Reaction mechanism of carboxymethyl starch-based wood adhesive

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Abstract

The technology involved in manufacturing carboxymethyl starch-based adhesive was studied with the aim of enhancing its water-resistance. The optimum formula was based on previous research using a quadratic orthogonal rotation combination design to synthesise the carboxymethyl starch-based wood adhesive. Compared with the original starch, carboxymethyl starch improves the performance of starch adhesive due to its advantageous properties such as hydrophilicity and stability during freezing and thawing etc. Infrared spectroscopy and scanning electron microscopy were used to analyse the synthesis of the carboxymethyl starch-based adhesive. Many functional groups could be identified by their characteristic Fourier transformation infrared vibration frequency and this was used to explain the structural changes. At the same time, the microstructure of the adhesive was analysed by scanning electron microscopy (SEM), and porous, round or elliptical granules in the carboxymethyl starch were observed. An SEM of the main starch agent revealed a network structure; the granules did not aggregate together to form large groups due to the polyvinyl alcohol that prevented granule agglomeration. However, the SEM of the starch adhesive showed a smoother and more compact network structure, due to the large number of strong chemical bonds that were formed by the association of isocyanate with the main starch agent.

Keywords: carboxymethyl starch, wood adhesive, optimisation, mechanism

1 Introduction

In recent years, sustainability has gained greater attention due to the world’s heavy dependence on petroleum and natural gas for energy and various products; the development of alternatives to petrochemical-based products from renewable materials improves sustainability [1]. At present, urea-formaldehyde resin, phenolic resin and melamine formaldehyde resin are still widely used to synthesise wood adhesives; however, these are not sustainable in the long run. Furthermore, the emission of carcinogenic formaldehyde during their production has been a serious concern in recent years [2-4]. Natural resources have unique properties and advantages. Starch is an abundant natural polymer that is excellent for use in the manufacture of wood adhesives. For a long time, starch has been used as an additive in conventional adhesives [5-7] because it is easily obtained, the process is simple, it is easy to operate, it is low cost, gives good adhesion and is environmentally friendly; it is therefore potentially a useful product to investigate [8]. Li Lixia [9] achieved the best operating parameters of wet strength adhesive after bonding wood materials and analysed the effects of the formula and synthesis technology using a quadratic orthogonal rotation combination design. Shi Junyou [10] investigated the bonding mechanism of the starch-based aqueous polymer isocyanate and birch wood using Fourier transformation infrared (FTIR) and electron spectroscopy for chemical analysis (ESCA). Wang Zhenjiong [11] analysed starch-based wood adhesive by FTIR, nuclear magnetic resonance (NMR) and SEM.

These studies on starch wood adhesive led to significant progress, but there are still some issues such as problems of low starch content and poor water resistance. Compared with the original starch, carboxymethyl starch can improve the performance of starch adhesive due to its advantages, including hydrophilicity and good stability during freezing and thawing etc. Therefore, in this paper we investigated the optimal formula for the preparation of carboxymethyl starch-based wood adhesive [9]. We aimed to reveal the reaction mechanism of the starch-based adhesive through comparative analysis using infrared spectroscopy and SEM to analyse the starch, the main agents of starch and the starch-based adhesive. The ability to enhance the water resistance of starch-based adhesives is of great importance.

2 Material

Material: carboxymethyl starch (Heilongjiang Longfeng Modified Corn Starch Factory); polyvinyl alcohol (1788, Tianjin Kemiou Chemical Reagent Development Centre); two-component polysocyanate emulsion adhesiv Prefere. 6150 (Taiier Chemical (Shanghai) Co., Ltd.); carboxylic butadiene-styrene latex Nipol LX473D (Shanghai Lishen Chemical Co., Ltd., Shanghai, China).

Instruments: HH.SY11-Ni electric-heated thermostatic water bath (Beijing Changfeng Instrument Company), JJ-1 type power basic stirrer (Jintan City, Jiangsu Province Medical Instrument Factory), three-necked flask (250 ml; Sichuan Shubo Co., Ltd.), thermometer (100 °C), measuring cylinder (100 ml), pipetting device (20–200 L; Shanghai Dragon Medical Equipment Co., Ltd.), JMI102 electronic

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balance (Yuyao Jining Weighing Electronic Balance and Check Equipment Co., Ltd.), VECTOR22 Fourier transform infrared spectrometer (Swiss Bruker company), Scanning electron microscope and E-1010 ion sputtering apparatus (Japan Hitachi company).

3 Methods

3.1 PREPARATION OF THE ADHESIVE

The optimum formula for carboxymethyl starch adhesive was based on previous research using a quadratic orthogonal rotation combination design to synthesise the starch-based wood adhesive [9].

3.2 FOURIER TRANSFORMATION INFRARED (FTIR)

The starch and the samples of carboxymethyl starch adhesive were fully milled in an agate mortar, and samples were prepared by grinding the finely powdered starch with potassium bromide. The mixture was then pressed into tablets before measurement. The IR spectra were obtained using a VECTOR22 IR Spectra Scanner, and they were recorded over a wave range of 400–4000 cm⁻¹.

3.3 SCANNING ELECTRON MICROSCOPY (SEM)

The carboxymethyl starch-based wood adhesive was synthesised using the optimal parameters from the above-mentioned experiment. A sample was placed on the carrier using a pipette, then it was solidified in a drying vessel. The dehydrated samples were coated with gold powder to avoid charging the sample under the electron beam. Finally, the microstructure was observed using a scanning electron microscope.

4 Results and discussion

4.1 ANALYSIS OF FTIR

Infrared spectroscopy was used to analyse carboxymethyl starch, carboxymethyl starch main agent and carboxymethyl starch-based adhesive; the results of IR spectra are shown in Figure 1 (Figure 1a, Figure 1b and Figure 1c).

The information on chemical structure from FTIR spectroscopy in Figure 1a shows a broad band at 3400 cm⁻¹ attributed to O-H stretching [12-14]. This is due to the hydroxyl groups present in the starch molecules, and indicates that these hydroxyl groups are not free; they form large amounts of intramolecular and intermolecular hydrogen bonds [5]. Meanwhile, the C-H stretching vibration gave a strong signal at 2890–2940 cm⁻¹ [15-17]. The peak at 1650 cm⁻¹ was attributed to C=O stretching [18-20], and the peaks at 1350–1450 cm⁻¹ were related to the C-H bending of CH₂ [21-23], this indicated that the hydroxyl groups of starch molecules were carboxymethylated. The results were consistent with previous reports concerning different kinds of carboxymethyl starch. The peaks at around 1160 cm⁻¹ and 1090 cm⁻¹ were characteristic of C–O–H in starch [24-26], while the peak between 990 cm⁻¹ and 1050 cm⁻¹ was attributed to C-O bond stretching in the C-O-C group [27-29].

A similar phenomenon was observed in the absorption peaks present at 928 cm⁻¹ for skeletal mode vibrations of glycosidic linkages (C–O–C) [30]. Bands at 850 cm⁻¹ were due to the C(1)-H deformation of CH₂ in the glucose unit, and the bands at 575 cm⁻¹ and 750 cm⁻¹ related to the C–C stretching of skeletal modes in the glucose unit, this observation is similar to the results of Joshi et al. [23, 30].

Compared with Figure 1a, the information of chemical structure from FTIR spectroscopy in Figure 1b shows a smaller peak at 3740 cm⁻¹; this was attributed to the free O-H stretching. The band, which was displaced at 3600 cm⁻¹, as a sharper and smaller peak in carboxymethyl starch main agent was the characteristic absorption peak for the stretching vibration of O-H groups because of the complex vibrational stretching associated with intramolecular and intermolecular bound hydroxyl groups. In addition, this peak had a high transmittance in the spectrum of carboxymethyl starch main agent attributed to the introduction of polyvinyl alcohol and carboxylic butadiene-styrene latex. The results indicated that the reaction of the hydroxyl and carboxyl weakened the peak intensity and wave number of hydroxyl absorption, and hydroxyl groups were blocked to proper lever in the carboxymethyl starch main agent. The band occurring at 2350 cm⁻¹ was most probably due to the presence of carbon dioxide in test samples. The absorption bands at 1680 cm⁻¹ were attributed to C=O stretching and this is consistent with the results of Machová et al. [31, 32], indicating the presence of carboxyl in the samples. It was also observed that the absorption peak present at 1525 cm⁻¹ was characteristic for benzene [33-35], and the peaks at 1800–1950 cm⁻¹ indicated the vibrating property of monosubstituted benzene derivate, suggesting the presence of carboxylic butadiene-styrene latex. The presence of the carboxyl group and phenyls made significant improvements in the viscosity and adhesive strength of the polymer and thus improved the property of the adhesive.

The absorption bands between 2310 and 2350 cm⁻¹ were ascribed to - NCO antisymmetric stretching vibration (see, Figure 1c) and a large number of strong chemical bonds were formed by the association of –NCO groups and carboxymethyl starch main agent, which improved the wet strength of the adhesive. It was also observed that absorption peaks were present at 1550 cm⁻¹ for N-H bending deformation and C-N antisymmetric stretching vibration [36, 37]. The peaks at 1700 cm⁻¹ and 1650 cm⁻¹ were attributed to the C=O stretching vibration [38, 39]. Moreover, the broad band at 1250 cm⁻¹ was attributed to N-CO-O asymmetric stretching vibration, indicating the introduction of isocyanate. This significantly increased the viscosity and wet strength of the adhesive.
4.2 ANALYSIS OF SEM

The microstructure of starch-based adhesive that was analysed by scanning electron microscope is shown in Figure 2. As can be seen in Figure 2a, round or elliptic shaped granules were present in the cornstarch [40-43] and the surface of the cornstarch had a smooth, full and compact structure [44-46]. The starch granules appeared to agglomerate due to the strong interaction of intermolecular and intramolecular hydrogen bonds in the starch molecules [47]. Compared with Figure 2a, carboxymethyl starch (see, Figure 2b) was still present in a granular form and it was similar in shape to the corn starch. However, holes were apparent on the surface of granules that increased the surface area thus improving solubility and adsorption. This observation suggests that the starch crystallinity was altered, thus allowing the etherifying
agents to have more access to the starch molecules for the carboxymethylation processes [48, 49]. The changes observed on the modified starch granules were also due to the breakage of chemical bonds in starch molecules affected by the strong alkaline environment together with heat treatment, this means that the carboxymethyl reaction took place both on the surface and within the starch granules [50]. The network structure following the introduction of a carboxyl group, benzene and polyvinyl alcohol can be seen in Figure 2c. This significantly improved the viscosity and adhesive strength of the polymer and improved adhesive properties. Each granule still maintained its individual entity but the granules did not agglomerate to form large groups (see, Figure 2c). This was due to the polyvinyl alcohol, which prevented granules agglomerating and accelerated the emulsifying process. When compared with Figure 2c, the much smoother and more compact network structure can be seen in Figure 2d. The starch adhesive was highly compatible because the uptake of isocyanate greatly improved the adhesive strength. The isocyanate was uniformly distributed in the water-soluble solvent of emulsifying by polyvinyl alcohol as long as it was reacting with the main agent and then forming solid amine fat keys, urea key chemical bonds and so on. Subsequently, these chemical bonds reacted with hydrogen, forming a network of structural molecules that increased the wet strength.

5 Conclusions

1) FTIR of carboxymethyl starch revealed a broader band at 3400 cm\(^{-1}\) attributed to the large number of hydrogen bonds that were formed by the association of hydroxyl and carbonyl. The C-H stretching vibration gave a strong signal at 2890-2940 cm\(^{-1}\) and the primary and secondary alcohols of the bands at 990-1160 cm\(^{-1}\) indicated C-O stretching. The FTIR of carboxymethyl starch main agent showed absorption bands at 1680 cm\(^{-1}\) attributed to C=O stretching, thereby indicating the introduction of carboxyls. It was also observed that the absorption peaks present at 1525 cm\(^{-1}\) were characteristic of benzene, and the peaks at 1800–1950 cm\(^{-1}\) had the vibrating property of monosubstituted benzene derivative; this indicated the introduction of phenyl of carboxylic butadiene-styrene latex. The introduction of polyvinyl alcohol and carboxylic butadiene-styrene latex made the viscosity and adhesive strength of the polymer increase significantly and thus improved the adhesive property. The FTIR of carboxymethyl starch adhesive absorption bands at 2310 -2350 cm\(^{-1}\) were ascribed to the - NCO antisymmetric stretching vibration, and isocyanate was introduced into the carboxymethyl starch adhesive.

2) Round or elliptic shaped granules appeared in the carboxymethyl starch and the granule surfaces became pocked with a number of holes. The carboxymethyl starch granules appeared to become agglomerated due to the strong interaction of the intermolecular and intramolecular hydrogen bonds of the starch molecules. The SEM of carboxymethyl starch main agent presented a network structure; however, each granule maintained its individual entity while the granules did not bind together to form large groups as compared with Figure 1b. This was due to the polyvinyl alcohol that prevented granule agglomeration and improved stability. In addition, the SEM of the carboxymethyl starch adhesive displayed a smoother and more compact network structure, due to the large number of strong chemical bonds that were formed by the association of isocyanate and the starch main agent.
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