

論文の内容の要旨

生物材料科学専攻

平成 26 年度博士課程進学

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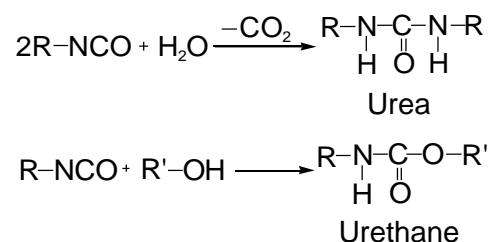
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論文題目： *In-Situ* Chemical Structure Analysis of Cured Glue-Line of Aqueous Vinyl Polymer-Isocyanate Adhesive for Wood Using FT-NIR and FT-IR Spectroscopy

(FT-NIR および FT-IR による水性高分子-イソシアネート系木材接着剤の接着層の *in-situ* 化学構造分析)

Chapter 1: Introduction

Aqueous Vinyl Polymer-Isocyanate Adhesive for Woods (API adhesive) is prepared by using aqueous polymer solution or water-based emulsion as base resin and isocyanate component as cross-linker. API adhesive is one of environmentally friendly adhesives and which is used for furniture and housing construction. After the application onto wooden adherends, water in API adhesive evaporates and permeates into wood gradually. In the meanwhile, NCO reacts with labile hydrogen. This process, ‘curing’ of adhesive, normally takes about 24h. After that, API adhesive solidifies into glue-line. NCO reactions (Scheme 1) still can carry on in glue-line, forming urethane and urea then leading to the increasing of mechanical property. This process is called ‘post-curing’. FT-NIR spectroscopy detects only the overtone and combination tone of chemical bond fundamental vibration. Compared with IR, NIR light has admirable transmitting ability that allows it to be performed on un-pretreated sample.



Scheme 1. Main NCO reactions in API adhesive glue-line.

In this study, chemical and physical properties of cured API adhesive film were studied by using FT-IR and DMA first to confirm the formation of cross-linking structure. In addition, the increasing of bond strength during post-curing was confirmed by cross-lap testing. After that, the chemical structure variation of API adhesive in glue-line sandwiched between two adherends was studied by using FT-NIR. In order to obtain a stronger post-cured glue-line, the influences of aging conditions and adhesive components on chemical structure were studied. Finally, to better understand the bonding mechanism of API adhesive to wood, the product of NCO-cellulose reaction was studied by using FT-IR.

Chapter 2: Post-Curing Process of API Adhesive

In this chapter, three materials, PVA, SBR and pMDI, were used to prepare API adhesive. FT-IR, TGA, DSC and DMA were used to

study the chemical structure and physical properties of post-cured API thin film and API film. Bond strength of API adhesive was also measured by using cross-lap testing.

Experimental: PVA aqueous solution (base resin), SBR latex (base resin), and pMDI (polymethylene polyphenyl polyisocyanate) (cross-linker) were mixed to prepare API adhesive. Then, API adhesive was used to prepare API film (thickness of 0.2mm), API thin film (thickness of 0.03mm) and cross-lap adhesive tests.

Results and Discussion:

By using DMA test, rubbery plateau was observed on storage modulus, where cross-linking density was calculated. DMA result indicated that the density of cross-linking increased with post-curing time. The chemical structure variation of API thin film during post-curing process was confirmed by using FT-IR spectroscopy (Fig. 1). Band decreasing at 2274cm^{-1} (N=C=O asymmetric stretching) implied the consumption of NCO. C=O stretching bands of urethane and urea, two products of NCO reactions, were detected at 1715cm^{-1} and 1639cm^{-1} , respectively. Besides, urea band intensity increased faster than urethane band intensity, where NCO-H₂O reaction is faster than that of NCO-hydroxyl. The result of cross-lap test indicated that urethane and urea generations during post-curing process led to increasing bond strength.

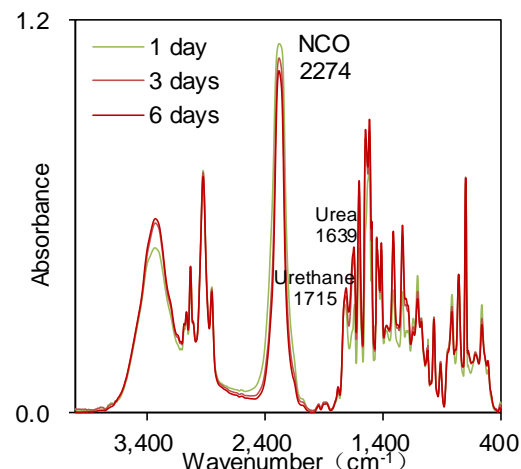


Fig. 1. FT-IR spectrum of aged API thin film.

Chapter 3: *In-Situ* Analysis of API Adhesive Glue-Line by Using FT-NIR Spectroscopy

The chemical and physical properties of post-cured API adhesive film were studied in chapter 2. However, post-cure of API adhesive normally occurred between adherends. In this chapter, two model compounds (MUT and DPU) were synthesized to assign the NIR absorptions of urethane and urea. In addition, to enhance resolution of FT-NIR spectrum, 2nd derivative spectrum was used. Then, API adhesive was sandwiched by two pieces of filter paper, and the chemical structure analysis of post-cured API adhesive in glue-line was carried out by using FT-NIR spectroscopy.

Experimental: Two model compounds, DPU (1, 3-Diphenylurea) and MUT (Di-2-butyl 4, 4'-diphenylmethane dicarbamate), were synthesized from phenyl isocyanate, water and 2-butanol. API adhesive was used to prepare API paper sample which had both glue-line and adherends. Temperature dependent FT-IR and FT-NIR spectroscopies were employed for band assignment since hydrogen bonded amide is sensitive to elevated temperature.

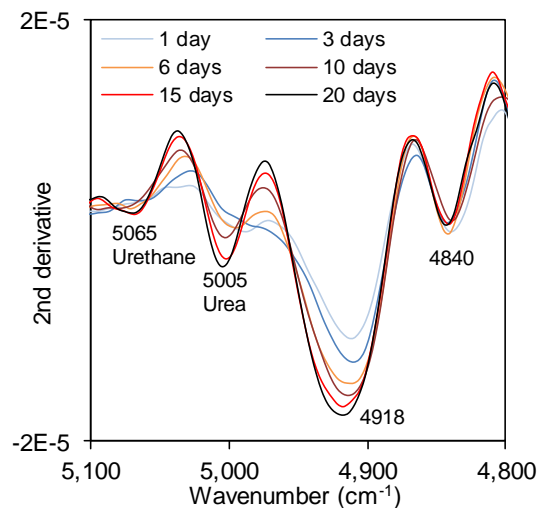


Fig. 2. 2nd derivative spectra of glue-line.

Results and Discussion:

Model compounds: Specific absorptions of urethane in NIR region were assigned at 5050cm^{-1} (N-H stretching/amide II combination tone), 4932cm^{-1} (C=O stretching second overtone) and 4867cm^{-1} (N-H stretching/amide I combination tone). Those of urea were assigned at 5019cm^{-1} and 4984cm^{-1} (N-H stretching/amide II combination tone or N-H stretching/N-H bending combination tone), 4935cm^{-1} (C=O stretching second overtone) and 4880cm^{-1} (N-H stretching/amide I combination tone).

API paper sample: The band assignments were carried out for API paper sample: 5065cm^{-1} was assigned to N-H stretching/amide II combination tone of urethane, 5005cm^{-1} was assigned to N-H stretching/amide II combination tone of urea, and 4918cm^{-1} was assigned to C=O stretching overtone of urethane and urea. Finally, the generations of urethane and urea in API paper sample during post-curing were tracked by using FT-NIR spectroscopy. The result indicated that urethane and urea were formed continuously from 1 day to 20 days during the post-curing process (Fig. 2).

Chapter 4: Influences of Adhesive Components and Aging Conditions on The Chemical Structure of API Adhesive Glue-Line

To investigate the practicability of FT-NIR test on glue-line, FT-NIR was used to study the influences of adhesive components and aging conditions on urethane and urea generating reactions. In addition, DMA and bonding test were also carried out.

Experimental: API adhesives were prepared in the same process as chapter 2 described. In this chapter, different PVAs and SBR latex mass ratios were used. Then, API adhesive was used to prepare API paper sample, API film and cross-lap bond strength. Variant humidity conditions (RH0%, RH50% and RH98%) and heat treatment (80°C) were also employed for sample aging.

Results and Discussion:

Different PVAs: At first, PVA with low DS (degree of saponification) was expected to mix and react better with pMDI. However, there was almost no disparity on the chemical structures of three PVAs based adhesives. The adhesive with high molecular weight PVA showed high bond strength.

Different SBR latex mass ratios: FT-NIR result demonstrated that the adhesive with less SBR latex produced more urethane and urea, due to high pMDI and PVA contents. After 6 days aging, cross-lap with less SBR latex content had been fully post-cured and thus displayed high bond strength.

Different humidity conditions: Aging humidity was found out to have significant influence on both chemical structure and physical property of glue-line. The glue-line aged in dry condition had much less urethane and urea (Fig. 3) generation amounts and showed worse bonding performance.

Heat treatment: After heat treatment, the amounts of the two linkages were increased, because high temperature was considered to accelerate NCO reactions. However, the generation rates of both urea and urethane decreased after heat treatment. This phenomenon could be explained as that cross-linking structure in glue-line restricted molecular mobility as well as NCO reactions. Cross-lap test also indicated that heat treatment increased bond strength.

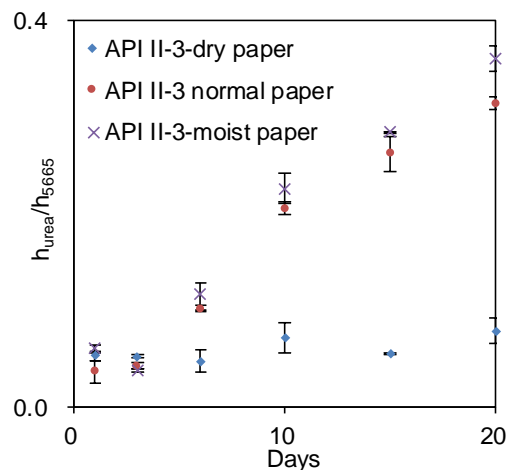


Fig. 3. Urea generations in glue-lines.

Chapter 5: Further Studies on NCO Self-Reactions and Urethane Generation Reactions

One advantage of API adhesive is considered as that NCOs can react with hydroxyls of wood components, forming urethane linkages between glue-line and wood. In addition, the reaction of between NCO and PVA hydroxyl inside API adhesive generates another type of urethane linkage. In this chapter, FT-IR spectroscopy was carried out to study those two urethanes, one generated from NCO-cellulose reaction and the other one generated from NCO-PVA reactions.

Experimental: Several compounds, including dimer, trimer and carbamates, were synthesized for FT-IR band assignment. Then, temperature dependent FT-IR spectroscopy was utilized to study the band variation under elevated temperature.

Results and Discussion:

NCO Self-Reactions: Dimerization and trimerization of NCO are very slow at room temperature. But those two reactions could not be ignored, especially for highly reactive aromatic isocyanate. FT-IR result indicated that dimerization of NCO processes slowly in API thin film during aging period.

Urethane Generation Reactions: Results of the carbamates suggested that firstly the thermal decomposition of urethane formed NCO and hydroxyl, then NCO thermal decomposition produce the substituted urea. Temperature dependent FT-IR was performed on pMDI-cellulose mixture to confirm the urethane linkage generated from NCO-cellulose reaction. Hydrogen bonded urethane band appeared at 1712cm^{-1} and non-hydrogen-boned urethane band appeared at 1730cm^{-1} . The bands of 1642cm^{-1} and 1660cm^{-1} are assigned to hydrogen boned urea and non-hydrogen-boned urea, respectively. Under elevated temperature, urethane and hydrogen bonded urea bands decreased, due to thermal decomposition and hydrogen bond dissociation. On the other hand, isocyanurate and substituted urea generations contributed to bands increasing at 1716cm^{-1} and 1660cm^{-1} (Fig. 4).

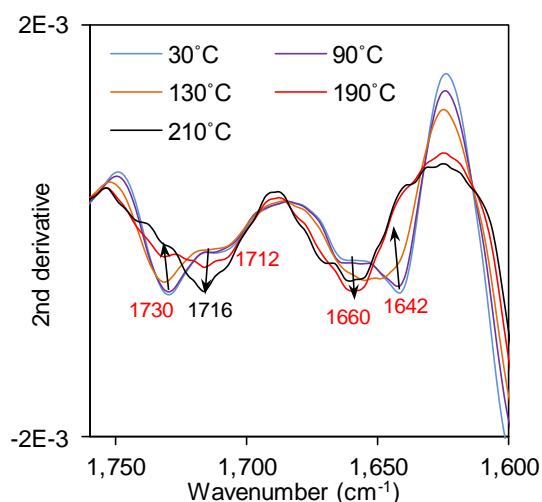


Fig. 4. Temperature dependent 2nd derivative spectra of cellulose-pMDI mixture.

Chapter 6: Summary

Residual NCO in cured API adhesive glue-line still can react with hydroxyls, forming chemical linkages and contributing to the increasing bond strength. In the experiment, FT-NIR spectroscopy was employed for the *in-situ* chemical structure analysis of glue-line. Further, the influences of adhesive components and aging conditions on the chemical structure of glue-line was studied. For better understanding of the bonding mechanism of API adhesive to wood, the reaction of between pMDI (cross-linker) and cellulose (one wood component) were confirmed.

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