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In-situ chemical structure analysis of aqueous vinyl polymer solution-isocyanate adhesive in post-cure process by using Fourier transform near infrared spectroscopy

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ABSTRACT

API (aqueous vinyl polymer solution-isocyanate) adhesive was prepared from PVA (polyvinyl alcohol) aqueous solution, SBR (styrene-butadiene rubber) latex and pMDI (polymethylene polyphenyl polyisocyanate). A paper sample was prepared by sandwiching API adhesive between two pieces of filter paper, which could be regarded as the model for an actual bonded structure in a practical application. In a post-cure process an *in-situ* chemical structure analysis of the adhesive layer in the paper sample was carried out using FT-NIR (Fourier transform near infrared) spectroscopy. The absorption bands of urea and urethane, two primary products generated from the chemical reactions of isocyanates, were assigned on a 2nd derivative spectrum at 5005 cm^{-1} and 5065 cm^{-1}, respectively. Band intensities of urea and urethane increased with time during the post-cure process, indicating the advance of chemical reactions in the adhesive layer. DSC was utilized to analyze the thermal properties of the API adhesive film sample, together with the cross-linking density in the API adhesive film sample which was tested using DMA. In addition, FT-IR spectroscopy was used to confirm the chemical reactions of isocyanate in the API adhesive thin film sample.

1. Introduction

In the building industry, wood construction has been widely use due to the various benefits such constructions can provide relating to, for example, aesthetic and artistic attributes, thermal insulating characteristics and environmental considerations. Furthermore, in order to deal with the increasing forest thinning, small-diameter wood and process residue are normally taken into account. For example, plywood, glulam and particleboard, which can be manufactured from small-diameter wood or wood chip with adhesive, has been utilized. API (aqueous vinyl polymer solution-isocyanate) adhesive is an environmentally friendly wood adhesive which does not exhibit formaldehyde release during cure and use and also has the advantage of water resistance in comparison with UF (urea-formaldehyde) resins and moderate temperature curing in comparison with PF (phenol-formaldehyde) and epoxy resins. In the 1940s, isocyanate was first employed in industrial production for the synthesis of polyurethanes in Germany, and thereafter the application has been expanded around the world. In 1971 API adhesive was developed by Kuraray Co., Ltd, Koyo Sango Co., Ltd and Asahi Plywood Co., Ltd in Japan, and which is currently used for the manufacture of glulam, plywood, etc. The high reactivity of NCO (isocyanate) allows it to react with labile hydrogens, generating chemical bonding strength not only within an adhesive but also between adhesive and adherend. API adhesive is a two-component system, comprising an aqueous soluble polymer based emulsion and an isocyanate based cross-linker.

API adhesive has excellent bonding characteristics which can give bonding strength to both wood-wood and metal-wood bonded structures [1]. NCO reacts with a variety of functional groups such as hydroxyl, amine, amide and, even, itself forming dimer and trimer (Scheme 1) [1,2]. The reaction between NCO and water has the highest reaction rate, forming carbamic acid which soon releases carbon dioxide and generates amine. At last urea is formed in the reaction between amine and another NCO. The other primary reaction takes place between NCO and hydroxyl producing urethane, to which a lot of attention has been paid in consideration of the chemical bonding generated between adhesive and adherend [3]. The generation rate of urea is much higher than that of urethane due to the much better mobility of water, and this phenomenon has been confirmed in previous research [4,5]. Biuret and allophanate generated from reactions between urea or

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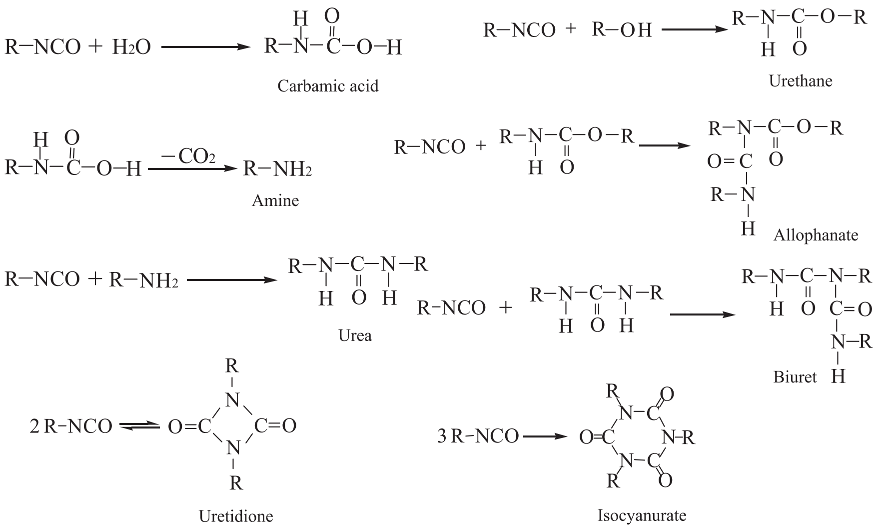


Scheme 1. Reactions of NCO, R: any functional group not reacting with NCO.

urethane with NCO, and uretdione and isocyanurate generated from the self-reactions of NCO are regarded as by-products and barely occur at room temperature [6].

The reactions of NCO mentioned above give API adhesives potential for various applications, but the complicated cross-linking structure attributed to these reactions makes the analysis of chemical structure very difficult. Patel et al. assigned bands at 1700 cm^{-1} and 1270 cm^{-1} to urethane linkages, whilst bands at 1640 cm^{-1} and 1255 cm^{-1} have been attributed to urea linkages in poly (urethane-urea)s [7]. Gao et al. used the $C{=}O$ stretching vibration band of urethane at 1705 cm^{-1} to confirm the cross-linking reaction in whey protein-based aqueous polymer API adhesive [8]. The reaction between isocyanate and wood was studied using NMR, where 99% ^{15}N-1abelled polymeric methylenebis (phenylisocyanate) resin was sandwiched between two pieces of wood flakes and ^{15}N CP/MAS NMR had been performed on resin-wood powder by Wendler and Frazier [9]. According to their results, biuret was produced more at high temperature or low wood moisture, however a urethane band in the NMR spectrum was indefinite because of the covering effect of a urea band. He et al. researched the reactions between NCO and wood using differential scanning calorimetry and clarified that wood moisture could affect the reactivity of NCO [10]. The rheological characteristics of API adhesive films under elevated temperature have been studied by Ling et al. [11]. Nevertheless, all previous research has barely covered the *in-situ* chemical structure analysis of an API adhesive layer following a post-cure process. Post-cure is an important process for an API adhesive, in which physical and chemical interactions arise between molecular chains, contributing to an increase in bonding strength. API adhesive solidification over a 24h period following application to an adherend, has been attributed to water evaporation and NCO reactions. Post-cure processes after 24 h have been shown to occur, lasting for several days, via reactions involving NCO, generating urea, urethane, etc. [12].

In this study, the *in-situ* chemical structure analysis of an API adhesive layer sandwiched between two adherends was carried out using FT-NIR (Fourier transform near infrared) spectroscopy. On account of the admirable transmitting ability, FT-NIR was performed directly on raw samples without any pretreatment. FT-NIR detects the overtone and combination tone of fundamental vibrations [12,13] and band overlapping arises significantly, so derivative calculation is normally utilized to enhance the resolution [14].

2. Experimental

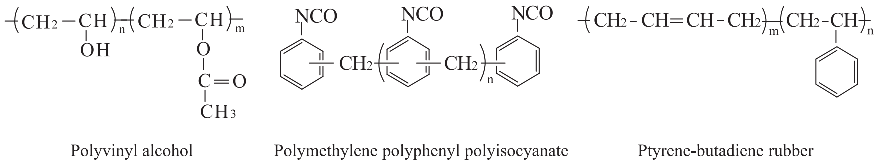
2.1. Materials

PVA (polyvinyl alcohol), with a degree of saponification of 99.1% and a M_W of 1 × 10^4 g/mol, was purchased from Wako Chemicals (Japan). SBR (styrene-butadiene rubber) latex was used as a softener, supplied by NIPPON A & L (Japan), with a solids content of 51.7% and a styrene/ butadiene mass ratio of 3/7. pMDI (polymethylene polyphenyl polyisocyanate, MR-200), supplied by Nippon Polyurethane (Japan) had an NCO content of 30.5-32.0% (Scheme 2). Filter paper (Whatman) made of 100% cellulose had a thickness of 0.2 mm. Teflon sheet (thickness 2mm) and vinyl tape (thickness 0.2mm) were also used. All water used in this experiment was purified by using Elix UV 3/5/10 (Millipore, Japan). Phenyl isocyanate (Wako Chemicals, Japan) and N, N-dimethylformamide (Wako Chemicals, Japan) were used to prepare the urea model compound, DPU (1, 3-Diphenylurea). 4, 4'-diphenylmethane diisocyanate (Wako Chemicals, Japan), 2-butanol (Wako Chemicals, Japan) and n-hexane (Wako Chemicals, Japan) were used to prepare the urethane model compound, MUT (di-2-butyl 4, 4'-diphenylmethane dicarbamate).

2.2. Preparation of API adhesive [12]

PVA aqueous solution: 15 g PVA powder was added into a three-neck flask with 85 g water. The mixture was stirred for 4 h at ≈95 °C and then for 14 h at room temperature.

API adhesive: 3 g PVA aqueous solution and 3 g SBR latex were mixed together in a plastic container (50 ml), stirred for 1 min and degassed for 30 s using a Hybrid Mixer HM-500 (Keyence, Japan). Then 1.5 g pMDI was added into the PVA-SBR mixture, stirred for 2.5 min and degassed for 30 s.



Scheme 2. Three raw materials used for the preparation of API adhesive.