Incorporation of Guanidine and Ethylguanidine into Thermosetting Resins

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ABSTRACT: Guanidine- and arginine-containing proteins are commonly used in the manufacture of formaldehyde-based thermosetting resins; however, the polymer structures of these resins were not known. ^{13}C-NMR spectroscopy has now been applied to demonstrate that guanidine does react and form crosslinks in formaldehyde reactions. Ethylguanidine was used to model arginine in soy proteins, and the NMR analysis indicates that guanidine side chains in proteins also react and form crosslinks in biobased adhesives. Furthermore, these reaction products change with pH demonstrating that the formation of desired polymer species can be controlled and optimized. Finally, the products of the two most widely manufactured amino resins, melamine–formaldehyde and urea–formaldehyde, were then compared with those of guanidine–formaldehyde and ethylguanidine–formaldehyde.
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Key words: adhesives; biopolymers; NMR; resins; crosslinking

INTRODUCTION

The reactivity of formaldehyde with guanidine moieties has been largely unexplored despite the use of guanidine salts and proteins with guanidine side chains in formaldehyde-based resins. Guanidine in the form of guanidine carbonate has previously been investigated as an additive in phenol–formaldehyde resins.[1] The authors concluded that the carbonate counter-anion was mainly responsible for the observed effects rather than guanidine itself; however, the evidence for this conclusion was indirect, as the chemical structures in the resin were not fully characterized. Soy proteins containing arginine units are used in the manufacture of biobased adhesives[2–10] due to soy being an environmentally friendly alternative to petroleum based counterparts, melamine, urea, and phenol. Wheat gluten also contains arginine and has been reported to be a potential binder for fiber composites.[9–11] The bonds that form in the polymerization process of protein-based resins have not been fully characterized presumably due to the large structures of proteins making the polymerization process difficult to analyze. Soy proteins contain 7.5% guanidine side chains, which is the fourth most commonly found side chain in these proteins.[7] Lysine side chains have been cited as reactive in soy resins,[12] whereas arginine side chains have been largely ignored as potential crosslinking groups despite the fact that guanidine side chains are more common than lysine (6.2%) in soy proteins. Although Wescott et al.[7] listed arginine as a potentially reactive side chain in soy, they reported that lysine could copolymerize with phenol and not arginine. Furthermore, guanidine side chains have three reactive nitrogen groups compared with just one on lysine. Therefore, it seems likely that guanidine side chains could be a significant contributor to the polymerization process in biobased adhesives.

Polymerization in amino resins is a two-step process. The first is hydroxymethylation, followed by condensation resulting in methylene and/or dimethylene–ether crosslinks. The degree to which methylene links are formed compared with dimethylene–ether links greatly affects the properties of the resulting resin.[13–16] Methylene links are more resistant to hydrolysis than dimethylene–ether bridges and therefore the proportion of these links influences the water resistance of the resin and the resulting composite.[13–16] Furthermore, formaldehyde emission from wood composites results from hydrolysis of hydroxymethyl groups and dimethylene–ether bonds and not from methylene links. It has been reported in biological systems that arginine, with guanidine side chains, readily reacts with formaldehyde to form hydroxymethyl derivatives; however, the presence of crosslinks was not investigated.[17]

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Tome and Naulet[18] used ^{13}C-NMR spectroscopy to study reactions between formaldehyde and amino acids; however, they stated that possible arginine condensation products were not able to be characterized. A recent study reported[19] that reactions between 8-hydroxyquinoline, guanidine, and formaldehyde resulted in the formation of terpolymers and not crosslinks between guanidine moieties. Work by Alferov et al.[20] suggested that guanidine reacts at basic pH with formaldehyde to produce hydroxymethyl derivatives, which then condense to form dimethylene–ether links but not methylene bridges; however, these studies were performed around 40 years ago and the evidence was indirect as microanalysis was used for structural analysis.

In more recent times, NMR spectroscopy has been widely used to elucidate protein as well as synthetic polymer structures.[21,22] NMR spectroscopy is commonly applied to the structural elucidation of thermosetting resins.[14,23–28] ^{13}C-NMR is particularly useful for resin analysis because the carbon resonances in thermosets are distinct.[14,27,28] It has been reported that pH is the major factor governing the proportion of methylene to dimethylene–ether crosslinks formed in melamine–formaldehyde (MF) and urea–formaldehyde (UF) resins.[16,29] Guanidine has pK_a 12.8, which differs greatly to those of melamine and urea, at 6.8 and 0.8, respectively. We now show that guanidine does react with formaldehyde, and the formation of crosslinks is affected by pH and differs for MF and UF systems. These results demonstrate that the polymer structure of guanidine-based resins can be controlled by pH. The ability to analyze and control resin structures should give rise to structure–function relationships leading to the synthesis of more durable products.

EXPERIMENTAL

Materials and instruments

Guanidine hydrochloride, sodium hydroxide, and formaldehyde were purchased from Sigma-Aldrich Chemical Company and dimethyl sulfoxide (d_6-DMSO) was purchased from Cambridge Isotope laboratories. ^{13}C-NMR spectra were recorded using a Varian Inova 500 spectrometer. Chemical shifts (δ values) are given in parts per million (ppm) and spectra were referenced against residual solvent (d_6-DMSO).

Resin preparation

Typical pH and temperature were used for resin preparation, however, dilute formaldehyde solution (5% w/w) was used to limit polymerization, thus simplifying structural analysis by preventing ^{13}C-NMR line-broadening.[30] The reaction products were therefore low-molecular weight species and were not subjected to physical analysis.

Guanidine–formaldehyde experiments

In a 5 mL reaction vessel, guanidine hydrochloride (0.100 g, 1.04×10^{-3} mol) was dissolved in aqueous formaldehyde solution (1.87 g of 5% w/w [3 eq formaldehyde]) and the pH was adjusted to 10 or 12 using sodium hydroxide solution (11 M and 1 M). The vials were then heated at 60 °C or 90 °C for 20 min, by which time the pH values had fallen to 7 and 9, respectively. The samples for ^{13}C-NMR spectroscopy were prepared by adding 0.3 mL d_6-DMSO and storing at 4 °C until analysis.

Ethylguanidine–formaldehyde experiments

In a 5 mL reaction vessel, ethylguanidine hemisulfate (0.145 g, 1.04×10^{-3} mol) was dissolved in aqueous formaldehyde solution (1.87 g of 5% w/w [3 eq formaldehyde]) and the pH was adjusted to 10 or 12 using sodium hydroxide solution (1 M and 0.2 M). The vials were then heated at 90 °C for 20 min, by which time the pH values had fallen to 7 and 9, respectively. The samples for ^{13}C-NMR spectroscopy were prepared by adding 0.3 mL d_6-DMSO and storing at 4°C until analysis.

RESULTS AND DISCUSSION

Guanidine–formaldehyde reactions

^{13}C-NMR spectroscopy was used to analyze products from guanidine–formaldehyde (GF) reactions. The ^{13}C-NMR spectrum in Figure 1 is of products from a reaction of guanidine with formaldehyde performed at pH 7 at 90°C for 20 min. The resonances of the starting materials are at δ 82.3 ppm and δ 165.0 ppm for formaldehyde and guanidine, respectively. Formaldehyde dimers and trimers are also present in the reaction indicated by resonances at δ 84.0 ppm and δ 86.0 ppm, respectively. It is clear from analysis of the NMR spectrum in Figure 1 that guanidine does in fact react with formaldehyde as there are numerous resonances not attributed to the starting materials.

Guanidine presumably reacts with formaldehyde in the same manner as urea, resulting in hydroxymethyl derivatives as well as methylene and dimethylene–ether bridges (Scheme 1). These guanidine-derived structures have analogous resonances to their urea counterparts because the carbons are in similar chemical environments. Resonances of products in UF resins are known[14,23] and are at δ 66.6–71.0 ppm for hydroxymethyl groups, δ 48.8–61.6

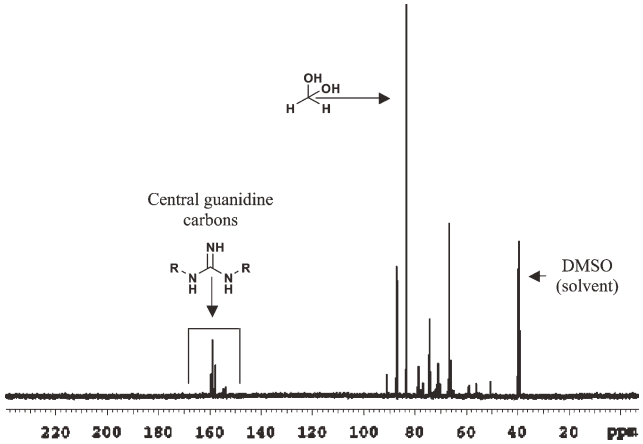
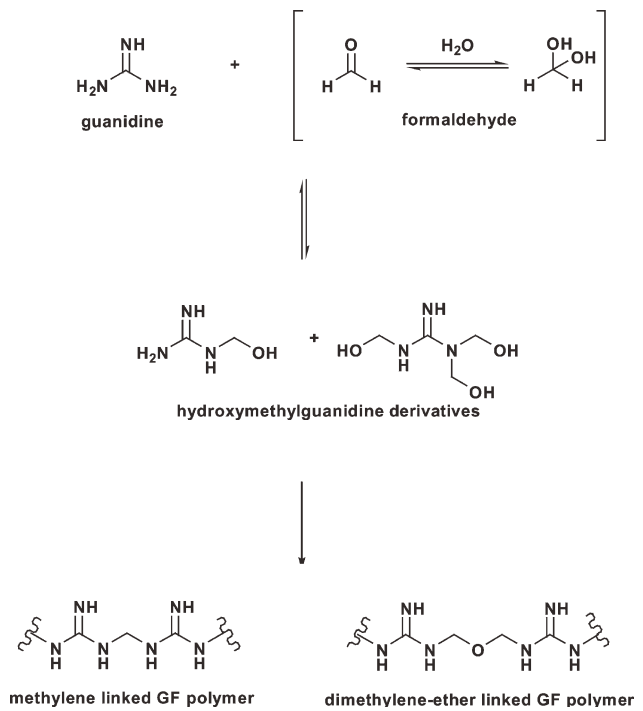


Figure 1 GF ^{13}C-NMR spectrum (5% formaldehyde, 20 min, 90°C, pH 7).

ppm for methylene bridges and δ 69.9–76.2 ppm for dimethylene–ether links. Carbons in GF resins would, therefore, have similar chemical shifts.

From analysis of the GF NMR data, the species shown in Scheme 1 can be identified. The main region of interest is that spanning the chemical shifts of the ether links, hydroxymethyl groups and methylene links (δ 45–85 ppm), and this region is therefore displayed in Figure 2. Dimethylene–ether links formed in the GF reaction are evident by ^{13}C-NMR signals from δ 68–80 ppm and have been labeled in Figure 2 accordingly. The peaks representing hydroxymethyl-derivatives are also highlighted in Figure



Scheme 1 Possible GF reaction scheme based on known UF and MF reactions.

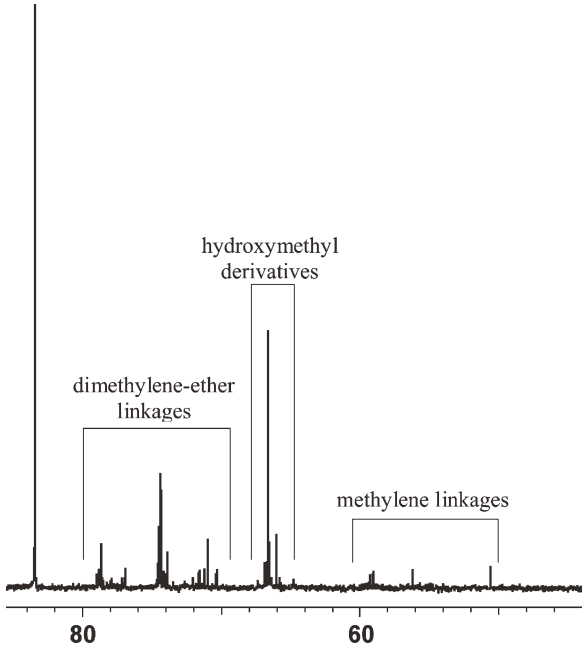


Figure 2 GF ^{13}C-NMR spectrum (5% formaldehyde, 20 min, 90°C, pH 7).

2. Finally, it is also clear that methylene links have formed under the specified reaction conditions as ^{13}C-NMR resonances corresponding to such links are observed and labeled in Figure 2 (δ 45–60 ppm). These results establish unambiguously that methylene links form during the reaction between guanidine and formaldehyde.

Figure 3 displays segments of ^{13}C-NMR spectra of GF reaction products at pH 7 and 9. These pH values were chosen because commercial resins are commonly manufactured in this pH range.[14] The formalin peaks are referenced to the same intensity (δ 82.3 ppm) to allow comparison of spectra. It can be seen that at pH 7 the most apparent species are ether links (groups of signals at $\sim$ δ 70, 73, and 78 ppm) and hydroxymethyl groups (δ 65.3 and 65.5 ppm),

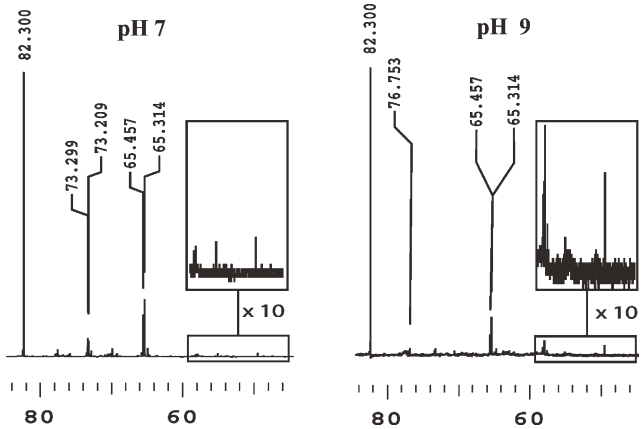


Figure 3 ^{13}C-NMR spectra of GF reaction products at pH 7 and 9 (5% formaldehyde, 20 min, 90°C).

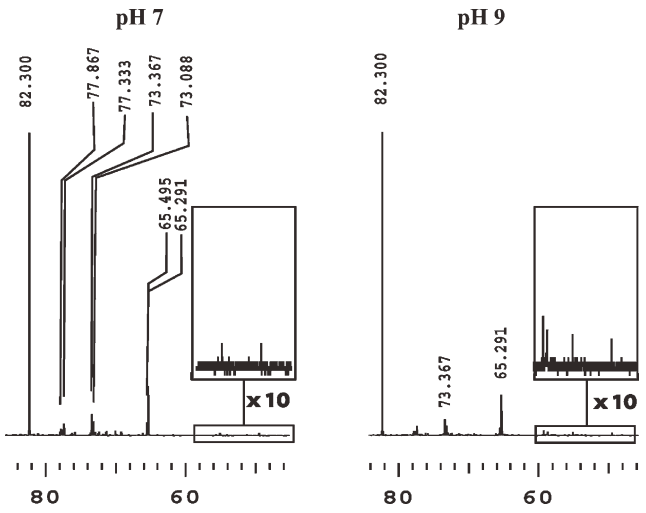


Figure 4 ^{13}C-NMR spectra of eGF reaction products at pH 7 and 9 (5% formaldehyde, 20 min, 90°C).

whereas at pH 9 hydroxymethyl groups (δ 65.3 and 65.5 ppm) and methylene links (δ 49.4, 57.9, and 58.1 ppm) dominate. The increase in proportion of GF methylene signals from pH 7 to 9 was unexpected, because UF and MF methylene links decrease with increasing pH.[14]

The NMR data shown in Figures 1–3 confirm that guanidine is indeed capable of being integrated into the main framework of amino resins, thus leading to the conclusion that the improvements in resin properties through use of guanidine carbonate as a resin additive may be due to guanidine itself rather than carbonate. The formation of methylene bridges at high pH is of special interest as these are particularly important for durability in the final wood composites.[13,16]

Ethylguanidine–formaldehyde reactions

To investigate the effect of substitution on guanidine reactivity to mimic the substituted guanidine in arginine, and therefore, soy proteins, the previous reactions were repeated using ethylguanidine.

The ethylguanidine–formaldehyde (eGF) system was investigated in a similar manner to the GF system. The reaction products at pH 7 and 9 were analyzed by ^{13}C-NMR spectroscopy (Fig. 4) and the formalin peak was referenced to the same intensity (δ 82.3 ppm) to allow comparison of spectra. It can be seen in Figure 4 that at pH 7 hydroxymethyl groups (δ 65.3 and 65.5 ppm) and dimethylene ether links (δ 69.1–71.3, 73.1, 73.4, 77.3, and 77.9 ppm) are clearly visible. Very small methylene signals are also present at δ 49.4 and 57.9 ppm. Two main changes in the appearance of the ^{13}C-NMR spectrum are seen on increasing from pH 7 to 9 (Fig. 4). First, the dimethylene–ether peaks, observed at pH 7, are somewhat diminished; secondly, further methylene bridge signals at ~59 ppm are observed. It is thought that these correspond to methylene link attached to the substituted nitrogen. There is not a notable difference between the GF and eGF NMR spectra. It is therefore concluded that there is little qualitative difference between the reactivity of guanidine and ethylguanidine in formaldehyde reactions, with ether bridges dominating at pH 7 and methylene bridges becoming more apparent at pH 9 in both systems (Figs. 3 and 4).

Comparison of GF and eGF reactions to UF and MF reactions

The results obtained in the GF and eGF systems were then compared with those of UF and MF reactions. Spectra recorded of UF and MF reactions, along with those for GF and eGF reactions, can been seen in Figure 5, again with the formalin peak scaled and referenced to δ 82.3 ppm. It can be seen in the NMR spectra of the MF system that hydroxymethyl groups (δ 64.5 ppm) and dimethylene ether links (δ 69.7 ppm) form at both pH 7 and 9, while an additional signal at δ 49.3 ppm, corresponding to the methylene bridge, is also observed at pH 7. Similarly, for the UF reactions, hydroxymethyl groups (δ 64.0 and 64.1 ppm) and dimethylene ether links (δ 70.1 ppm) are observed at pH 7 and 9, and methylene links (δ 49.4 ppm) are observed at pH 7 only.

When comparing UF and MF spectra to those of GF and eGF, the first observation to be made is the difference in methylene bridge formation between the systems at pH 7 and 9 (Fig. 5). Methylene bridges are known to form under more acidic conditions than ether bridges in MF resins; this is seen in the UF and MF systems, where methylene bridges (δ 49.4 ppm) are observed at pH 7 and absent at pH 9. For the GF and eGF systems not only did methylene bridges form at pH 9 (δ 49.4 and 58.1 ppm), but these were more apparent than those at pH 7.

The second observation to be made is that UF and MF reactions give fewer individual species with only one signal appearing in each of the hydroxymethyl (δ 61.4 ppm [UF] and 64.6 ppm [MF]), methylene (δ 49.4 ppm), and dimethylene ether regions (δ 70.1 ppm [UF] and 69.7 ppm [MF]), suggesting that under the present conditions it is most likely that only one substitution per $-NH_2$ group occurs. This is in contrast to results obtained during reactions of guanidine and ethylguanidine, where a large number of different products are formed in each region, determined by the presence of several ^{13}C-NMR signals of low intensity. This suggests the formation of crosslinked products, indicating that the initial guanidine products react further to form polymer networks.

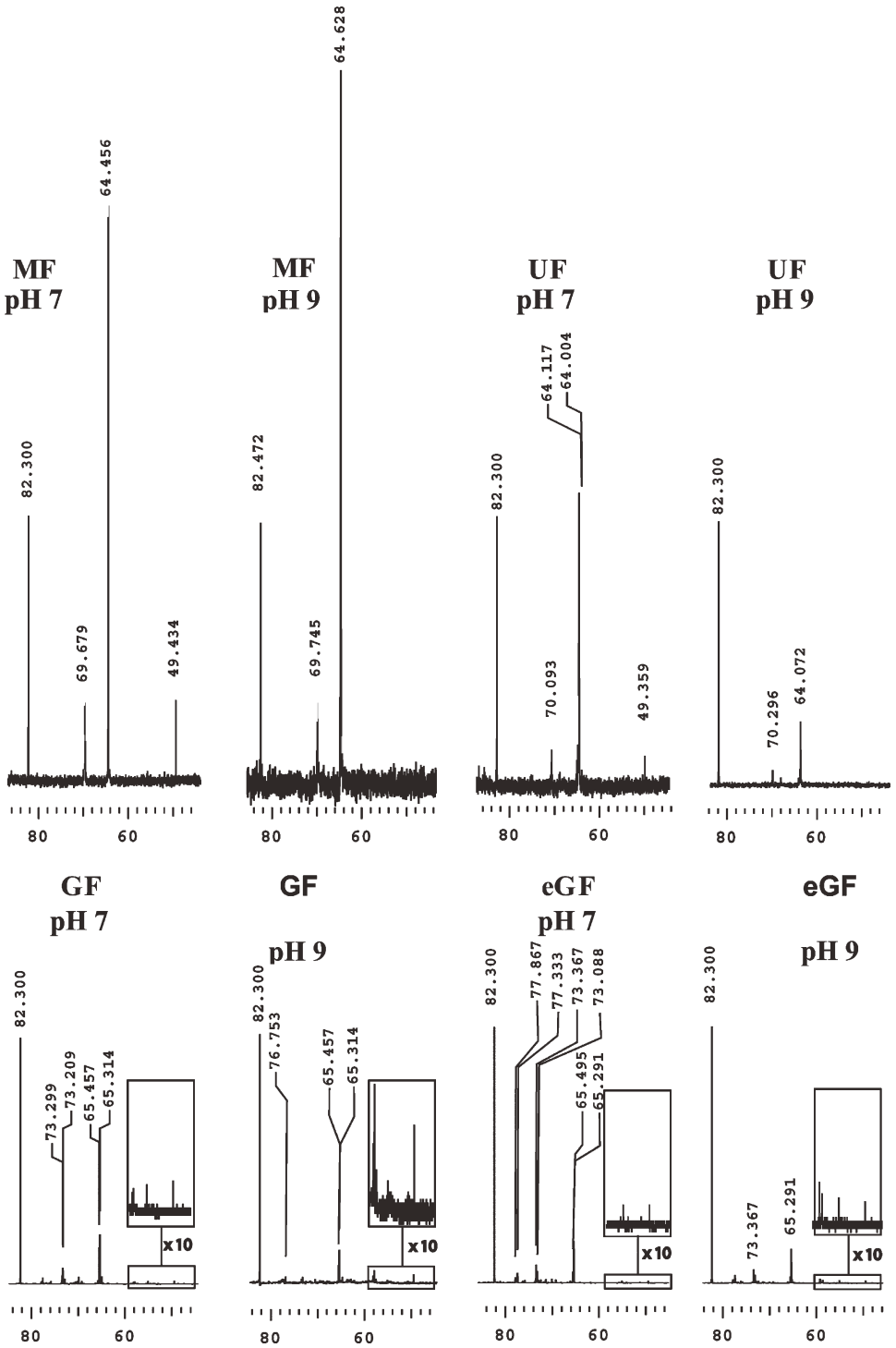


Figure 5 ^{13}C-NMR spectra of reaction products from melamine, urea, guanidine, or ethylguanidine and formaldehyde (5% formaldehyde, 20 min, 90°C, pH 7 and 9).

CONCLUSION

Guanidine and ethylguanidine react with formaldehyde and form hydroxymethyl derivatives as well as dimethylene–ether and methylene links. Using ^{13}C-NMR spectroscopy, polymer crosslinks in guanidine formaldehyde reactions have been directly identified and characterized. These are similar to species formed in commercially produced MF and UF amino thermosets. Therefore, when guanidine salts and/or soy proteins are added to thermosetting resins, the guanidine groups are presumably incorporated into the resin, thus affecting the properties of the resulting composite. Reactions were performed at pH 7 and 9 and changes in GF and eGF products

were observed, which demonstrated the potential to control the formation of polymers in guanidine reactions by pH. Products from UF, MF, GF, and eGF were then compared using NMR spectroscopy. The notable difference was that guanidine and ethylguanidine form methylene links at pH 9 and MF/UF reaction do not. This is of particular interest as it is known that methylene links do not degrade to formaldehyde and that they are more durable than their dimethylene–ether counterparts. It has been demonstrated that ^{13}C-NMR can be used to monitor structures of amino resins, including guanidine and ethylguanidine resins, enabling correlations between polymer structures and resin properties. The ability to control the formation of GF crosslinks, a major component of biobased adhesives, should result in the optimization of composite parameters such as durability.

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