropylene component. The increased  $T_{1\rho}$  relaxation parameter for the crystalline cellulose component may be a sign of iPP nucleating the cellulose crystals. The change in the  $T_{1\rho}$  relaxation parameter for the crystalline cellulose after compression molding may be from increased iPP mobility at the press temperature (above the  $T_m$  of iPP). In other words, the iPP may reorganize away from the cellulose crystalline surface when iPP is raised above its melting temperature.

Extracted polypropylene from the co-processed material showed signs of oxidation by chemiluminescence [2]. However, it is assumed that the fractionation process removed the least oxidized portion from the material. Other work has demonstrated chemical bonding of oxidized polyolefin to model cellulose fibers [31]. Solid state NMR allowed the investigation of *in-situ* chemical groups. However, there was poor signal to noise ratio for the portion of the  $^{13}\text{C}$  NMR spectra where carbonyls and peroxides are located. In spite of these limitations, there were chemical changes noted in the aromatic and some acetal regions for the co-processed wood and

iPP. Additionally, after pressing the co-steam-exploded material a new shoulder developed on the methine peak for polypropylene. It is suggested that co-steam-explosion processing forms the initial labile bonds that then undergo reaction during heat molding. These labile bonds may arise from the oxidized polypropylene chemically bonded to lignin, cellulose, or some intermediates from lignin or hemicellulose degradation, such as quionone methides or furfural aldehydes.

## Conclusions

NMR analysis shows chemical, morphological, and mobility/relaxation changes in the co-refined steam-exploded wood and polypropylene. The most noticeable chemical changes were found in the aromatic region of the spectra (110-155 ppm). Additionally, the cellulose crystallinity ratio increased for the co-steam-exploded material relative to the control sample. The crystallinity increase was a result of both amorphous cellulose hydrolysis and amorphous cellulose crystallization.

Relaxation parameters of the co-steam-exploded wood material also changed as a result of steam-explosion. Four observations were noted for  $T_{1\rho}$ :

- 1.) polypropylene relaxations were similar for control and co-steam-exploded material
- 2.) amorphous and crystalline cellulose had different  $T_{1\rho}$  values for the co-steam-exploded material with the crystalline cellulose value similar to the value for polypropylene
- 3.) lignin  $T_{1\rho}$  value was reduced for the co-steam-exploded material in the range of amorphous cellulose
- 4.)  $T_{1\rho}$  values for the co-steam-exploded material reverted to values similar to the control when compression molded

Together these relaxation values indicate a complex interaction among the lignin, polypropylene, and cellulose that arises as a result of co-steam-explosion processing: this is symptomatic of a meta-stable molecular arrangement.

Analysis of the  $T_g$  of lignin for the co-steam-exploded material is complicated by the melting of the iPP in the same temperature region, while the  $T_g$  of polypropylene is not shifted, but the transition is broadened. These trends point to a minimal interaction on the nanoscale between co-steam-exploded wood and polypropylene. However, evaluation of interaction arising from co-steam-explosion processing is complicated by increasing the thermal processing

when compression molding the material into a composite. A meta-stable enhanced-interaction may occur that is erased by the press temperature. Solid-state NMR supports this claim.

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