

Biomimetic Organic-Inorganic Hybrid Magnesium Oxychloride Cement as Green Adhesive for Wood Industry

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Abstract. *Benefiting from the negative carbon footprint of wood, wood composites have been considered as eco-friendly alternative building materials. However, adhesives for bonding wood components are mainly formaldehyde-based resins, which are highly combustible and continuously release volatile hazardous substances during service. Therefore, the development of magnesium oxychloride cement (MOC) as wood adhesive is highly compliant with environmental regulations and green material requirements. Unfortunately, the extensive application of MOC adhesive is hindered by poor water resistance and weak interfacial interaction with wood. Herein, an oyster-inspired organic-inorganic hybrid strategy was proposed to develop MOC with high adhesion strength and excellent water resistance. Specifically, the renewable chitosan (CS) and tartaric acid (TA) were selected as organic reinforcing constituents to construct a dense double chelating network in MOC, which induced the structural regulation at the bonding interface, thus enhancing the cohesion strength and interfacial properties. Thanks to the biomimetic organic-inorganic hybrid structure, the dry and wet shear strength of the MOC-CS-TA reached 3.08 MPa and 1.77 MPa, making increases of 27.27% and 53.91% compared to the control sample, respectively. Meanwhile, the MOC-CS-TA adhesive presented excellent flame-retardant properties compared with urea-formaldehyde resin adhesives and soy protein adhesives. The design path presented here provides workable guidance for the preparation of eco-friendly cementitious materials and green wood composites in further applications.*

Keywords: *Magnesium oxychloride cement, Wood adhesive, Organic-inorganic hybrid, Double chelating network, Eco-friendly building materials.*

1 Introduction

With the increasing emphasis on green, low-carbon, sustainable concepts, the development of wood building materials has received considerable attention. However, the most of adhesives used in wood construction is still “maldehyde-based and petroleum-derived” adhesive, which are highly combustible and continuously release volatile hazardous compounds during the preparation and application (Xu et al. 2021). Therefore, it is urgent to develop the non-formaldehyde and flame-retardant wood building materials using cementitious adhesives.

Magnesium oxychloride cement (MOC) is an air-harden cementitious material composed of MgO-MgCl₂-H₂O ternary system (Sorel 1867). Under the normal temperature and pressure, their hydration products are mainly phase 5 (5Mg(OH)₂·MgCl₂·8H₂O) and phase 3 (3Mg(OH)₂·MgCl₂·8H₂O) (He et al. 2020). Compared with Portland cement (PC), MOC presents the advantages of high mechanical strength, low alkalinity (pH=8-9.5), and better compatibility with wood, which making it more suitable for the design of wood building materials (Li et al. 2020). However, there are still many challenges in the large-scale applications of MOC as wood adhesives.

The weak interfacial interactions between MOC and wood result in poor interfacial adhesion strength. To improve the interfacial interactions, numerous strategies have been conducted to increase the active specific surface area by pretreating the surface of wood, such as NaOH alkali treatment, coupling agent grafting, emulsion polymer coating, etc. (Wang et al. 2021, Zuo et al. 2018). However, these researches neglected the relationship between the MOC structures at the bonding interface and the final properties of wood composites.

In addition, the filtering effect of wood will destroy the reasonable composition ratio of MOC at the bonding interface, which generates more unstable phase 3 and $Mg(OH)_2$, thus affecting the final adhesion strength and durability of MOC/wood composites (Zhou et al. 2021).

In nature, many marine organisms, such as nacre, oysters and barnacles, have evolved a unique organic-inorganic hybridization mechanism to maintain their stable mechanical strength and excellent adhesion strength underwater (Li et al. 2018, Metzler et al. 2016). Inspired by these marine organisms, the construction of organic-inorganic hybrid system in MOC is expected to enhance the interactions between MOC and wood and mitigate the filtering effect of wood.

Chitosan (CS) is a natural and biodegradable linear carbohydrate containing massive $-NH_2$ groups, which can serve as chelating reaction sites for various metal ions (Ben Seghir and Benhamza 2017). However, CS is insoluble in water or alkali environments. Therefore, it is urgent to choose a weak acid as the solvent. Tartaric acid (TA) contains abundant $-COOH$ groups, which can construct a stable double-chelating network with CS through electrostatic adsorption and hydrogen bonding interactions (Cadogan et al. 2014).

In this work, inspired by marine organisms, a facile and eco-friendly method was proposed to fabricate MOC wood adhesives with organic-inorganic double-chelating structures using CS and TA as organic reinforcement. The main merits and novelties may be concluded by the following aspects. (1) The double chelating structure was optimized by adjusting the CS and TA content, which can introduce more active sites as the nucleation of phase 5, thus achieving the structural regulation of the bonding interface and enhancing the interactions. (2) The construction of CS/TA double chelating network can form an encapsulation with MgO particles, improving the permeability of MOC adhesives into the wood layers. (3) Compared with other linear carbohydrates and organic acids, CS and TA are mainly extracted from the wastes or by-products of the mariculture industry and wine production industry, which is conducive to the high-value recycling of waste resources and promoting the sustainable development of MOC. In conclusion, this study will provide theoretical basis and technical support for the preparation of high-performance MOC/wood composites, and for promoting the development of low-carbon and energy-saving wood building materials.

2 Materials and Methods

2.1 Materials

Light-burnt MgO (64% activity), Magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$, 98% purity), CS (viscosity: 50-800 mPa·s, degree of deacetylation: 80.0-95.0), TA (99.5% purity) and Basswood (3 mm).

2.2 Preparation of MOC/CS/TA Adhesives

The molar ratio of MgO: MgCl₂: H₂O was controlled to be 5: 1: 13. First, CS (0.1, 0.2, 0.3 and 0.4 wt.% weight of MgO) was dissolved in TA solution (2 wt.% weight of MgO). Then, the MgCl₂ was added into the mixture with stirring to obtain a homogeneous solution. Next, the MgO powder was subsequently added into the resultant mixture with stirring for 5 min. Finally, the prepared MOC paste was poured into the mold (2 mm × 2 mm × 2 mm) and cured at 25 °C and 60 ± 5 % relative humidity for 7 days before any further measurements. The resultant adhesive is denoted as MOC-CS-TA.

To further investigated the effect of TA content on the properties and structure of MOC-CS-TA adhesives, a series of MOC composites were prepared with various TA contents (1, 2, 3 and 4 wt.% weight of MgO) using 0.2 wt.% CS.

2.3 Preparation of MOC/CS/TA Wood Composites

The prepared MOC/CS/TA adhesive was evenly spread onto the basswood veneer (65 mm × 25 mm × 3 mm) with a spreading rate of 400 g/m² and an adhesive bonding area of 25 mm × 25 mm using a paintbrush. Next, two basswood veneers were overlapped by the single lap shear principle and cold-pressed for 24 h with 0.7 MPa, then stored at 25 °C and 60% relative humidity for 7 days before further tests.

3 Results and discussion

To evaluate the flame-retardant performance of MOC adhesives, the heat release rate (HRR) and total heat release (THR) of MOC adhesive were compared with those of urea-formaldehyde resin adhesives and soy protein adhesives, as shown in Fig 1. Compared to that, the peak heat release rate (PHRR) and THR of MOC markedly decreased to 4.9 W/g and 0.9 KJ/g, respectively, confirming that MOC as the wood adhesive can alleviate the fire hazard problem of traditional wood-based panels.

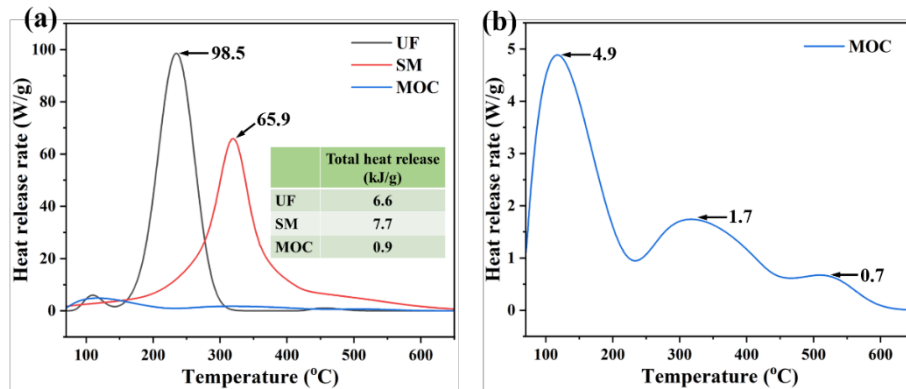


Figure 1. Heat release rate of UF, SM and MOC.

As presented in Fig.2, the initial MOC/wood has the lowest dry and wet shear strengths of 2.42 MPa and 1.15 MPa, respectively, suggesting the weak interfacial interaction between MOC and wood. Consistently, the addition of CS and TA into MOC induced significant improvement in dry and wet shear strengths for MOC-CS-TA. Particularly, the MOC/CS-0.2@TA-2 exhibited the maximum dry and wet shear strength of 3.08 MPa and 1.77 MPa,

accounting for 27.27% and 53.91% increases compared to the MOC, respectively. The improvement can be ascribed to the construction of CS/TA organic-inorganic double chelating network, which improves the stability and permeability of cement particles, thus effectively improving the adhesion property of MOC/wood composites and alleviating the filtering effect of wood. However, the shear strengths of MOC-CS-TA/wood composites presented a decreasing trend with the further addition of CS and TA.

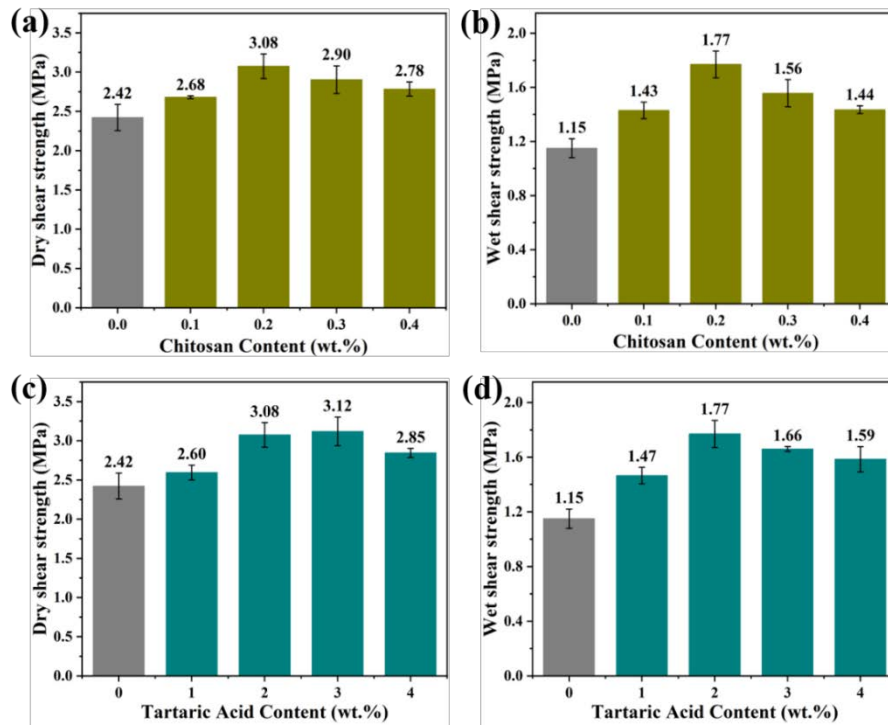


Figure 2. Dry/wet shear strength of MOC-CS-TA bonded wood composites: (a, b) with different CS contents and (c, d) with different TA contents.

To further reveal the effect of CS/TA organic-inorganic double chelating network on the adhesion properties and bonding interface of MOC/wood composites, the phase composition, morphologies and adhesive permeability at the bonding interface were characterized. As shown in Fig.3, the pristine MOC/wood composite presented the lowest phase 5 content of 48% and the highest MgO content of 43%. After the addition of CS and TA, the phase 5 content increased and the MgO content decreased at the interface, indicating that the organic-inorganic double chelating network can effectively mitigate the filtering effect of wood, improve the stability of cement particles and reduce the formation of weak interfacial layers. In particular, with the addition of 0.2 wt.% CS and 2 wt.% TA, the MOC/CS-0.2@TA-2 exhibited the maximum phase 5 content at the interface of 56%, and the minimum MgO content of 34%. The improvement of phase 5 content was mainly attributed to the following two aspects. (1) The addition of TA can promote the dissolution of partial MgO particles, which can more easily participate in the hydration reaction in wood pores to produce phase 5, thus improving the permeability of adhesive. (2) The construction of CS/TA double chelating network can form an encapsulation with MgO particles to improve the stability, and promote the formation of “MgO-

MgCl₂-H₂O” stabilization system at the bonding interface, thus effectively mitigating the filtering effect of wood. However, when further increasing the CS and TA content, MOC/CS/TA/wood composites exhibited a reduced phase 5 content, which was attributed to the excessive reactive sites destroying the stability of the double chelating network and hindering the formation of phase 5.

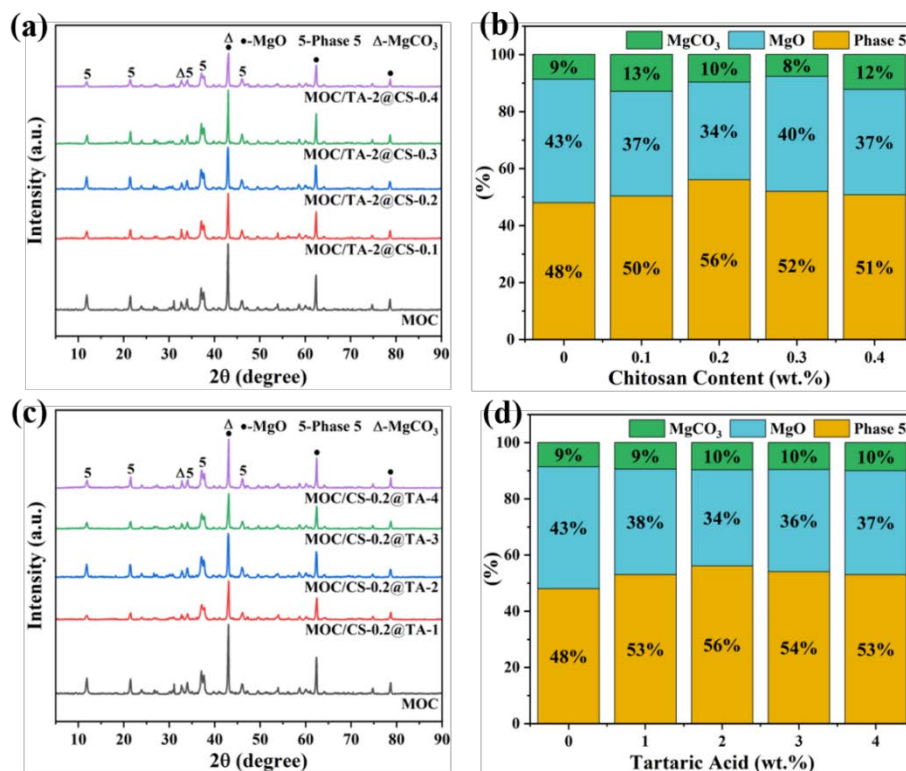


Figure 3. (a) XRD patterns and (b) quantitative analysis at the bonding interface.

As shown in Fig. 4a, the pristine MOC/wood composite presented a smooth fracture surface, indicating a cohesive failure in the pristine MOC and the weak interfacial interaction between MOC and wood layers. In contrast, the MOC/CS-0.2@TA-2 showed a rougher fracture surface with many pulling fibers and rod-like phase 5 structures (Fig. 4b). These results suggested that the construction of CS/TA double chelating network not only promoted cohesion but also improved the surface attachment of the adhesive to wood. However, with the further increase of CS, the phase 5 structure at the bonding interface in MOC/TA-2@CS-0.4 disappeared, indicating that the excessive CS would hinder the generation of phase 5, which is consistent with the XRD results (Fig. 4c). With the further increase of TA, for the MOC/CS-0.2@TA-4, it was observed that the gel-like phase 5 structure and a large number of obvious cracks on the fracture surface. These results indicated that the excessive TA would increase the internal stress of MOC and induce more cracks within the MOC, thus destroying the structural integrity of the bonding interface (Fig. 4d).

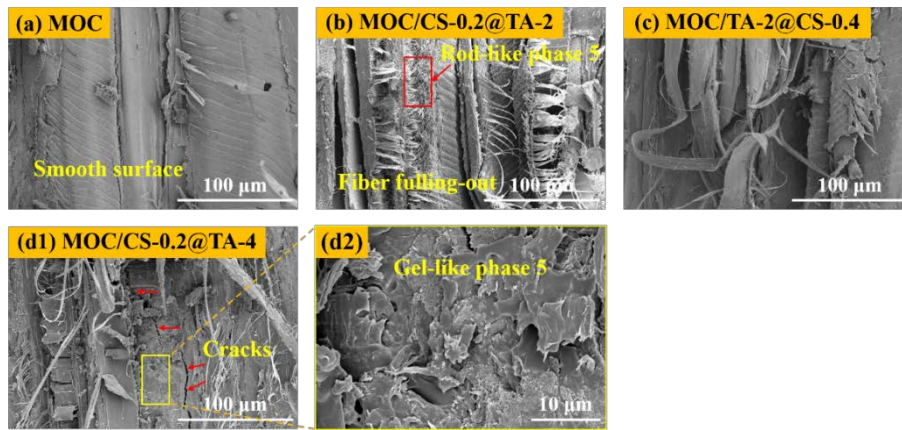


Figure 4. SEM images of wood fracture surface for (a) MOC, (b) MOC/CS-0.2@TA-2, (c) MOC/TA-2@CS-0.4, (d1) MOC/CS-0.2@TA-4 and (d2) enlarged image of MOC/CS-0.2@TA-4

To further investigate the effect of CS/TA on the permeability of MOC, the element distribution at the vertical section were analyzed by SEM-EDS test. As shown in Fig.5, with the addition of CS and TA, the relative concentration and location of Mg element along the scan line of the MOC/CS-0.2@TA-2/wood composite are deeper than the pristine MOC/wood composite. These results suggested that CS/TA can significantly improve the penetration of MOC into the wood and promote the formation of strong adhesive “nail” structure at the bonding interface, thus improving the adhesion properties of MOC/wood composites.

The aforementioned investigations demonstrated, the introduction of CS and TA can not only improve the cohesive strength of the MOC adhesives, but also promote the generation of adhesive “nails” structure and phase 5 at the bonding interface. The enhancement of adhesion properties was mainly derived from the following factors. (1) The introduction of CS/TA provided more nucleation sites for phase 5, which promoted the generation of phase 5 at the bonding interface and induced the transformation of gel-like phase 5 and gel-like chelating products, thus enabling them to act as a water-resistant barrier to effectively impede the erosion of water on the adhesive and bonding interface. (2) The construction of CS/TA double chelating network could not only improve the cohesive strength of MOC against external loading, but also enhance the surface attachment and interfacial interaction with wood. (3) The CS/TA double chelating network can absorb on the surface of MgO particles to promote them partial dissolution and uniform dispersion, thus improving the permeability and stability of adhesive.

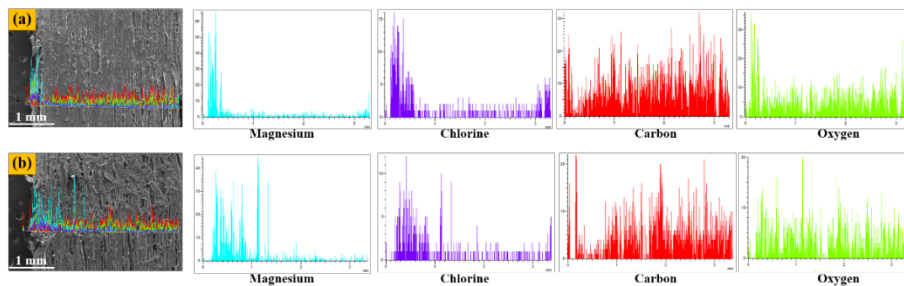


Figure 5. SEM images and EDS spectrum of section of (a) MOC and (b) MOC/CS-0.2@TA-2.

4 Conclusions

In summary, inspired by marine organisms, an eco-friendly MOC wood adhesive with excellent flame retardancy, adhesion strength, water resistance and interfacial properties was prepared by constructing CS/TA organic-inorganic double chelating network. The specific conclusions are as follows:

- Compared with the traditional UF and SM adhesives, MOC wood adhesives exhibited excellent flame-retardant properties, which can alleviate the problem of fire hazards of traditional wood-based composites and expand the application scope, thus promoting the green, flame retardant and high-quality development of the wood-based panel industry.
- Compared with the pristine MOC, the phase 5 content at the bonding interface of MOC/CS-0.2@TA-2/wood composite increased from 48% to 56%, and the MgO content decreased from 43% to 34%, which effectively alleviated the filtering effect of wood. Meanwhile, the dry and wet shear strengths increased to 3.08 MPa and 1.77 MPa, accounting for 27.27% and 53.91% increments in comparison with the pristine MOC/wood composite.

Therefore, this strategy is expected to pave a new way for designing high-performance inorganic wood adhesives with integrated economic and environmental benefits.

References

- Ben, S.B., and Benhamza, M.H. (2017). *Preparation, optimization and characterization of chitosan polymer from shrimp shells*. Journal of Food Measurement and Characterization, 11, 1137-1147.
- Cadogan, E.I., Lee, C.H., Popuri, S.R., and Lin, H.Y. (2014). *Effect of solvent on physico-chemical properties and antibacterial activity of chitosan membranes*. International Journal of Polymeric Materials and Polymeric Biomaterials, 63, 708-715.
- He, P., Poon, C.S., and Tsang, D.C.W. (2020). *Water resistance of magnesium oxychloride cement wood board with the incorporation of supplementary cementitious materials*. Construction and Building Materials, 255, 119145.
- Li, A., Jia, Y., Sun, S., Xu, Y., Minsky, B.B., Stuart, M.A.C., Colfen, H., von Klitzing, R., and Guo, X. (2018). *Mineral-enhanced polyacrylic acid hydrogel as an oyster-inspired organic-inorganic hybrid adhesive*. ACS Applied Materials & Interfaces, 10, 10471-10479.
- Li, Q., Zhang, L., Gao, X., and Zhang, J. (2020). *Effect of pulverized fuel ash, ground granulated blast-furnace slag and CO₂ curing on performance of magnesium oxysulfate cement*. Construction and Building Materials, 230.
- Metzler, R.A., Rist, R., Alberts, E., Kenny, P., and Wilker, J.J. (2016). *Composition and structure of oyster adhesive reveals heterogeneous materials properties in a biological composite*. Advanced Functional Materials, 26, 6814-6821.
- Sorel, S. (1867). *On a new magnesium cement*. Comptes Rendus Science, 65, 102-104.
- Wang, J., Wang, S., Zuo, Y., Xiao, J., and Wu, Y. (2021). *Construction of compatible interface of straw/magnesium oxychloride lightweight composites by coupling agents*. Construction and Building Materials, 281, 122600.
- Xu, Y., Han, Y., Chen, M., Luo, J., Shi, S.Q., Li, J., and Gao, Q. (2021). *Constructing a triple network structure to prepare strong, tough, and mildew resistant soy protein adhesive*. Composites Part B: Engineering, 211.
- Zhou, W., Ye, Q., Shi, S.Q., Fang, Z., Gao, Q., and Li, J. (2021). *A strong magnesium oxychloride cement wood adhesive via organic-inorganic hybrid*. Construction and Building Materials, 297, 123776.
- Zuo, Y., Xiao, J., Wang, J., Liu, W., Li, X., and Wu, Y. (2018). *Preparation and characterization of fire retardant straw/magnesium cement composites with an organic-inorganic network structure*. Construction and Building Materials, 171, 404-413.