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STUDY ON THE PERMEATION AND FIXATION OF ACQ-C IN POPLAR

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ABSTRACT

In this paper, the effects of atmospheric pressure, vacuum and vacuum pressure impregnation on the permeability of alkaline copper quat in poplar were studied, and the permeability and fixation of preservatives were improved by pretreatment of poplar. The results show that the volume loading of wood can be increased by about 60 - 150% after 30 min of vacuum treatment, so the vacuum method is a simple and efficient preservation treatment method. In addition, ethanol treatment, heat treatment and microwave treatment can increase the fixation rate of copper ions by 5 - 10%, but the fixation rate of copper ions dropped by 17.83% after NaOH treatment for the dissolution of partial hemicellulose.

KEYWORDS: Fixation, permeation, preservation, alkaline copper quat, poplar.

INTRODUCTION

The permeation and fixation of preservatives in wood seriously affect the preservative effect of wood. Permeability and fixation are not only related to the preservation treatment process, but also affected by the chemical groups and microstructure inside the wood.

Alkaline copper quat (ACQ) is a commonly waterborne preservative with good permeability and handling in wood (Dhyani et al. 2012, Morris et al. 2017, Qin et al. 2019, Sivrikaya et al. 2017, Yu et al. 2011). However, the loss of copper ions and some ammonium species deteriorates the resistance of the wood because of the active ingredient in ACQ is soluble in water (Druz et al. 2001, Li et al. 2006, Civardi et al. 2015, Tang et al. 2018). In production, the volume loading of ACQ in the wood was improved by increasing the pressure, and classify the wood's corrosion resistance level (Liu et al. 2019, Yildiz et al. 2010, Jin et al. 2016). In fact, large volume loading does not guarantee better durability of the preservative wood, because these processes cannot improve the fixation of ACQ in wood (Tascioglu and Tsunoda 2012). Many scholars are dedicated to studying the fixation of preservative in wood (Stirling et al. 2015, Yu et al. 2013). Tascioglu used ACQ and ethanolamine copper (CuMEA) to treat Red pine sapwood and found that the fixation rate of copper in the treated material can significantly increased at temperature of 50°C (Tascioglu et al. 2005). Gao prepared three different kinds of ammonia-soluble copper alkylammonium, and carried out wood anti-corrosion and anti-leak experiments (Gao et al. 2005). It was found that the fixation rate of ACQ in neutral environment (distilled water extraction) reached 75%. The fixation rate in acetic acid extraction and alkali ammonia extraction environment is significantly reduced. Maria et al. (2013) conducted a leaching experiment on *Pinus sylvestris* treated with CBA (copper-boron) preservative and found that copper leaching is the result of complexation reaction. Tebuconazole interacts with hydroxyl groups in wood and is affected by the effect of pH. Lee studied the adsorption and cation exchange capacity of ethanolamine copper (Cu-MEA) in wood, and found that the cation exchange capacity of Red pine increased with the increase of pH (Lee et al. 2010). At the same time, the project team used ERP method to study the dissolution and reaction of copper ions in ultra-fine copper treated wood. It was found that copper in basic copper carbonate can form chemical bonds rapidly with wood and has good resistance to loss (Lee et al. 2012). The above findings indicate that the penetration and fixation of the preservative is related to the type and characteristics of the wood. Poplar is commonly used fast-growing tree species, which is susceptible to decay, but how to improve the fixing effect of preservatives in poplar is still blank.

This paper studied the effects of production process and pretreatment method on the penetration and fixation of ACQ-C in poplar, and provided theoretical basis for improving the traditional wood anticorrosion process, improving the antiseptic effect of ACQ anticorrosive wood and reducing production cost.

MATERIAL AND METHOD

Materials

Poplar (*Populus russkii* Jabl.), obtained from the Wulumuqi region of Xinjiang Province) was 20 years old and the diameter was 200-230 mm. The density of poplar was 0.45 $g \cdot cm^{-3}$, and the moisture content of the panels was adjusted to 12%. The sapwood was sawn into a 20 × 20 × 20 mm piece, and placed at a constant temperature of (20 ± 3)°C and a relative humidity of (65 ± 5)%. The concentration of the ACQ-C was 15% (Guangdong Academy of Forestry, where the mass fraction of CuO and BAC (Dodecyl benzyl dimethyl ammonium chloride) are 66.7% and 33.3%, resp.). The ACQ-C was diluted with distilled water to the specific concentration required for the test in subsequent experiments.

Impregnation process

The wood was impregnated by atmospheric pressure, vacuum and vacuum pressurization, and the impregnated test piece was washed by water to investigate the amount of copper ions absorbed and fixed in the wood.

In normal pressure impregnation, the concentration of ACQ-C was diluted to 1.8%, 3.0%, 4.2%, and 5.4%, respectively, and the test piece was placed in a glass beaker containing 200 ml of ACQ-C, with 5 samples each group. A glass block was placed on the test piece to prevent the wood from floating, and the beaker was sealed with a plastic film, and allowed to stand at room temperature (about 25°C) for 12 h. In the vacuum impregnation method, the vacuum degree is set to -0.1 MPa and applied for 30 min, then 200 ml ACQ-C is sucked into the treatment tank to completely immerse the wood, and stand at room temperature for 2 h. The pressure of vacuum pressure impregnation was 0.5 MPa, and the immersion time was 2 hours.

In this study, volume loading was defined by Eq. 1:

$$A = [(G_1 - G_0) \times C / V_1] / 10^{-6} \quad (1)$$

where: A is the volume loading (kg·m^{-3}), G_1 is the mass of wood after impregnation(g), G_0 is the mass of wood before impregnated (g), V_1 is the volume of the wood after immersion (mm^3), and C is the concentration of the ACQ-C (%).

The wood was immersed and stirred in distilled water and the distilled water was replaced at intervals of 6 h, 8 h, 24 h and 48 h then collect the filtrate until 14 days, and detected the copper ion content by atomic absorption spectroscopy (Spectr AA 220FS/220Z, USA), which was consulted to American AWPA standard E11-97.

Effect of pretreatment on impregnation and fixation

The poplar specimens were treated with NaOH, ethanol extraction, heat treatment and microwave treatment respectively, and then were immersed in ACQ-C by vacuum method and investigate volume loading and copper ion fixation rate. NaOH pretreatment: Wood pieces were immersed in 200 ml of 1% NaOH solution and treated in a 90°C water bath for 1 h, 2 h, 2.5 h, 3 h. Ethanol extraction pretreatment: Wood pieces were immersed in 500 ml of ethanol solvent, and extracted in a constant temperature water bath of 70-80°C for 1 h, 2 h, 3 h, 4 h. Heat treatment: Wood pieces were placed in a constant temperature drying oven at 100°C, 120°C, 140°C, 160°C for 2 h. Microwave pretreatment: Wood pieces were placed in a microwave oven with microwave power of 700 W, 350 W, and 100 W, the processing time of each group was 30 s, 80 s, and 120 s, respectively.

RESULTS AND DISCUSSION

Effect of impregnation process on volume loading

It can be seen from Fig. 1 that the volume loading of poplar increases with the increase of ACQ-C concentration, and vacuum treatment can significantly increase the volume loading. The volume loading by vacuum impregnation was increased by 166.3%, 82.8%, 61.6%, and 86.9%, when the concentration of ACQ-C solution was 1.8%, 3.0%, 4.2%, and 5.4%, resp. A partial vacuum is created inside the wood under vacuum, thereby creating a pressure drop inside and outside the wood, by which ACQ-C enters the wood. The vacuum pressure impregnation has a small increase compared to the vacuum impregnation, but it is not significant.

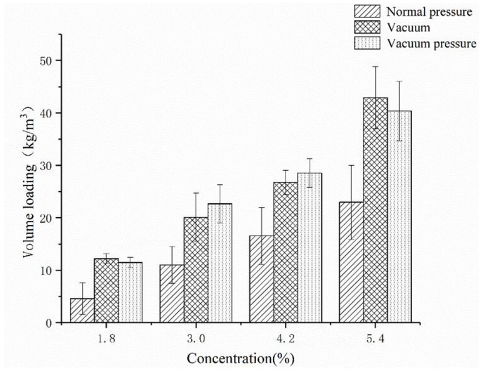

Fig. 1: Volume loading of poplar.

The effect of pretreatment on volume loading

In Fig. 2a, the volume loading of poplar increased by about 6% ~ 20% after NaOH treatment. When the time increased from 1 h to 2.5 h, the volume loading increased from 22.56 kg·m^{-3} to 25.95 kg·m^{-3}, but the amount of volume loading began to decrease after more than 2.5 h.

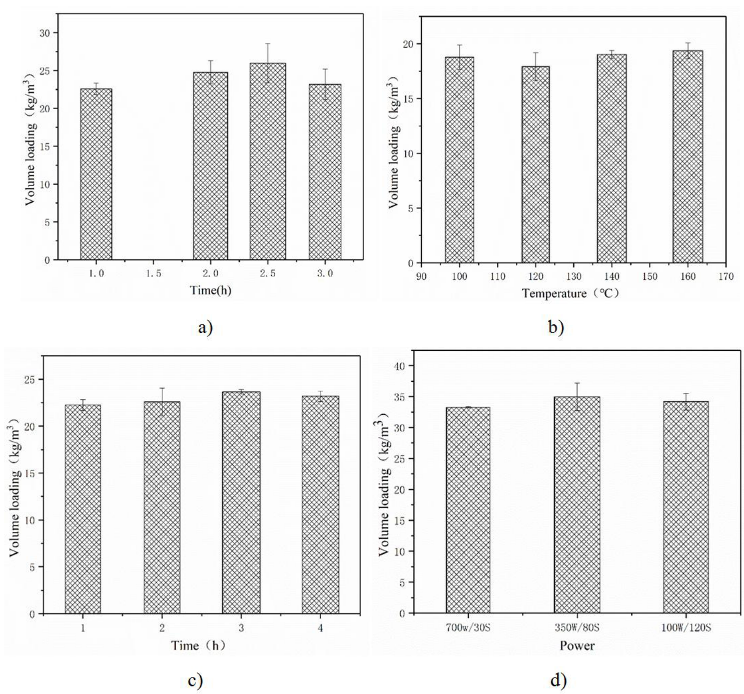

Fig. 2: Effect of pretreatment on the volume loading: a) NaOH pretreatment, b) heat treatment, c) ethanol extraction, d) microwave treatment.

Some hydrogen bonds on the cell wall are opened by limited swelling after a short period of NaOH treatment, so the hydrophilic and permeable of wood is increased with the increase in the number of hydroxyl groups. However, the lignin and hemicellulose degrade in some degrees, and the crystallinity increases, which destroys the inherent strength and morphology of the fiber. The volume loading is reduced because of the weaken of the capillary and microcapillary effects.

The heat treatment temperature in this experiment was 100°C-160°C. At lower treatment temperatures, part of the extracted surface in the wood is volatilized and the lignin is softened, thereby affecting the permeability of the wood. However, the extracting components in poplar wood are less, so the heat treatment has little effect on the volume loading.

The volume loading of ACQ-C increased by 8.1%, 9.7%, 14.8%, and 11.7%, when the poplar extracting in ethanol solution at 70°C - 80°C for 1 h, 2 h, 3 h, and 4 h, respectively. That was shown in Fig. 2c. After ethanol treatment, most of the pores are still in the middle position, and the occlusion rate of pores can be kept as low as that of the raw material state. So the ethanol extraction dissolves resin, tannins, pigments, some carbohydrates, and trace amounts of lignin in wood (Chen 1994). The crust material on the pore film is reduced, at the same time, the internal passage of the wood is smoother because the loss of invading material, so that the permeability and diffusibility of the wood are improved, and the volume loading is increased.

The volume loading of poplar increased by 47.38%, 54.96% and 51.55% after microwave treatment of 700 W/30 s, 350 W/80 s and 100 W/120 s, respectively, as shown in Fig. 2d. Microwave radiation generates electromagnetic fields that are frequently alternating, which causes the water molecules in the wood to rotate rapidly, rub each other, and generate heat, so the water to evaporate quickly (Jiang et al. 2006). In a short period of time, a large amount of water vapor generated inside the wood cannot be discharged in time, which will cause an impact on the interior of the wood. The impact destroys some weak parts such as cell walls or pits and creates cracks. These cracks are new channels, which improve the permeability of wood.

Fixation of copper ions

In Tab. 1, the copper ion fixation rate attended more than 80%, which was treated by the ethanol extraction, heat treatment and microwave.

Tab. 1: Fixation rate of effective components (Cu) in different pretreatment methods.

	NaOH pretreatment	**Heat treatment**	**Ethanol extraction**	**Microwave treatment**	**Control**
Copper ion fixation rate (%)	56.37	80.51	80.06	84.87	74.20
Volume loading ($kg \cdot m^{-3}$)	28.93	20.24	23.93	33.58	20.60

However, the copper ion fixation rate in wood decreased by about 20% after NaOH treatment. The main active ingredient of ACQ-C is copper and dodecyl benzyl dimethyl ammonium chloride (BAC), which can be dissolved in an amine/aqueous ammonia solution to form a stable amine/ammonia-copper system. Ethanol treatment can produce more carboxyl groups in the cellulose and provide more fixation points for the amine/ammonia-copper system, thereby increasing the fixation rate of copper ions. In addition, hemicellulose in wood is easily hydrolyzed to form acetic acid in a high-temperature, high-humidity treatment environment (Li et al. 2009). In an acidic environment, copper ions are dissolved in ethanolic ammonium in ACQ-C, which can carry out acidic ion exchange reaction with substances in the cell wall, that is, copper ions in the wood can displace H+ in the acidic place and form water-insoluble compounds with cell wall material to fix in wood. Therefore, the fixation rate of copper is increased. The

NaOH treatment dissolves the low degree of polymerization of cellulose, hemicellulose and other saccharides in the amorphous region of the wood while improving the permeability of the wood. Therefore, the dissolution of hemicellulose reduces the effective fixation point of copper ions. At the same time, alkali treatment converts some of the amorphous regions in the wood cellulose into crystalline regions (Yang et al. 2010), and the crystallinity of the wood is improved.

It can be seen from Fig. 3 that the peak of poplar at 1736 cm^{-1} disappears after NaOH treatment, and this portion just reflects the characteristic peak of C = O on the acetyl group and the carboxyl group which are different from the other components in hemicellulose. This indicates that partial hemicellulose is dissolved by the action of NaOH, so that the main medium capable of fixing copper ions is reduced, which is in agreement with the results analyzed above.

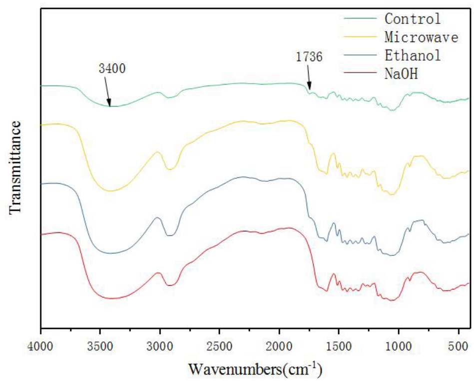

Fig. 3: Infrared spectrum of poplar.

The vibration absorption peak was R-COOH at 1750 cm^{-1} - 1770 cm^{-1}, after ethanol treatment, the peak appeared at 1751 cm^{-1} because ethanol treatment produced more carboxyl groups in the cellulose and increased the fixation rate of copper ions.

CONCLUSIONS

The volume loading of wood can be increased by about 60 - 150% after 30 min of vacuum treatment, and it is not much different from the volume loading by vacuum pressure but much higher than normal pressure. So vacuum impregnation is a good handleability method. Proper pretreatment can not only significantly increase volume loading, but also affect the fixation of copper ions. Ethanol treatment, heat treatment and microwave treatment can increase the fixation rate of copper ions by 5.86%, 6.31%, 10.67%, respectively. New cracks in microwave processing provide new channels for wood and increase wood permeability. But the fixation rate of copper ions dropped by 17.83% after NaOH treatment because of the dissolved of partial hemicellulose. Therefore, the wood can be pretreated before the impregnation treatment, which can improve the fixation effect of copper ions in the wood and improve the anticorrosive performance.

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