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STRUCTURAL AND THERMAL CHARACTERIZATION OF HYDRAZINE SULFATE-MODIFIED UREA-FORMALDEHYDE RESINS

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Abstract. This study focuses on the structural characterization and thermal degradation behavior of eco-friendly urea-formaldehyde resins (UFR) modified with hydrazine sulfate ($N_2H_6SO_4$). The chemical framework, cross-linking dynamics, and thermal stability of the modified resins were investigated using Raman spectroscopy and thermogravimetric analysis coupled with differential thermal analysis (TGA/DTA). Raman spectroscopic analysis confirmed the successful incorporation of hydrazine sulfate into the polymer matrix through characteristically intensified bands corresponding to symmetric framework vibrations, C-N linkages, and sulfate group interactions. Thermogravimetric investigations revealed a four-stage thermal degradation process, demonstrating enhanced thermal stability with an elevated initial decomposition temperature and a prominent exothermic peak at 284.74 °C. The synergistic evaluation of Raman and TGA data confirmed that hydrazine sulfate acts not only as an efficient formaldehyde scavenger but also as a structural reinforcing agent that significantly improves the thermal resistant network of UFR-based adhesives.

Keywords: Urea-formaldehyde resin, hydrazine sulfate, modification, Raman spectroscopy, thermogravimetric analysis (TGA/DTA), thermal stability, cross-linking network.

Annotatsiya. Mazkur tadqiqot gidrazin sulfat ($N_2H_6SO_4$) bilan modifikatsiyalangan ekologik xavfsiz karbamid-formaldegid smolalarining strukturaviy tavsifi hamda termik

parchalanish xususiyatlarini o'rganishga bag'ishlangan. Modifikatsiyalangan smolalarning kimyoviy karkasi, polimerizatsiya darajasi va termik barqarorligi Raman spektroskopiyasi hamda differensial termik tahlil bilan birga olib borilgan termogravimetrik tahlil (TGA/DTA) yordamida tadqiq qilindi. Raman spektroskopiyasi tahlillari karkasning simmetrik tebranishlari, C-N bog'lanishlari hamda sulfat guruhlarining o'zaro ta'sirlariga mos keluvchi cho'qqilar intensivligining ortishi orqali gidrazin sulfatning polimer matritsasiga muvaffaqiyatli birikkanligini tasdiqladi. Termogravimetrik tahlil natijalari to'rt bosqichli termik parchalanish jarayonini hamda 284.74 °C dagi aniq ekzotermik cho'qqi va yuqori dastlabki parchalanish harorati bilan xarakterlanuvchi oshirilgan termik barqarorlikni ko'rsatdi. Raman va TGA ma'lumotlarining birgalikdagi tahlili gidrazin sulfat nafaqat samarali formaldegid biriktiruvchisi (skavenger), balki KFS asosidagi yelimlarining termik chidamli karkasini sezilarli darajada mustahkamlovchi agent sifatidagi rolini isbotladi.

Kalit so'zlar: Karbamid-formaldegid smolasi, gidrazin sulfat, modifikatsiya, Raman spektroskopiyasi, termogravimetrik tahlil (TGA/DTA), termik barqarorlik, polimer karkasi.

Аннотация. Данное исследование посвящено структурной характеристике и термическому разложению экологически безопасных мочевино-формальдегидных смол, модифицированных сульфатом гидразина ($N_2H_6SO_4$). Химический каркас, степень сшивки и термическая стабильность модифицированных смол были изучены с помощью комбинационного рассеяния света (Рамановской спектроскопии) и термогравиметрического анализа, совмещенного с дифференциальным термическим анализом (ТГА/ДТА). Рамановская спектроскопия подтвердила успешную интеграцию сульфата гидразина в полимерную матрицу за счет характерного усиления полос, соответствующих симметричным колебаниям каркаса, C-N связям и взаимодействия сульфатных групп. Термогравиметрический анализ выявил четырехстадийный процесс термической деструкции, продемонстрировав повышенную термостойкость с более высокой температурой начального разложения и выраженным экзотермическим пиком при 284.74 °C. Совместный анализ данных Рамановской спектроскопии и ТГА подтвердил, что сульфат гидразина выступает не только в роли эффективного акцептора формальдегида, но и в качестве структурирующего агента, существенно укрепляющего термостойкую сетку клеев на основе мочевино-формальдегидных смол.

Ключевые слова: Мочевино-формальдегидная смола, сульфат гидразина, модификация, Рамановская спектроскопия, термогравиметрический анализ (ТГА/ДТА), термическая стабильность, полимерная сетка.

Introduction. Urea-formaldehyde resins (UFR) remain among the most widely utilized thermosetting adhesives in the wood-based panel industry due to their high reactivity, excellent adhesion performance, and cost-effectiveness. However, traditional UFR systems suffer from critical limitations, including susceptibility to hydrolytic degradation, low water resistance, and the continuous emission of toxic free formaldehyde. To address these environmental hazards and structural drawbacks, extensive research has focused on introducing chemical scavengers and bio-based nanomaterials into the resin matrix.

Recently, Deng et al. [1] demonstrated that modifying UFR with nanocrystalline cellulose (NCC) and nanofibrillated cellulose (CNF) significantly reorganizes the hydrogen-bonding network and enhances cross-linking density. Their comprehensive evaluation via FTIR, XRD, DSC, TGA, and SEM showed that CNF superiorly improved thermal stability, water-resistant bonding strength (up to 1.13 MPa), and reduced free formaldehyde content to 0.14%, lowering plywood emissions to 0.35 mg/L.

While nanocellulose provides effective physical reinforcement, chemical modifiers such as hydrazine sulfate ($N_2H_6SO_4$) enable direct chemical scavenging of unreacted formaldehyde while forming highly stable cross-linked networks. To thoroughly evaluate these structural transformations and thermal behavior beyond standard FTIR analysis, complementary analytical methods are necessary.

Raman spectroscopy offers precise insights into symmetric framework vibrations and skeletal C-N linkages, while thermogravimetric analysis coupled with differential thermal analysis (TGA/DTA) elucidates multi-stage thermal degradation. Therefore, this study employs a combined Raman and TGA/DTA approach to investigate the structural characterization and thermal stability of hydrazine sulfate-modified urea-formaldehyde resins.

In recent literature, several innovative approaches have been explored to enhance the thermal and mechanical performance of UF resins while reducing formaldehyde release. For instance, Esmaeili et al.[2] reported a novel bio-based modification of UF resins using 5-hydroxymethylfurfural (HMF). Their thermal characterization via TGA and DSC demonstrated that the incorporation of HMF—featuring active hydroxyl groups and furan rings—significantly improved the thermal stability, char yield, and film-formation ability of the resin. Furthermore, particleboards bonded with HMF-modified UF resins exhibited enhanced mechanical properties (higher modulus of rupture and elasticity), reduced thickness swelling, and a substantial decrease in formaldehyde release compared to conventional UF adhesives.

Additionally, Arshad et al. [3] investigated the morphology, thermal stability, and thermal degradation kinetics of cellulose-modified urea-formaldehyde (UFC) resins. Their structural characterization using SEM, FTIR, and XRD revealed a homogenous, partially crystalline structure with a distinct urea-formaldehyde/cellulose interface morphology. Non-isothermal thermogravimetric and differential thermal analyses (TGA/DTA) demonstrated that cellulose modification significantly improved the inherent thermal stability of the resin, as elucidated by the integral procedure decomposition temperature. Furthermore, isoconversional kinetic analysis confirmed a complex, multi-step thermal degradation mechanism involving parallel and consecutive reactions, where activation energy varied substantially with the advancement of thermal decomposition.

Furthermore, Hong et al. [4]conducted a comprehensive thermal analysis study on modified urea-formaldehyde (UF) resins to evaluate their degradation behavior and thermal endurance. Their findings demonstrated that chemical modification significantly alters the thermal decomposition profile, elevating characteristic degradation temperatures and improving overall structural stability compared to conventional UF systems. The integration

of modifying agents effectively reinforces the polymer network, resulting in enhanced thermal resistance and optimized cross-linking density, which plays a crucial role in suppressing rapid thermal breakdown and improving the durability of resin-based materials.

In addition, Siimer et al. [5] examined the thermal behavior and structural characteristics of industrial urea-formaldehyde resins modified with low levels of melamine using combined TG-DTA techniques and ^{13}C NMR spectroscopy. Their thermal analysis demonstrated that co-condensing melamine into the UFR matrix during synthesis causes a distinct shift in both the condensation exotherm and water evaporation endotherm toward considerably higher temperatures, signifying enhanced thermal endurance. The authors also compared the direct addition of melamine monomer prior to curing alongside urea incorporation as a formaldehyde scavenger, proving that structural modification during synthesis yields superior thermal network stability compared to post-synthesis blending.

Furthermore, Samaržija-Jovanović et al. [6] investigated the thermal stability and free formaldehyde content of urea-formaldehyde resins modified with hexamethylenetetramine (HMTA), melamine, ethylene urea (EU), and nano-SiO_2 using non-isothermal TG, DTG, DTA, and IR spectroscopy. Their findings demonstrated that modifying UF resins with ethylene urea (Resin 3) significantly shifted the DTG decomposition peaks toward higher temperatures, indicating enhanced thermal stability corroborated by FTIR analysis. Moreover, the integration of ethylene urea successfully minimized free formaldehyde down to an optimal minimum level of 6%, proving its dual effectiveness as a thermal stabilizer and scavenger.

Experimental Part

Materials

Urea (purity >= 99.0%) and aqueous formaldehyde solution (37.0 wt%) were used as precursors for resin synthesis. Hydrazine sulfate ($N_2H_6SO_4$, >= 99.0%, Sigma-Aldrich) was employed as a modifier and formaldehyde scavenger. Sodium hydroxide (NaOH) and ammonium chloride (NH_4Cl) were used for pH adjustment and curing catalysis, respectively. All aqueous solutions were prepared using distilled water.[7]

Synthesis of Unmodified and Modified Urea-Formaldehyde Resins

The synthesis of conventional and hydrazine sulfate-modified urea-formaldehyde resins was carried out in a three-necked glass reactor equipped with a mechanical stirrer, a reflux condenser, and a digital thermometer placed in a thermostated water bath.

Synthesis of Base UF Resin: The synthesis of urea-formaldehyde (UF) resin was carried out via a two-stage alkaline-acid condensation method in a reactor equipped with a mechanical stirrer, reflux condenser, and thermometer. Formalin was placed into the reactor, and the pH was adjusted to 7.8–8.2 using a 20% NaOH solution. The first portion of urea was added to achieve an initial formaldehyde-to-urea (F/U) molar ratio of 2.0:1.0. The reaction mixture was heated to 85–90 °C and maintained under constant stirring for 60 minutes.

Subsequently, the pH was adjusted to 4.5–4.8 using a 10% H_2SO_4 solution to promote polycondensation.[8] The reaction was continued until a target viscosity was reached. At this stage, calculated amounts of hydrazine sulfate ($N_2H_6SO_4$) modifier were incorporated into

the system. The pH was then raised back to 7.5–8.0 using NaOH to terminate the condensation reaction. Finally, the second portion of urea was introduced to adjust the final F/U molar ratio to 1.1–1.2:1.0, and the resin was cooled to room temperature. Unmodified UF resin was prepared under identical conditions without hydrazine sulfate as a control.

Raman Spectral Analysis.

The Raman scattering measurements of the cured resin samples were performed using a (HORIBA Scientific) Raman spectrometer equipped with a 532 nm semiconductor laser excitation source.

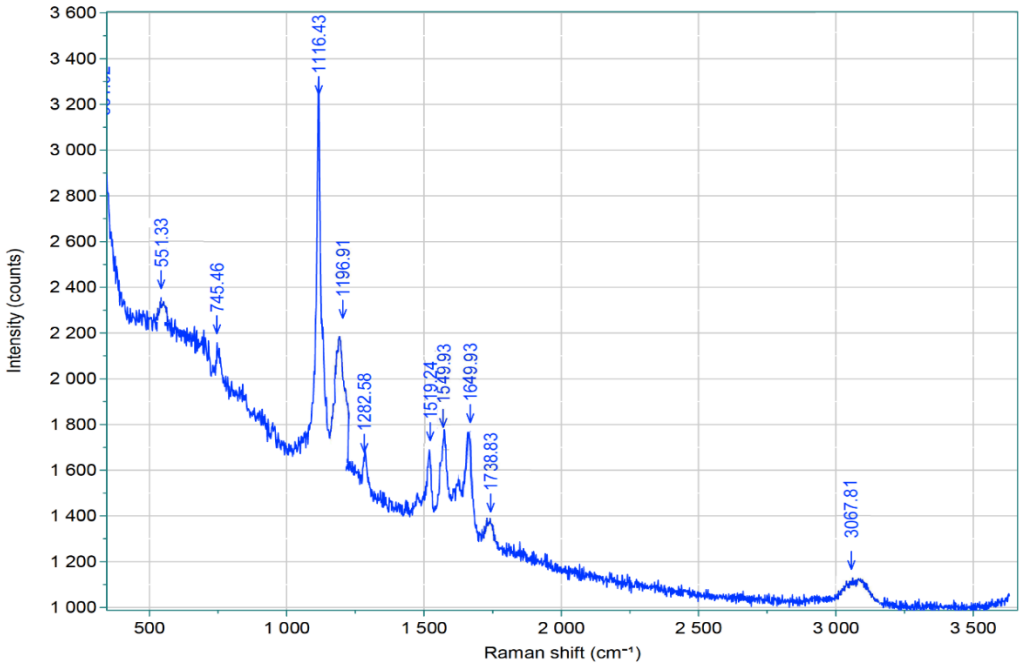

Fig. 1. Raman spectrum of the cured hydrazine sulfate-modified urea–formaldehyde resin matrix.

As shown in the spectrum, several characteristic vibrational bands confirm the formation of a densely cross-linked amino-resin network. The sharpest peak at 1116.43 cm^{-1} corresponds to symmetric C–O–C ether linkage and C–N skeletal stretching, indicating extensive methylene-ether bridge formation. Bands at 1196.91 cm^{-1} and 1282.58 cm^{-1} (Amide III region) alongside peaks at 1519.24 cm^{-1} and 1549.93 cm^{-1} (Amide II region) confirm the presence of primary and secondary amine groups within the polycondensation frame. The peak at 1649.93 cm^{-1} is assigned to Amide I carbonyl (C=O) and C=N azomethine stretching modes, validating successful condensation, while a minor band at 1738.83 cm^{-1} reflects weakly hydrogen-bonded carbonyls. Additionally, the broad band at 3067.81 cm^{-1} represents N–H/C–H stretching, and lower-frequency peaks at 551.33 cm^{-1} and 745.46 cm^{-1} are attributed to skeletal deformation modes. Overall, these spectral features confirm a highly cross-linked polymer structure rich in stable amide, ether, and imine linkages.[9]

Table 1. Characteristic Raman vibrational bands and structural assignments of cured hydrazine sulfate-modified UF resin

Wavenumber (cm^{-1})	**Vibrational Assignment**	**Structural / Functional Group Identification**

551.33 / 745.46	δ(skeleton)	Out-of-plane ring/chain skeletal deformation modes
1116.43	νs(C–O–C) / ν(C–N)	Ether bridges and skeletal polymer network
1196.91 / 1282.58	ν(C–N) + δ(N–H)	Amide III region (primary and secondary amines)
1519.24 / 1549.93	δ(N–H) + ν(C–N)	Amide II region (secondary amide units)
1649.93	ν(C=O) / ν(C=N)	Amide I region and azomethine linkages
1738.83	ν(C=O)	Free or weakly hydrogen-bonded carbonyl groups

Thermogravimetric and Differential Thermal Analysis

The thermal degradation behavior and thermostability of unmodified and hydrazine sulfate-modified UF resins were evaluated using TGA/DTA under a nitrogen atmosphere.

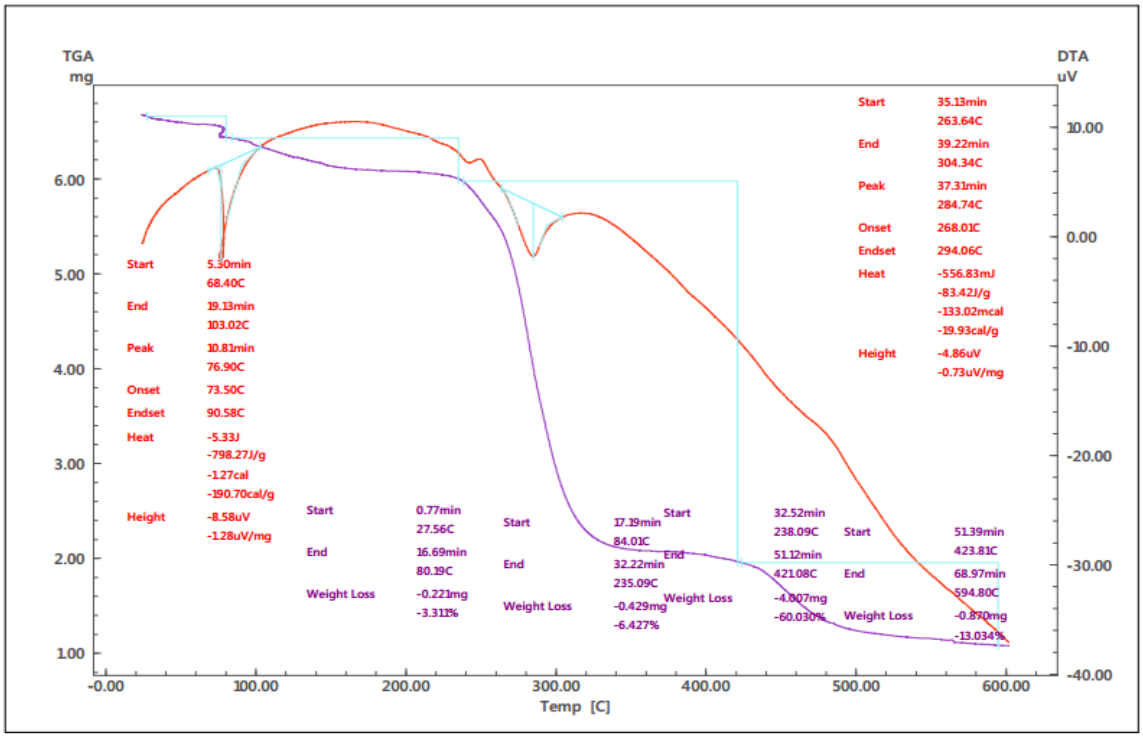

Fig 2. TGA and DTA thermograms of the cured hydrazine sulfate-modified urea–formaldehyde resin.

The thermal stability and degradation behavior of the modified resin were evaluated using thermogravimetric and differential thermal analysis (TGA/DTA). As depicted in the thermal curves, the decomposition process proceeds through distinct weight loss stages. In the first stage, spanning from 27.56 °C to 80.19 °C, an initial weight loss of 3.31% is observed, accompanied by an endothermic DTA peak at 76.90 °C, which is primarily attributed to arabic/physical moisture evaporation and volatile low-molecular-weight residues.[10] The second and primary thermal degradation stage occurs between 238.09 °C and 421.08 °C, accounting for a major weight loss of 60.03%. This sharp mass reduction corresponds to the thermal cleavage of methylene-ether bridges, methylene linkages, and the breakdown of secondary amide structures within the polymer network, accompanied by a

distinct thermal transition with an onset at 268.01 °C and a peak degradation temperature of 284.74 °C. Finally, in the third stage (423.81–594.80 °C), an additional weight loss of 13.03% occurs due to the extensive fragmentation of the cross-linked backbone and progressive carbonization.

Conclusion. Urea–formaldehyde (UF) resin was successfully modified with hydrazine sulfate via a two-stage alkaline-acid polycondensation process. Raman spectroscopy confirmed the formation of a densely cross-linked polymer matrix featuring key ether (1116.43 cm^{-1}), amide (1519.24–1549.93 cm^{-1}), and C=O/C=N (1649.93 cm^{-1}) linkages. Thermal analysis (TGA/DTA) demonstrated high thermal resistance, with primary decomposition occurring between 238.09 °C and 421.08 °C and a peak temperature of 284.74 °C. Initial moisture and volatile loss was limited to 3.31%. Overall, hydrazine sulfate modification effectively enhances the structural integrity and thermal stability of the resin for advanced binder applications.

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