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Chitosan-based adhesive reinforced with pine resin

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Keywords

chitosan
pine resin
adhesive
bond strength

Abstract

Commercial adhesives have a high bond strength and are resistant to water but harm the environment and humans. Chitosan can be regarded as a versatile bio-sourced alternative. The potential of chitosan as a wood adhesive which was produced from medium molecular weight chitosan and different ratio of Pine resin, was investigated in this study. The viscosity of chitosan-based adhesive was found from 1167 CP to 2871 CP. Also, the chemical compositions of chitosan-based adhesives were analyzed via Fourier transform infrared spectroscopy. Double-lap shear tests were used to determine the bond strength of different chitosan-based formulations. The bond strength of chitosan-based adhesive was found to vary between 0,47 MPa to 0,82 MPa.

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Introduction

As a safe, easy-to-use, aesthetic structure, wood has been used as a building and engineering material since ancient times. Wooden materials are preferred mainly due to their anatomical and chemical structures and mechanical and physical properties (Ergun, 2021). However, the increasing population and requirements led to waste and small-scale wood being converted into products such as particleboard, fiberboard, plywood, and glulam. Therefore, it demands high quantity adhesive. Also, adhesives are used to bond the solid wood. Formaldehyde-based adhesives such as melamine formaldehyde (MF), phenyl formaldehyde (PF), resorcinol formaldehyde (RF), urea-formaldehyde (UF) and are primarily used in the wood material sector. These adhesives show high water resistance and bond strength. Despite all these positive features, they produce dangers for the environment and human health due to the release of free formaldehyde (Abdelmoula et al., 2021). So, researchers are attempting to develop non-toxic wood or less-toxic adhesives by diminishing the molar ratio and adding a formaldehyde scavenger during preparation (Ji and Guo, 2018). In addition, petroleum resources used in producing PF, MF, and UF resins are rapidly depleting. Therefore, developing adhesives containing no formaldehyde from non-petroleum sources is essential. In this context, bio-based adhesives were emphasized (Umemura et al., 2003). Bio-based adhesives are derived from animals, fungi, bacteria, and plants. These can be polymers that play a variety of biological functions in plants, such as energy storage (starch), cellular communication (glycosaminoglycans), or cell wall forming (cellulose). These polymers can have high molecular weights (Sorlier et al., 2001). The main structural features of polysaccharides include mainly polar functional groups and high molecular weight to exhibit adhesive properties. Polysaccharides with hydrogen-bonding functional and polar groups, namely carboxylates, ethers, and hydroxyls, demonstrate superior adhesion to high-energy bonding woods and metals. The most investigated polysaccharides for adhesives are guar gum, starch, lignin, and chitosan (Mathias et al., 2016).

Chitosan, the second most abundant polysaccharide on earth (Yıldırım et al., 2022), has many applications, including but not limited to water treatment, biomedical, wood adhesive, and insulation materials (Ozen et al., 2021). In particular, chitosan is a suitable biopolymer for use in wood adhesives. Chitosan, acquired with the deacetylation of chitin, has gotten attention due to its high potential applicability as a bioadhesive. Bioadhesives have taken place in significant advances in the biomedical sector and, more recently, in the wood construction sector. In bioadhesives, the parameters affecting the attractive features of chitosan are the degree of deacetylation and molecular weight. Many studies showed that the adhesive features change when molecular weight and the degree of deacetylation decrease. Chitin is also extracted industrially from the exoskeletons of shrimp and crabs, primarily from seafood processing waste. These characteristics enable efficient and fashionable waste management using polysaccharides in the adhesive wood field (Mati-Baouche et al., 2014).

On the other hand, pine resin is an abundant natural renewable resource in Türkiye. The main component of the resin is a resin acid mixture with a hydrogenated phenanthrene ring structure (Mao et al., 2021). Pine resins are widely used in many fields, such as agriculture, cosmetics, and health.

This study aimed to examine the usability of the adhesive produced from chitosan and different amount of pine resin for the wood industry.

Methods and materials

Materials

The medium molecular weight chitosan (molecular weights: 310000 to 375000 Da), acetic acid, and glycerol were supplied from Sigma-Aldrich (Schnelldorf, Germany). Calabrian pine (Pinus brutia) resin was collected from calabrian pine trees in Dalaman / Mugla (Türkiye).

Methods

Both calabrian pine resin and chitosan can dissolve in acetic acid conditions, so %5 stock solution of acetic acid was prepared in distilled water. Firstly, calabrian pine resin was mixed at 1200 rpm in acetic acid for 2 h. Respectively, chitosan was added and stirred at 600 rpm for 6 h. All mixing processes were carried out at room temperature. Compositions of the adhesive are given in Table 1.

Table 1. Contents of chitosan-based adhesive

Code	Chitosan (gr)	Pine Resin (gr)	Acetic Acid (5%) (ml)	Glycerol (ml)
CPA-0	10	0	125	2
CPA-1	10	1.25	125	2
CPA-2	10	3.75	125	2
CPA-3	10	6.75	125	2

*CPA – chitosan-pine resin adhesive.

The preparation method of chitosan-based adhesive is shown in Fig. 1.

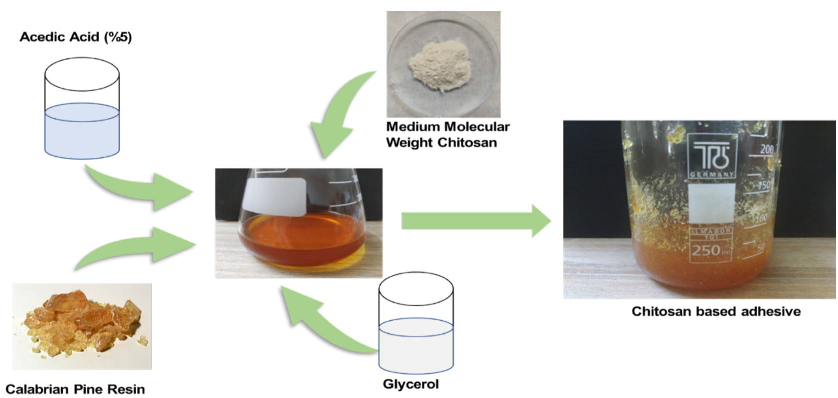

Fig. 1. Production of chitosan-based adhesive

Characterization

The viscosity of the produced glues was measured according to ISO 9665 standards with KU-2 viscometer (Brookfield, USA). Fourier transform infrared (FT-IR) analyses were carried out with a Nicolet IS FT-IR (iS10, Thermo Fisher Scientific, Massachusetts, USA) spectrometer. Each produced adhesive was measured at the spectra range of 400 cm^{-1} to 4000 cm^{-1}. Double lap samples were prepared with 5× 18 × 150 mm (thickness × width × length) dimensions, and the bonding area was 900 mm^2. 150 grams of adhesive per square meter was applied to the sample surfaces. The samples were dried at 60 °C without pressure for 6 h in the oven. The mechanical characterization of the double lap specimens was assessed on a Marestek universal test device (Mares Engineering Research Electronic Systems, İstanbul, Türkiye) according to ASTM D 3528-96 (2016) standard. After, the bond strength was calculated with the following Equation (1):

$$\sigma = \frac{F_{max}}{2A} \tag{1}$$

Where σ is the bond strength, F is the applied maximum force (N), and A is the lap area (mm^2).

Results and discussion

The viscosity of a fluid is a measurement of its resistance to gradual deformation and spreading. The viscosity properties of chitosan solutions provide essential information in adhesives. The viscosity of chitosan solutions is related to their pH and degree of deacetylation (Crini et al., 2009). In addition, temperature and concentration are other vital viscosity parameters (Mati-Baouche et al., 2014). The viscosity values of chitosan-based adhesive reinforced with pine resin are given in Fig. 2.

Depending on the pine resin concentration, the chitosan-based adhesive's viscosity ranged from 1167 CP to 2871 CP. As the amount of pine resin increased, the adhesive viscosity increased. The viscosity of chitosan-based adhesive increased due to chitosan and pine resin reacting with each other. In different studies, the viscosity values of chitosan ranged from 14 CP to 7132 CP (Jeon et al., 2002; Bajaj et al., 2011). Generally, it is desired to have high cohesion strength in adhesives, and therefore it is undesirable to use an excessive amount of filling material. Cohesion force, in a sense, determines the mechanical properties of the material. The cohesion force's magnitude

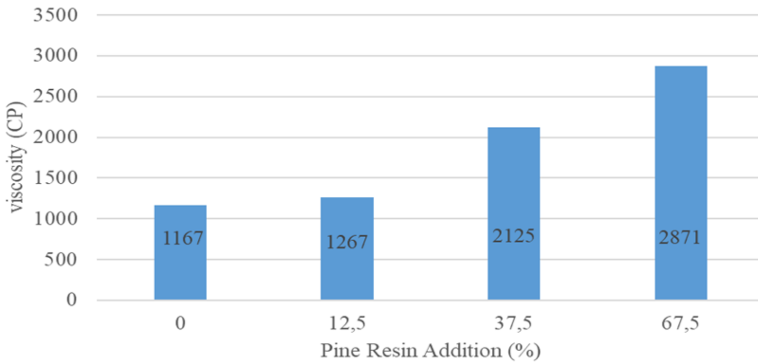

Fig. 2. The viscosity of the chitosan-based adhesive

depends on the adhesive's chemical structure, and using more than 40% filler on average affects the cohesion force in adhesion negatively (Senay, 1996).

Although the chemical structure of pine resins is very complex, all FTIR spectra of pine resins offer similar properties and, as a result, can be characterized by FTIR spectra when mixed with different polymers. FTIR spectra of chitosan, pine resin, and their mixtures are given in Fig. 3.

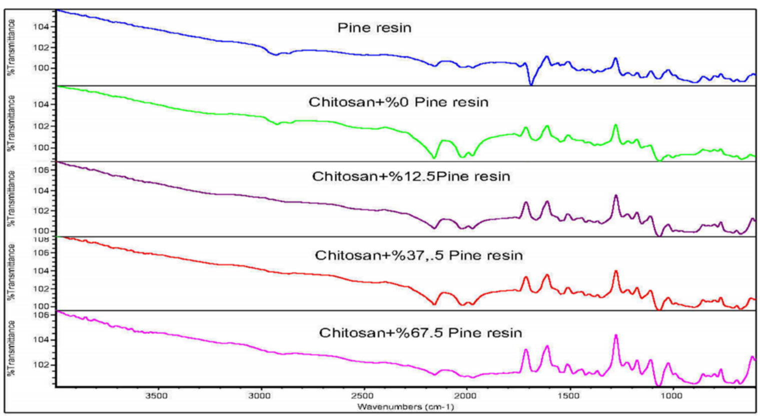

Fig. 3. FTIR results of chitosan-based adhesive

The spectra of pine resin displayed the following band: 2927 cm^{-1} could be assigned to the aliphatic C-H stretch group. This C-H stretch group is typical of highly branched and cycle-containing alkyl groups. Terpenoid compounds, the primary constituents of pine resins, contain these alkyl fragments. The presence of bands in 1689 cm^{-1} could be C–O stretching vibrations due to the carboxylic groups of resin acids. Due to C-O-C and C-O stretch vibrations, the bands are centered around 1000 cm^{-1}–1100 cm^{-1}. After the resins have been oxidized, these bands may appear in the spectra (Vahur et al., 2011). When the spectra of chitosan without pine resin were examined, 2922 cm^{-1} bands were related to C-H symmetric and asymmetric stretching, respectively. These bands are characteristics typical of polysaccharides and occur in different polysaccharide spectra, such as carrageenans (Silva et al., 2010), glucans (Wolkers et al., 2004), and xylan (Melo-Silveira et al., 2011). N-acetyl groups were affirmed at around 1665 cm^{-1} peak (C = O stretching of amide I), 1546 cm^{-1} (N-H bending of amide II), and 1380 cm^{-1} (C-N stretching of amide III), respectively. The second band (1546 cm^{-1}), characteristic of typical N-acetyl groups, was presumably overlapped by other peaks (Queiroz et al., 2014). The CH_2 bending and CH_3 symmetrical deformations were confirmed by the presence of band at around 1380 cm^{-1}. The absorption band at 1151 cm^{-1} can be attributed to the asymmetric stretching of the C-O-C bonds. The bands at 1063 cm^{-1} correspond to C-O stretching. Similar results are found in other studies (Vino et al., 2012; Song et al., 2013). As the amount of pine resin in the adhesive increased, the peak intensity observed at 2159 cm^{-1}, 2025 cm^{-1}, and 1974 cm^{-1} decreased. On the other hand, there was an increase in the C=O stress peak around 1600 cm^{-1}. In addition, the intensity of the peaks belonging to the CH_2 and CH_3 groups, found around 1380 cm^{-1}, was observed. All these changes are thought to be due to the interaction of pine resin and chitosan.

The bond strengths of the control and pine resin-reinforced chitosan-based adhesive applied to Scots pine wood are given in Fig. 4.

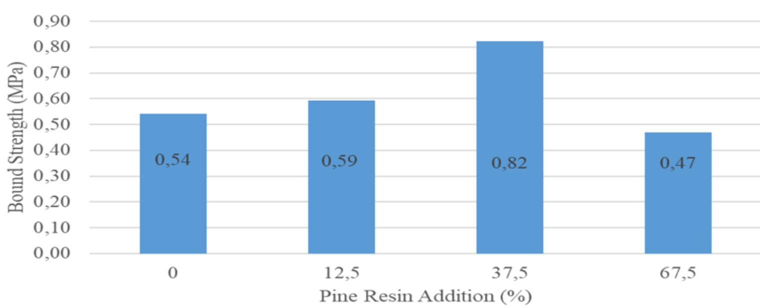

Fig. 4. The bond strength of the chitosan-based adhesive

The bond strength of chitosan-based adhesive varied between 0.47 MPa to 0.82 MPa. The highest value was obtained from CPA-2 with pine resin at %37.5 addition in the chitosan-based adhesive. CPA-3 gave the lowest bond strength value with 0.47 MPa. The bond strength of samples depended widely on the interaction between wood and adhesive. Wood has a tiny porosity. Typically, the roughness of the surfaces of adherents is of an upper order compared to this porosity. As a result of their low surface tension and adapted viscosity, chitosan solutions can penetrate deeply into these asperities. In wet conditions, positively charged chitosan (acid pH) interacts strongly with the negatively charged surface via electrostatic forces, van der Waals forces, and hydrogen bonds between D-glucosamine and the adherend or hydrated surface (Lee et al., 2013). Ji et al. (2017) produced MDF with an adhesive containing chitosan and glutaraldehyde. The bond strengths of the MDF were found to vary between 0.13 MPa and 1.22 MPa. On the other hand, the bond strengths of the adhesive produced from chitosan and lignin were between 0.9 MPa and 1.3 MPa (Ji and Guo, 2018). Patel et al. (2013) found the bond strengths of chitosan-based adhesives between 3.5 MPa and 6.1 MPa.

Conclusions

This work successfully produced novel adhesives that were fully biomass-based for wood. The viscosity of chitosan-based adhesive was found 1167 CP to 2871 CP. It was determined that the bond strength increased to 52% with the addition of pine resin compared to the control group. Also, it was found that the addition of excessive pine resin (CPA -3) had a negative effect on the bond strength. Although the chitosan-based adhesive has promising results, it is required to improve the mechanical properties using a crosslinker. Bond strengths will be evaluated in cold and hot water. In addition, the interaction between wood and adhesive will be examined with FTIR and Raman Spectrometer.

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