Decreasing the Formaldehyde Emission in Urea-Formaldehyde Using Modified Starch by Strongly Acid Process

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ABSTRACT: The incorporation of the modified starch (MS) in urea-formaldehyde resins at different stage of the synthesis was studied in this article. The synthesized resins were characterized by Fourier transform infrared spectroscopy, indicating that the ester bond can be introduced into the UF structure after the addition of MS. The curing reactions were examined with differential scanning calorimetry and it reveals that curing temperature of UF resin are slightly shifted to higher temperatures. To study the bonding strength and formaldehyde emission of the bonded plywood, the addition method and amount of MS are systematically investigated. The performance of the UF resins is remarkably improved by the addition of MS around 15% (weight percentage of the total resin) in the second stage. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40202.

INTRODUCTION

Urea-formaldehyde (UF) resins adhesive is a polymeric condensation product of formaldehyde with urea, and is considered as one of the most important wood adhesives. Reason for this is their high reactivity, and good adhesion to wood, but essentially due to their low price compared with other adhesives.[1] However, the UF adhesives have an obvious disadvantage for the practical application because of the high emission of formaldehyde.[2] Emissions have two origins: unreacted formaldehyde and hydrolysis of UF linkages.[3] Costa et al.[4] also reported that decomposition of hexamine formed as by-product during cure also contributes for formaldehyde release during lifetime of board. The formaldehyde emission from the panel used interior application was one of the factors affecting sick buildings syndrome in an indoor environment. Therefore, for UF resins, it is quite significant to investigate an effective way to depress the amount of formaldehyde emission. During the last three decades, many literatures were published relating different forms to reduce formaldehyde emission. One of the common effective methods to decrease the formaldehyde content of resin is to change the mole ratio of formaldehyde to urea in UF resins. Several works declared that the emission of formaldehyde from panels lessened as the mole ratio decreases, the other physical and mechanical properties were adversely affected.[5–8] The other

method has been the use of chemical additives called formaldehyde scavengers to reduce formaldehyde emitted from wood based panels. The most common scavengers are compounds containing primary or secondary amine such as urea, ammonia, melamine, and dicyandiamide.[9] Other additives such as casein, tannin, resorcinol, peroxides, and ammonia had been proved to effectively suppress the formaldehyde emission from wood-based composite panel.[10–14] Unfortunately, these additives had not succeeded to be not only cheap but also efficient enough for modified the UF resins.

Starch has been widely used in industry for a long time, due to its low cost, biodegradability, and renewability,[15] and has already been reported as a modifying agent for improving adhesive performance.[16] Tondi et al.,[17]observed an adhesion synergy between sugar and starch in wood adhesion. The hydroxyl groups of starch are easily subjected to various types of reactions, such as oxidation, esterification, etherification, etc.[18,19] In particular, the oxidation of starch has been extensively investigated. Hydroxyl groups, primarily at C-2, C-3, and C-6 positions, are easily transformed to carbonyl and/or carboxyl groups by oxidation.[20,21] However, comparing with the studies of melamine, phenol, and polyvinyl acetate, there are few reports describing the investigation of oxidized starch to modify UF resins. Therefore, it is necessary to further extend the study on

Additional Supporting Information may be found in the online version of this article.

modification of UF resins by using modified starch (MS). The aim of this work was to improve the bonding performance of UF resins and decrease the formaldehyde emission of plywood made from the modified UF resins.

In this work, starch was modified by α-amylase, saccharifying enzyme, and hydrogen peroxide. The effect of MS addition during the synthesis of UF resins at different pH environments and their influence on the performance of plywood were also investigated. Structures and properties of the modified resins were characterized by using Fourier transform infrared spectroscopy (FTIR) and Differential scanning calorimetry (DSC). The modified UF resins were further applied as wood adhesives to prepare plywood. To study the bonding strength and formaldehyde emission of the bonded plywood, the influences of addition method and amount of MS for the modification were investigated in detail.

EXPERIMENTAL

Materials

Urea pellets, melamine, and Formaldehyde solution 37% were obtained from Guangdong Guanghua Chemical Factory. Corn starch (containing 12% moisture) was purchased from Changchun hongyuan Industries. Hydrogen peroxide (30%) was obtained from Guangdong Guanghua Chemical Factory. Saccharifying enzyme and α-amylase were purchased from Hunan Hongyingxiang biochemistry Industry. The optimal pH of the saccharifying enzyme and α-amylase were 4.0–4.5 and 6.0–6.5, respectively. The recommended temperature was 60–65°C, and 90–95°C, respectively. The enzyme activity of α-amylase was 20,000 units/g, and for the saccharifying enzyme was 50,000 units/g. All the other chemicals like formic acid, $CaCl_2$, NaOH, $MgSO_4$, and $NaSO_3$ were used as received at commercially analytical grade.

Preparation of the MS

A corn starch slurry (pH 6–6.5) containing 45% dry solid and $CaCl_2$ (0.1% based on the mass of dry starch) and α-amylase (0.2% based on the mass of dry starch) was prepared, the starch slurry was gradually heated to 95°C while stirring continuously, held at 95°C for 30 min, and then cooled to 65°C. The pH of starch slurry was adjusted to 4.5 using 20 wt % of formic acid solution. Saccharifying enzyme (0.2 wt % based on the mass of dry starch) was then added into the slurry, and held at 65°C for 60 min. After this process the starch slurry was heated to 80°C and the pH was adjusted to 8.5–9 by using 30 wt % of sodium hydroxide solution. Magnesium sulfate (0.1 wt % based on the dry starch) was added as a catalyst and hydroxide peroxide solution (6 wt % based on the dry starch) was added dropwise over a period of 15 min to the reaction mixture, and held at 80°C for 60 min, trace amount of sodium sulfite was added into the slurry to terminated the Oxidation reaction and then cooled to room temperature. Freshly prepared MS slurry was used in the following experiments.

Synthesis of the Modified UF Resins

The modified resins were synthesized by three steps as the following described.

- Step I: methylolation and condensation in strongly acid environment (below pH 2) at controlled temperature and urea feed rate until a desired F/U molar ratio is reached.
- Step II: second methylolation at slightly alkaline environment (pH8-8.5), with addition of a second urea at controlled feed rate until a desired F/U molar ratio is reached, and a low amount of melamine (0.3% based on total weight of liquid resin) is added for improving hydrolysis resistance.
- Step III: condensation at lightly acid environment (pH 4.5–5) is reached. The reaction proceeded until the viscosity of the resin reach about 150 mPa/s, after the desired viscosity being reached, the reaction was stopped by alkalinization with sodium hydroxide solution and the final urea was then added into the mixture, yielding a final F/U ratio of 1.5.

MS was employed as modifier and added via three different methods to investigate the influence of the MS for the performance of UF resins as shown in Table I. Three different amounts (10, 15, and 20% based on total weight of liquid resin) of MS was added into the reaction mixture. Meanwhile, another synthesized resin under the same condition without the addition of MS was defined as the blank UF resin for comparison.

For the sake of convenience, the samples with different addition methods and amounts are designated hereafter as UFX-Y, where X stands for addition method, such as I, II, and III, and Y means the percentage of addition amount, such as 10, 15 and 20. For example, in UFII-10, IImeans the MS was added by method II, and 10 means the addition amount of MS is 10% in the weight percentage of total liquid resin. Thus, the samples studied in this work can be expressed as UFI-10, UFII-15, UFIII-10, etc.

Preparation and Testing of Plywood

Eucalyptus veneers with dimensions of $320 \times 320 \times 2.1$ mm^3 were used to prepare 3-ply plywood panels. The as-synthesized UF resins were first mixed with 5 wt % ammonium chloride solution (20 wt %, aq.) and then applied to double sides of a veneer at a spread rate of 350 g/m^2 (for double gluelines). The adhesive-coated veneer was then stacked between two uncoated veneers with the grain directions of two adjacent veneers perpendicular to each other. Thereafter, the assembled veneers were pre-pressed (pressure, 1 MPa) at room temperature for 1 h. After that, the pre-pressed veneers were hot-pressed at 120°C at the same pressure of 1 MPa. The thickness-dependent pressing time was applied for this process at 1 min/mm. The specimens were maintained at room temperature, for 24 h, sawn to get samples for the test of bonding strength and formaldehyde emission desiccator method, respectively, according to National Standard of Peoples' Republic of China GB/T 17657-1999.[22] The testing specimen was shown in Figure 1.

Table I. Different Addition Method of MS During UF Synthesis

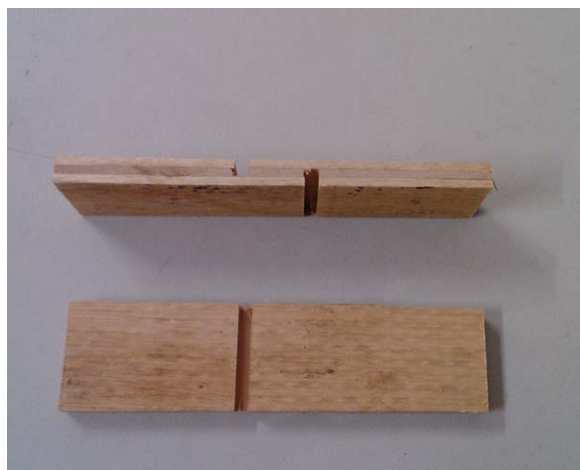| Code	Method
I	Added at the beginning of Step I
II	Added at the beginning of Step II
III	Added at the beginning of Step III

Figure 1. Testing Specimen. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Bonding Strength of Plywood

The bonding strength of plywood was measured by using a universal material testing equipment (CMT 4304 from Shenzhen, Xinsansi Material Testing).The three-layer plywood was cut into 25×100 mm of specimens with a notch of 20×25 mm in each piece. These specimens were merged into $63 \pm °C$ water for 3 h, and then cooled to room temperature for 10 min before measurement. The measurement was carried out in tension mode with the test loading speed of 10 N/mm^2. Twenty specimens were tested for each sample and the results were averaged.

Formaldehyde Emission

After the produced plywood was cooled down to room temperature, the three-layer plywood was immediately cut into 10 specimens with three-dimensional size of $10 \times 50 \times 150$ mm^3. Within 30 min after production, these samples were put into a 10 L of covered glass desiccators together with a petri dish filled with a specified amount of deionized water. The formaldehyde emission test lasted 24 h under 20°C. The emitted quantity of formaldehyde was obtained from the concentration of formaldehyde absorbed in the water by using a spectrometer based on the Hantzsch reaction, in which the formaldehyde can react with ammonium acetate and acetylacetone and the yield of diacetyldihydrolutidine was quantified by evaluating the characteristic UV peak centered at 412 nm.

Resin Characterization

The transmission FTIR spectra of samples were measured by a Perkin Elmer model Spectrun V10 instrument. Each spectrum was recorded in a frequency range of 400–4000 cm^{-1} using potassium bromide (KBr) disc. Thirty-two scans were accumulated with a resolution of 4 cm^{-1}. Discs were prepared by first mixing 1 mg of cured resins with 100 mg of KBr. The cured resins were prepared by drying the liquid resins in a convection oven at 120°C for 2 h.

DSC measurements were conducted on a NETZSCH 204 F1 differential scanning calorimeter. Dynamic scans were conducted in a temperature range of 25–150°C, at constant heating rate of 10°C/ min, under nitrogen atmosphere at a flux rate of 50 mL/min.

A freeze-dried sample of 6 mg was used in an aluminum crucible of 40 μL.

RESULT AND DISCUSSION

Properties of Plywood Bonding by Modified UF Resins

Plywood was prepared by using the synthesized UF resins serving as adhesives. The influences of addition methods as well as the amount of MS on the bonding strength of prepared plywood are compared in Figure 2. For all types of the modified resins, the plywood prepared by method I shows the worst bonding strength than that of blank UF resin, which is labeled as the dash line in Figure 2. The reason may be because at method I formaldehyde, which was supposed to offer the crosslink, was consumed by the reaction with glucose as shown in Figure 3.[23] The plywood made from resins prepared via method II and method III showed comparable bonding strength to that of blank UF resin. The bonding strength prepared by method II and method III with the addition amount of MS from 10 to 15% is superior to that of blank UF resin, which may be due to the introduction of the MS into the polymer chain of UF resins. From Figure 2, we can know that the UF resins made by method II and method III all have better result of bonding strength up to the standard of 0.7 MPa from National Standard of People's Republic of China GB/T9846-2004.[24] And all the resins prepared by different methods followed the same trend, the maximum bonding strength was reached at 15% additional amount and when the addition of MS increase to 20 wt % (based on total weight of liquid resin), the bonding strength of plywood was dropped down. The declining bonding strength is probably due to the exceeded hydroxyl content, which resulted in the decreasing water resistance of the prepared plywood.

Except for the bonding strength, formaldehyde emission is another important parameter for the practical application of plywood bonded by UF adhesives. The results of formaldehyde emission of plywood made from modified UF resins were listed in Table II. Meanwhile, the formaldehyde emission of plywood made from blank UF resin is 4.3 mg/L. As shown in Table II, all the UF resins made by different methods have lower
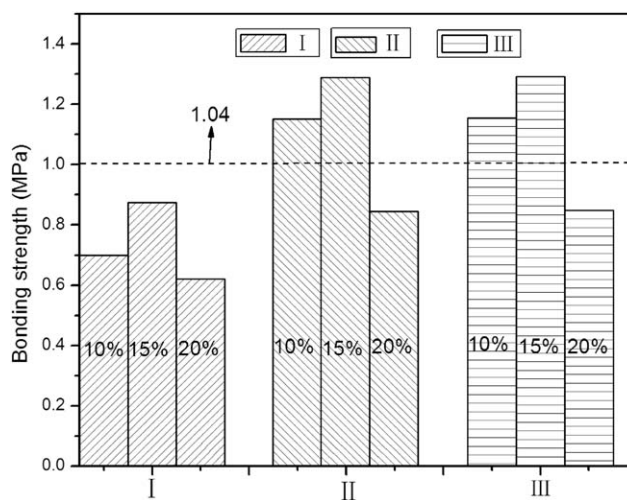

Figure 2. Bonding strength of plywood made from UF resins synthesized by different addition method with different MS addition amount.
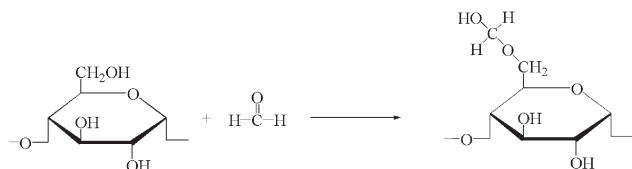
Figure 3. The reaction between glucose and formaldehyde.

formaldehyde emission than that of blank UF. This indicated that no matter when the MS added into the UF resins, the MS played a role in reducing formaldehyde emission. Moreover, with the same additional amount, UFII-15 and UFII-20 showed the lower formaldehyde emission, which may be due to the reaction between carboxyl and the methylolurea in step II. The plywood made from method III showed the highest formaldehyde emission, indicated that in this stage fewer dimethylolurea or formaldehyde reacted with the MS. As can be seen from Table II, when increase the additional amount of MS to 20%, the formaldehyde emission increase at the same time. This phenomenon may be because when increase the amount of MS, more MS may react with urea or hinder the reaction between urea and formaldehyde and this may cause more free formaldehyde remain in the resin, which could lead to a higher formaldehyde emission.

FTIR Analysis

FTIR spectra ($4000–400$ cm^{-1}; $1800–700$ cm^{-1}) of MS, UF, UFI-15, UFII-15, and UF III-15 were shown in Figures 4 and 5, respectively. For MS, a typical spectrum enclosed absorption bands at 3435 cm^{-1}, revealing the O—H stretching vibration of OH groups in the glucose units, and the peaks at 1450 and 1370 cm^{-1} ascribe to the C—H stretching and bending modes of the methylene.[25] The peaks at 1080 and 1020 cm^{-1} reflect the stretching mode of C—O—C linkages in the glucosidic rings.[26] The spectrum of the MS exhibit a characteristic peak at 1600 cm^{-1}, which is due to the asymmetric stretching of COO^- in carboxylate groups absorbing.[25] FTIR spectra of the four samples at different reaction stages with the same amount of MS and the blank UF are also compared in Figures 4 and 5. The broad band may be attributed to monomers such as water, formaldehyde, and glucose, whose O—H group may form hydrogen bonds with reactive functional groups as CH_2OH, NH_2, and NH. The small peaks at the area of $1320–1450$ cm^{-1} can be assigned to stretching C—N vibrations of amide I and II.[27] In the area of $1600–1650$ cm^{-1} multiple and some overlapped peaks appear in the spectra of the four UF resins. These are assigned to the C=O stretching of amide I and II, as well as the N—H scissors of amide I. The overlapped peaks at the area
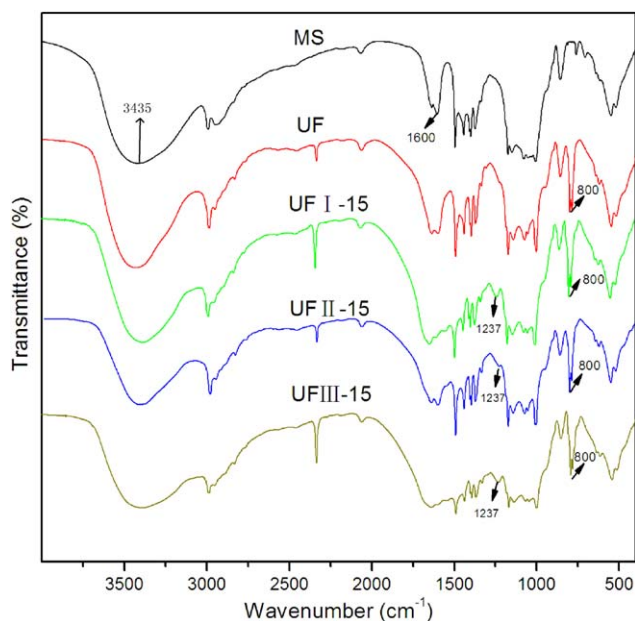

Figure 4. FTIR transmittance spectra ($4000–400$ cm^{-1}) of MS, UF, UFI-15, UFII-15, and UF III-15. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$1500–1600$ cm^{-1} are attributed to N-H bending vibrations of amide II.[27] From these two areas, we can find some differences among these four UF resins, which may be due to the reaction between COOH and N—H or N—H₂. From the spectra of UF, UFI-15, UFII-15, and UF III-15, we can clearly see there is a characteristic peak at 800 cm^{-1}, which is due to the C—O—C stretching vibrations in uron.[28] And after compared these four resins spectra with each other, we find one new peak 1237 cm^{-1} appear in the spectra of UFI-15, UFII-15, and UF III-15, which is due to the C—O—C asymmetrical stretching vibration in ester groups. The ester bond may be formed by the reaction
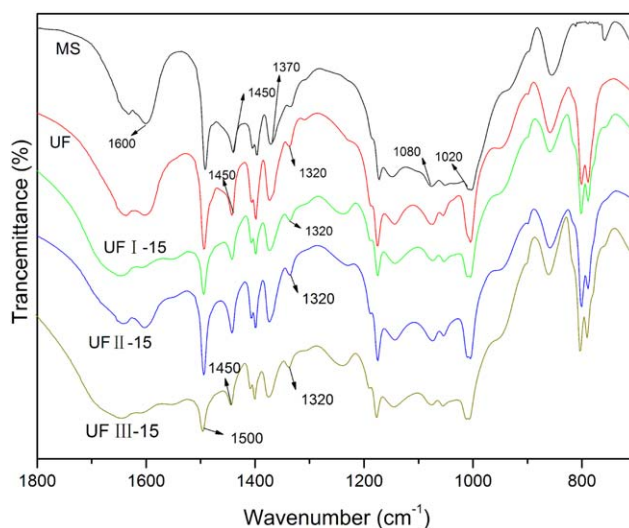
Table II. Formaldehyde Emission of Plywood Made from Modified UF Resins

Addition	UF (mg/L)	I (mg/L)	II (mg/L)	III (mg/L)
0	4.30	–	–	–
10%	–	1.05	1.69	1.72
15%	–	1.52	1.21	2.12
20%	–	1.71	1.42	2.53

Figure 5. FTIR transmittance spectra ($1800–700$ cm^{-1}) of MS, UF, UFI-15, UFII-15, and UF III-15. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
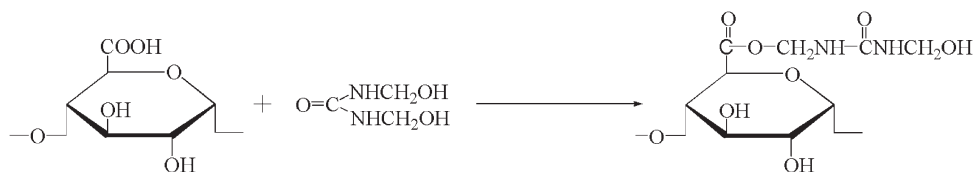
Figure 6. Reaction between ─COOH on glucose and the ─OH on dimethylolurea.

between the ─COOH on glucose and the ─OH on dimethylolurea, which is shown in Figure 6.

DSC Analysis

The DSC curves of UF, UFI-15, UFII-15, and UF III-15 are presented In Figure 7. It revealed that all resins follow the same curing trend, for the blank UF resin, the maximum peak temperature was recorded at 110°C, while for the other UF hybrids that peak was slightly shifted to higher temperatures. The UFI-15 showed the peak temperature at 116°C, and the peak temperature for UFII-15 and UF III-15 was 120 and 116.2°C, respectively. Although the shift is considered rather small, we can say that this is an indication that MS hinder the cross linking reactions of UF resins. The reason could be because some functional groups like hydroxyl and carboxyl in MS interact with the polymer chain, possibly by forming bonds with it or participate in the condensation reactions and thus, in both case the polymer chain needs more energy in order to crosslink. As can be seen from Figure 7, the UFII-15 showed the highest curing temperature,which may be because when the MS added in method II the UF chain can be more open to the functional groups like carboxyl and hydroxyl in glucose ring. When more functional groups in glucose ring were introduced into the polymer chain, it needed more energy to finish the process of curing, so the curing temperature increased at the same time. The XRD spectra of four samples are also showed in the Supporting Information, which do not show large differences between the different resins.
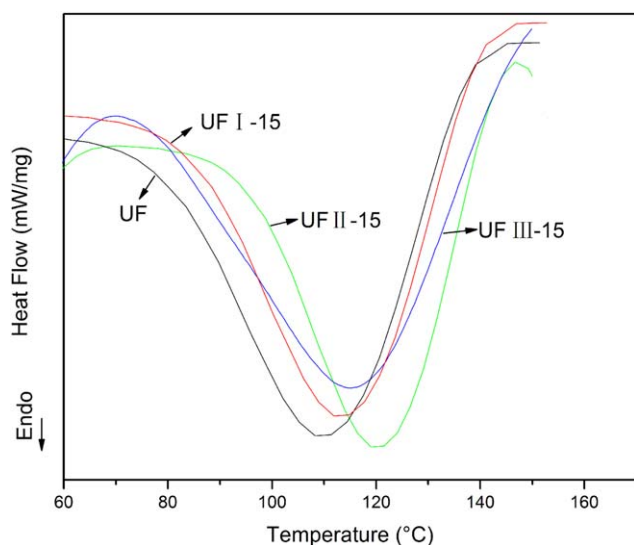

Figure 7. DSC curves of UF, UFI-15, UFII-15, and UF III-15. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSION

The ultimate goal of the MS addition is to improve the properties of the UF resin. In this particular work, UF resins were modified by using MS during the synthesis of UF resins at different pH environments. The MS with some functional groups such as carboxyl, hydroxyl, etc., can react with the UF resins, which was verified from FTIR spectroscopy. This was also verified from DSC analysis since the peak curing temperature was found to be slightly higher than that of the blank UF resin, which implies the formation of bonds between the MS and the polymer chain in UF resins. With the plywood prepared by the resins adhesives, the influence of the addition method and the amount of MS used in modification on the bonding strength as well as the formaldehyde emission of the plywood were investigated. The best way to introduce MS into UF resins is adding MS in the methylolation stage. With the increasing addition amount of MS, the bonding strength of plywood first improved and then decreased, and a maximum value was observed at the addition amount of 15% in the weight percentage of the total resin. The formaldehyde emission of plywood was decreased significantly with the addition of MS. Considering the cost and performance, method I with 10% of MS, method II with 10 and 15%, and method III with 10% are all the effective way to improve the resin properties. The 15 and 10% of MS (in the weight percentage of the total resin) added in the UF resin by method IIcan improve the bonding strength of plywood to 1.28 and 1.17 MPa, respectively, and decrease the formaldehyde to 1.21 and 1.69 mg/L, respectively, which is 1.04 MPa and 4.3 mg/L of the corresponding value of the blank UF resin, respectively. Since the industry requires compromises between the best performance and the lowest cost, the results of this study are considered satisfactory. From this work, it has been shown that MS are promising materials for the improvement of the UF resin performance and so, further studies to this direction are worthwhile.

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