Preparation of Novel Melamine-Urea-Formaldehyde Resin—MUF Post-Print Preparation Using High-Concentration Formaldehyde and Soy Protein Hydrolysate

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Abstract

Melamine-urea-formaldehyde (MUF) resin was synthesized using melamine, high-concentration formaldehyde, urea, and soy protein isolate (SPI) hydrolysate as raw materials. The properties of the modified MUF were compared, and the structural changes and thermomechanical properties were analyzed using carbon-13 nuclear magnetic resonance (13C-NMR), Fourier transform infrared spectroscopy (FT-IR), and dynamic mechanical analysis (DMA). The results showed that MUF synthesized with high-concentration formaldehyde exhibited a 52% reduction in free formaldehyde, while the internal bond strength and modulus of rupture of the prepared particleboard increased by 25% and 64%, respectively. MUF synthesized with high-concentration formaldehyde and SPI hydrolysate showed a 56% decrease in free formaldehyde, with the internal bond strength and modulus of rupture of the prepared particleboard increasing by 48% and 97%, respectively. FT-IR analysis indicated that a crosslinking reaction occurred between the protein hydrolysate and the MUF resin. 13C-NMR and DMA results demonstrated that the MUF resin prepared with high-concentration formaldehyde possessed a high methylene ether bond content and a high degree of polycondensation, conferring very high initial strength but poor thermal stability. The MUF resin prepared with high-concentration formaldehyde and SPI hydrolysate exhibited a high degree of polycondensation, with significantly increased methylene bridge bond content, which could partially offset the instability caused by ether bond cleavage and rearrangement at high temperatures, endowing the resin with high thermomechanical properties, thermal stability, and low free formaldehyde.

Full Text

Preamble

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Synthesis of a New Melamine-Urea-Formaldehyde Resin–Preparation of MUF with Degradated Liquid of Soy-Protein and Concentrated Formaldehyde

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Abstract

A new melamine-urea-formaldehyde (MUF) resin was prepared using melamine, concentrated formaldehyde, urea, and degradated liquid of soy protein isolate (SPI) as raw materials. The performance of modified MUF was compared, and structural changes and thermo-mechanical properties were analyzed using ^{13}C-NMR, FT-IR, and DMA. The results show that MUF synthesized with concentrated formaldehyde alone reduced free formaldehyde by 52%, while the internal bond strength and modulus of rupture (MOR) of prepared particleboard increased by 25% and 64%, respectively. MUF synthesized with both concentrated formaldehyde and SPI degradated liquid reduced free formaldehyde by 56%, with internal bond strength and MOR increasing by 48% and 97%, respectively. FT-IR analysis confirmed that the protein degradated liquid underwent crosslinking reactions with the MUF resin. ^{13}C-NMR and DMA results indicated that MUF resin prepared with concentrated formaldehyde contained higher amounts of methylene ether bonds, exhibited high condensation degree, and possessed high initial strength but poor thermal stability. In contrast, MUF resin prepared with concentrated formaldehyde and SPI degradated liquid showed higher condensation degree and significantly elevated methylene bridge bond content, which could partially offset the instability caused by ether bond cleavage and rearrangement at high temperatures, endowing the resin with superior thermo-mechanical properties, thermal stability, and lower free formaldehyde content.

KEY WORDS organic polymer materials, melamine-urea-formaldehyde resin, high concentration formaldehyde, soy protein, structure characteristics, thermal mechanical properties

1. Experimental

1.1 Materials

Soy protein isolate (SPI, protein content 90%); formaldehyde (37%, analytical grade); concentrated formaldehyde (50% formaldehyde content); mixed wood particles (moisture content 5%); other chemical reagents such as NaOH and urea (all analytical grade).

1.2 Degradation of Soy Protein and Performance Testing

A round-bottom three-neck flask equipped with a mechanical stirrer, thermometer, and condenser was charged with 150 g of a 9% (mass fraction) solution. After heating to 90°C, 84 g of soy protein isolate was added and the reaction was maintained for 3 hours before cooling and discharging, yielding a tea-brown transparent liquid. The SPI degradated liquid had a solid content of 36% and a viscosity of 32.5 mPa·s.

1.3 Preparation of SPI-Degradated Liquid Modified MUF Resin

In a round-bottom three-neck flask equipped with a mechanical stirrer, thermometer, and condenser, 97.8 g of concentrated formaldehyde was added at room temperature. The pH was adjusted to 9.2, and the temperature was raised to 50°C. The first addition of urea (U_1) 37.6 g and a specific proportion of SPI degradated liquid was made, followed by the first addition of melamine (M_1) 5.95 g. The temperature was increased to 92°C, pH adjusted to 5.2-5.3, and the reaction continued until the viscosity reached 90 mPa·s. The pH was then adjusted to 8.7-8.9, and the temperature was reduced to 86-88°C. When the pH dropped to 8.0-8.5, the second addition of melamine (M_2) 34.725 g was made. The reaction was maintained until water miscibility reached 100%, then the pH was immediately adjusted to 9.0 and cooling commenced. At 45°C, the second addition of urea (U_2) 8.55 g was made, and the product was discharged and stored at pH 8-8.5.

The modified melamine-urea-formaldehyde resins prepared with SPI degradated liquid additions of 0%, 5%, 10%, and 20% were designated as HMUF0, S1HMUF, S2HMUF, and S3HMUF, respectively. Using the same method, a melamine-urea-formaldehyde resin was prepared with conventional formaldehyde at the same molar ratio and designated as MUF0.

Viscosity, solid content, pH value, and free formaldehyde content of the adhesives were determined according to the methods specified in national standard GB/T 14074-2006.

1.4 Particleboard Preparation and Performance Testing

Single-layer particleboards with dimensions of 350$×310×10*mmwerepreparedusingsprayapplicationat*10^{2}$ temperature of 140°C, and pressing time of 8 minutes. After surface sanding, dry internal bond strength and other properties were measured according to GB/T 17657-1999.

1.5 Characterization Methods

^{13}C-NMR Analysis: Performed on a Bruker Avance high-resolution superconducting NMR spectrometer. Sample preparation: 300 mL of deuterated dimethyl sulfoxide (DMSO-d_6) was used as solvent, with 300 mL of sample injected into the NMR tube and mixed uniformly. Measurement parameters: pulse sequence zgig, internal standard DMSO-d_6, accumulation times 500-800, spectral width 39062.5 Hz.

FT-IR Analysis: Conducted on a Varian 1000 Fourier transform infrared spectrometer using KBr pellet method, scanning range 400-4000 cm^{-1}, 32 scans.

DMA Analysis: Performed on a NETZSCH DMA-242 instrument with NETZSCH Proteus software. Three-point bending mode was used with heating rate of 5 K/min, temperature range 40-300°C, frequency 50 Hz, and dynamic force 1.5 N. Poplar wood specimens (50 mm$×10*mm*×$3 mm) were used with adhesive application of 0.125 g.

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2. Results and Discussion

2.1 Degradation of SPI and Modification Mechanism of MUF

Soy protein molecules possess a spherical structure with numerous hydrophobic and active groups hidden inside. Only by degrading the globular protein and exposing these hydrophobic and active groups can active sites be generated. Soy protein contains various amino acids, and formaldehyde can react with amino groups at the ends of amino acid chains, such as the amine groups of glycine, lysine, histidine, and arginine. The degradation schematic of soy protein is shown below, using glycine as an example:

During MUF preparation, multiple reactions occur after adding SPI degradated liquid: (1) reaction between SPI degradated liquid and formaldehyde; (2) hydroxymethylation reaction between urea and formaldehyde; (3) reaction between hydroxymethyl urea and melamine; (4) reaction between hydroxymethyl protein and melamine.

The crosslinking reaction between SPI degradated liquid and melamine-urea-formaldehyde forms sufficient chemical bonds and a compact skeleton, which improves the bonding strength of the resin. Moreover, introducing degradable soy protein structures into the final crosslinked molecular network enhances biodegradability when the material is discarded and buried in soil through microbial action.

2.2 Physicochemical Properties of SPI-Modified MUF

presents the basic properties of melamine-urea-formaldehyde resin prepared with conventional formaldehyde (MUF0), concentrated formaldehyde (HMUF0), and concentrated formaldehyde with SPI degradated liquid (S1HMUF, S2HMUF, S3HMUF). Compared with MUF0, HMUF0 showed significantly increased viscosity and solid content, with free formaldehyde content decreasing from 0.136% to 0.066% (a 52% reduction). The internal bond strength and modulus of rupture of particleboard increased by 25% and 64%, respectively. According to chemical equilibrium principles, increasing formaldehyde concentration promotes the forward reaction, leading to more complete reactions, higher condensation and crosslinking degrees, thus consuming more formaldehyde and reducing residual free formaldehyde while improving resin strength.

Further modification was conducted by adding SPI degradated liquid to HMUF0. When 10% SPI degradated liquid was added, S2HMUF exhibited the best performance. Compared with MUF0, S2HMUF reduced free formaldehyde content by 56% and increased internal bond strength and modulus of rupture by 48% and 97%, respectively. This is because degraded soy protein becomes a mixture of amino acids and polypeptides with exposed active groups, and 10% addition maximizes crosslinking with MUF. However, excessive addition results in low-molecular-weight SPI degradated liquid existing independently in MUF, which deteriorates performance.

2.3 ^{13}C-NMR Analysis

Using methanediol at 83 ppm as the reference peak, all absorption peaks were integrated, and the sum of all methylene carbon integration areas was calculated. The ratio of each chemical bond's integration value to the total methylene carbon integration value represents the percentage content of each methylene carbon type. Based on conclusions from Section 2.1, quantitative NMR analysis was performed on MUF0, HMUF0, and S2HMUF. The ^{13}C-NMR spectra are shown in [Figure 1: see original paper], [Figure 2: see original paper], and [Figure 3: see original paper], respectively, with quantitative analysis results listed in .

According to the peak assignments in Table 2, in the ^{13}C NMR spectrum, hydroxymethyl groups in hydroxymethylated products correspond to chemical shifts at 63-65 ppm. Peaks at 54-56 ppm and 46-48 ppm are primarily methylene bridge bonds, while methylene ether bonds appear mainly at 67-70 ppm. Absorption peaks at 74-75 ppm and 77-78 ppm are attributed to methylene ether bonds generated from co-condensation reactions between melamine and urea, which can also serve as characteristic absorption regions for co-condensation reactions.

Hydroxymethyl groups are the foundation for molecular chain growth and crosslinking reactions in resins. The hydroxymethyl content in the final product reflects the degree of resin condensation. Higher hydroxymethyl content indicates more thorough addition reactions, while higher proportions of methylene bridge and ether bonds result from hydroxymethyl consumption during the reaction. Higher methylene bridge and ether bond proportions indicate deeper condensation and higher resin strength.

MUF0 contained 49.6% hydroxymethyl, 16.4% methylene bridge, 18.5% methylene ether, and 10.5% methylene ether from melamine-urea co-condensation. HMUF0 contained 44.1% hydroxymethyl, 12.7% methylene bridge, 28.3% methylene ether, and 10.8% from co-condensation. The total methylene bridge-ether bond contents were 34.9% for MUF0 and 41% for HMUF0, indicating that MUF prepared with concentrated formaldehyde had higher condensation degree. This also explains why HMUF0 consumed more formaldehyde and had lower residual free formaldehyde, consistent with experimental results. High-concentration formaldehyde affects UF resin condensation degree; increased formaldehyde concentration accelerates reaction rate and polycondensation, raising ether bond content and condensation degree, thereby improving bonding strength—precisely why HMUF0 showed significantly increased internal bond strength and modulus of elasticity.

However, MUF resin prepared with concentrated formaldehyde contains substantial ether bonds that affect service performance. Therefore, SPI degradated liquid was added during HMUF0 preparation for modification. S2HMUF contained 48.0% hydroxymethyl, 19.0% methylene bridge, 27.8% methylene ether, and 3.4% from co-condensation. The total methylene bridge-ether bond content of S2HMUF was 46.8%, higher than HMUF0. Consequently, S2HMUF exhibited higher strength than HMUF0, and the significantly increased bridge bond content helped improve thermal stability.

Combined with the strength data, MUF resin prepared with concentrated formaldehyde and SPI degradated liquid showed significantly improved condensation degree and bridge bond content, thereby enhancing mechanical properties and reducing free formaldehyde content.

2.4 FT-IR Analysis

Based on literature [23-26], the functional group assignments for melamine-urea-formaldehyde resin absorption peaks are: 3300-3500 cm^{-1} for N-H stretching vibration, 1660 cm^{-1} for C=O vibration, 1553 cm^{-1} for N-C=N bending and ring deformation in triazine ring, 1372 cm^{-1} for -CH$_2$ bending vibration, 1257 cm^{-1} for CH$_3$O- asymmetric stretching, 1130 cm^{-1} for C-O-C symmetric stretching, ~1000 cm^{-1} for strong -CH$_2$OH absorption (C-O stretching in hydroxymethyl and N-H rocking), 900 cm^{-1} for C-H deformation between C in triazine ring and adjacent external H, 815 cm^{-1} for characteristic out-of-plane ring vibration of melamine, and ~770 cm^{-1} for C-H deformation in amide.

[Figure 4: see original paper] shows FT-IR spectra of MUF0, HMUF0, and S2HMUF resins, with essentially consistent peak shapes. However, S2HMUF shows that the amide characteristic absorption bands at 1530-1600 cm^{-1} and 1600-1630 cm^{-1} changed from distinct double-shoulder peaks to single-shoulder peaks, indicating increased protein groups. This suggests that free amino and carboxyl groups of proteins underwent crosslinking reactions with the melamine-urea-formaldehyde resin.

2.5 DMA Analysis

[Figure 5: see original paper] presents DMA results for MUF0 prepared with conventional formaldehyde, HMUF0 prepared with concentrated formaldehyde, and S2HMUF prepared with 10% SPI degradated liquid and concentrated formaldehyde, all with 1% ammonium chloride.

DMA analysis can simulate the hot-pressing process of wood-based panels and reflect resin curing behavior. As temperature increases, resin fluidity gradually improves and elastic modulus begins to decrease. At approximately 100°C, HMUF0 began curing earlier than MUF0 and S2HMUF, with elastic modulus increasing rapidly. As crosslinking progressed and molecular chains grew, storage modulus increased rapidly, reaching maximum values within a short temperature range (HMUF0 > S2HMUF > MUF0).

MUF0, HMUF0, and S2HMUF showed modulus changes starting at 128°C, 115°C, and 115°C, respectively. HMUF0 exhibited the largest modulus variation, followed by S2HMUF, while MUF0 showed relatively stable curves. MUF0 had relatively low methylene ether content and condensation degree, resulting in good thermal stability but low strength. HMUF0 contained more methylene ether bonds, which were unstable during heating, macroscopically manifested as large modulus changes. However, at the same temperature throughout the heating process, HMUF0' s elastic modulus remained higher than MUF0' s.

The reason is that S2HMUF resin had higher condensation and crosslinking degrees, ensuring sufficient mechanical strength. Although S2HMUF also contained relatively high ether bonds, whose cleavage and rearrangement caused some modulus changes with temperature, the relatively high bridge bond content could partially offset the instability from ether bond cleavage, macroscopically showing smaller modulus changes than HMUF0.

These results demonstrate that MUF resin prepared with concentrated formaldehyde has high initial strength but poor stability. MUF resin prepared with concentrated formaldehyde and SPI degradated liquid exhibits high thermo-mechanical performance and thermal stability.

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3. Conclusions

Melamine-urea-formaldehyde (MUF) resin can be synthesized using melamine, concentrated formaldehyde, urea, and soy protein isolate (SPI) degradated liquid as raw materials. MUF resin prepared with concentrated formaldehyde increased particleboard internal bond strength and modulus of rupture by 25% and 64%, respectively, while reducing free formaldehyde by 52%. MUF resin prepared with concentrated formaldehyde and SPI degradated liquid increased internal bond strength and modulus of rupture by 48% and 97%, respectively, while reducing free formaldehyde by 56%. The protein degradated liquid underwent crosslinking reactions with the MUF resin. MUF prepared with concentrated formaldehyde contained high methylene ether bond content and high condensation degree, resulting in high initial strength but poor thermal stability. MUF prepared with concentrated formaldehyde and SPI degradated liquid exhibited high condensation degree and significantly increased methylene bridge bond content, which could partially offset the instability from ether bond cleavage and rearrangement at high temperatures, endowing the resin with high thermo-mechanical performance, thermal stability, and low free formaldehyde content.

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