

MODIFICATION OF POLYURETHANE FINISHING AGENT USING COLLAGEN HYDROLYSATE FROM CHROME SHAVINGS**

by

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ABSTRACT

Finishing with traditional polyurethane finishing agents often dramatically decreases the permeability of finished leathers. Continuing attempts have been made in recent years to develop aqueous polyurethanes (PU) finishing agents with better overall balance of properties while retaining characteristic high durability. Research in our industry has also included many studies to optimize use of the collagen available from chrome shavings. Collagen hydrolysate may contain a number of hydrophilic groups such as carboxylic, hydroxylic, amino, imino, and amide. The reactions between these collagen hydrolysate active groups and the urethane reactive groups (-NCO) resulted in the synthesis of new polyurethane finishing agents which offered increased permeability. The optimum collagen hydrolysate modifying condition for this polyurethane finishing agent was found to be: DMPA, 5% of the monomers by weight, reaction temperature of 80°C and reaction time of 2.5 hours. When the collagen hydrolysate is in the range of 0.6-0.8% of IPDI by weight, a range of good properties is achievable. For example, when collagen hydrolysate is 0.6% of IPDI by weight, the modified polyurethane finishing agent has high strength appropriate for use in basecoat or topcoat finishes. When the collagen hydrolysate is 0.8% of IPDI by weight, the modified polyurethane finishing agent has good elongation at break and extensibility, indicating a potential application in leather sealing finishes.

RESUMEN

El acabado con los tradicionales agentes de poliuretano muy a menudo disminuyen dramáticamente la permeabilidad [a los gases] de los cueros terminados. Continuados intentos se han efectuado durante los últimos años para desarrollar agentes de acabado basados en poliuretanos (PU) acuosos con propiedades más ecuanimes, pero reteniendo su característica alta durabilidad. Investigación en nuestra industria ha incluido muchos estudios para optimizar el uso del colágeno disponible desde rebajaduras de cuero al cromo. Hidrolizados del colágeno podrían contener un número de diversos grupos hidrófilos tales como carboxilo, hidroxilos, amino, imino y amida. La reacción entre estos grupos activos en los hidrolizados y los grupos reactivos en los uretanos (-NCO) resultó en la síntesis de nuevos agentes de acabado poliuretánicos con incrementada permeabilidad. La óptima condición del hidrolizado para este agente modificado de acabado poliuretánico se encontró ser: DMPA, 5% por peso de los monómeros, temperatura de reacción de 80°C y tiempo de reacción 2.5 horas. Cuando el hidrolizado de colágeno es del orden de 0,6-0,8% del IPDI por peso, un rango de buenas propiedades es alcanzable. Por ejemplo, cuando el hidrolizado de colágeno es 0,6% del IPDI por peso, el agente de acabado de poliuretano modificado confiere alta resistencia apropiada para la capa de base o la del acabado final. Cuando el hidrolizado del colágeno es 0,8% del IPDI por peso, el agente de acabado resultante del poliuretano modificado tiene buena elongación a la rotura y extensibilidad, indicando su potencial aplicación en acabados para cuero.

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INTRODUCTION

Polyurethane finishing agents have excellent properties such as flexibility, wearability, resistance to solvent, and anti-aging.¹ Aqueous polyurethane is widely used in leather making as a finishing agent, because it is environmentally friendly. However, the properties of aqueous polyurethanes are not comparable in many cases to solvent-based polyurethanes. Disadvantages such as small elongation (extensibility), bad adhesion, easy yellowing, and brittle do exist in aqueous polyurethane finishing agents. The permeability of leathers is usually remarkably affected by finishing with polyurethane finishing agent. Many attempts have been made in recent years to modify aqueous polyurethanes (PU)²⁻⁵ in order to produce finishing agents with excellent properties. In the modification of polyurethane finishing agents, hydrophilic groups are needed and are usually introduced.

Statistical data suggest that, in the leather making process, only a small part of the raw materials are transformed into leathers to be sold and the rest are discarded as waste including chrome shavings. Chrome shavings contain plenty of collagen. If discarded, both severe pollution to the environment and an enormous waste of resources are caused.⁶⁻⁷ In the past 20 years, knowledge of the favourable functional properties of collagen hydrolysate has increased and research for applications of collagen hydrolysate has been more and more active.⁸ There are many hydrophilic reactive groups on collagen hydrolysate, such as amino (-NH₂), carboxyl (-COOH), imino (-NH-), and hydroxyl (-OH). These groups may react with diisocyanate, -NCO, an active group in the preparation of polyurethane. Consequently the properties of polyurethane finishing agents may be improved by the introduction of collagen hydrolysate.

In the present paper, collagen hydrolysate from tannery wastes was used to modify aqueous polyurethane finishing agents. By the reaction between collagen hydrolysate with the reactive groups (-NCO) in the synthesis of the polyurethane finishing agent, new finishing agents with superior properties were obtained.

EXPERIMENTAL

Materials and apparatus

Isophorone diisocyanate (IPDI), dimethylol propionic acid (DMPA) and polytetrahydrofuran (M2000) were purchased from Wanhua Synthetic Leather Co. Ltd, Yantai, China. Polytetramethylene ether glycols, PTMG-1000, with a hydroxyl value of 112mg KOH/g, and hydroxyethyl methacrylate (HEMA) were also purchased from Wanhua Synthetic Leather Co. Ltd, Yantai, China. Diethylene glycol and triethylamine (TEA) were all analytically pure and

purchased from Tianjin No. 1 Chemical Reagent Co. Ltd., China. Collagen hydrolysate (powder) was provided by Jinxing Biochemistry Co. Ltd, China. It was prepared by a comprehensive hydrolysis method⁹. The chrome content was 0.33mg/kg, the ash content was no more than 0.85% in weight, and molecular weight was widely distributed. It only dissolved in polar media and was easily attacked by microorganisms. The computer controlled electronic universal testing machine, CMT6000, was made by Sans Testing Machine Co. Ltd., Shenzhen, China. The flourier transform infrared spectrometer, FTIR-8700, was from Shimadzu Co. Ltd, Japan.

Procedures

Preparation of collagen hydrolysate modified polyurethane finishing agent

In a three-necked flask equipped with a condenser, thermometer, and stirrer, calculated amounts of DMPA, collagen hydrolysate, and PTMG were added. After being heated to a certain temperature, a calculated amount of isophorone diisocyanate (IPDI) was dropped over an hour. After a certain time of reaction, diethylene glycol was added over 30 minutes. The mixture was allowed to react for another 30 minutes, and cooled to 60 °C Triethylamine (TEA) was added over 30 minutes. Eight times the volume of water was added and the mixture was stirred for another 2 hours to yield the collagen hydrolysate modified polyurethane emulsion.

Determination of residual -NCO groups in the mixture

The residual -NCO group content in the mixture was determined according to the method described in reference 10.

Preparation of polyurethane films

The polyurethane emulsion was put into a 15×10cm mould prepared in our laboratory. After drying at 50 degree centigrade for 72 hours, an additional 48 hours of drying occurred at room temperature. The films were peeled carefully and air-conditioned at 23°C and RH=65% for determining the mechanical behaviour and water absorption. For FTIR characterization, the film was placed in a desiccator with silica for more than a week to achieve constant weight.

Finishing

The crust pigskin leather samples were finished with different finishing agents. The finishing agents were diluted with distilled water to a solid content of 5%. In order to know the influence of finishing with different finishing agents on the permeability of leathers, no other finishing components were employed in the finishing. Approximates 68g/m² of the finishing agent was manually brushed on the grain side of leather samples. After being air-dried, the samples were air-conditioned at 23°C and RH=65% before determining the water vapor permeability.

Characterization

Mechanical behavior: The mechanical properties of the different PU films were obtained using the CMT6000 computer controlled electronic universal testing machine. A standard dumbbell-shaped cutter was used to obtain the sample specimens. The specimens were stretched at a speed of 500mm/min. The average of at least three tests was calculated and reported.

FTIR: FTIR was employed to acquire information on the chemical structure of the polyurethane film. Through measurement and analysis of the resulting spectra, the chemical structure of the product was deduced.

Water absorption: After vacuum drying at 70°C and 0.09MPa for more than 5 hours to constant weight, the films were weighed, giving a mass m_1 . They were then put in water for several hours to obtain the water absorption ratio. The weight of the samples after soaking in water was recorded as m_2 . The water absorption ratio was calculated as:

$$\text{Water absorption ratio} = \frac{m_2 - m_1}{m_1} \times 100\% \quad (1)$$

Water absorption ratios were then plotted against water soaking time to yield water absorption curves.

Water Vapor Permeability: All the samples were air-conditioned at 23°C and RH=65% for at least two weeks to constant weight. The water vapor transmission rate (WVTR) was measured by the permeation cup method¹⁰. A stainless steel cup (body diameter of 45.0mm and top diameter of 30.0 mm) was filled with 50mL of distilled water. A leather sample was mounted to the top of the cup. An O-ring was used to hold the sample in place. After the initial weight of the test cups were taken, the cups were placed in a desiccator with 98wt% H₂SO₄. Weight loss measurements were taken by weighing the test cup with an electronic scale (Ohaus, Switzerland) after 24h. The water vapor transmission rate (WVTR) of the sample was calculated as:

$$\text{WVTR} = \frac{W_1 - W_2}{At} \quad (2)$$

where W_1 is the weight of the cup before test (mg), W_2 is the weight of the cup after 24h of incubation (mg), A is the area of exposed film (an instrument constant, 7.07cm²), and t is the time of experiment (24h). The average of at least three tests was reported.

RESULTS AND DISCUSSION

Factors affecting the modification

Effect of temperature and time

When DMPA was 5.0% of the total monomers in weight and collagen hydrolysate was 0.8% of IPDI in weight, collagen hydrolysate modified polyurethane emulsions were prepared after reacting for different times at 60°C, 70°C, 80°C, and 90°C respectively. The results are shown in Table 1 and Figure 1.

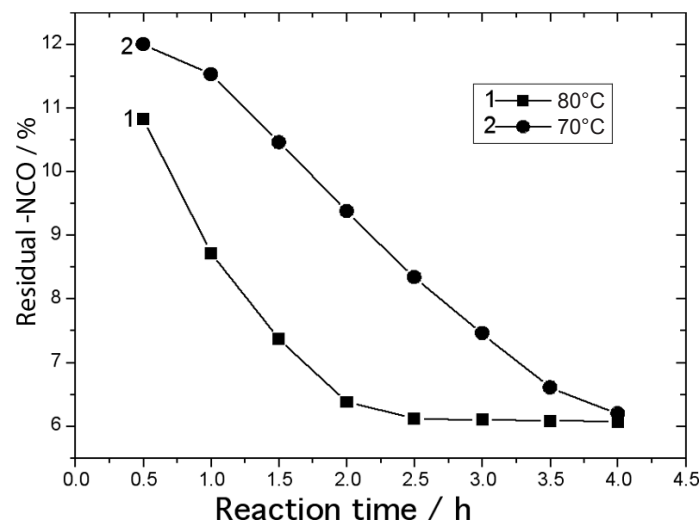
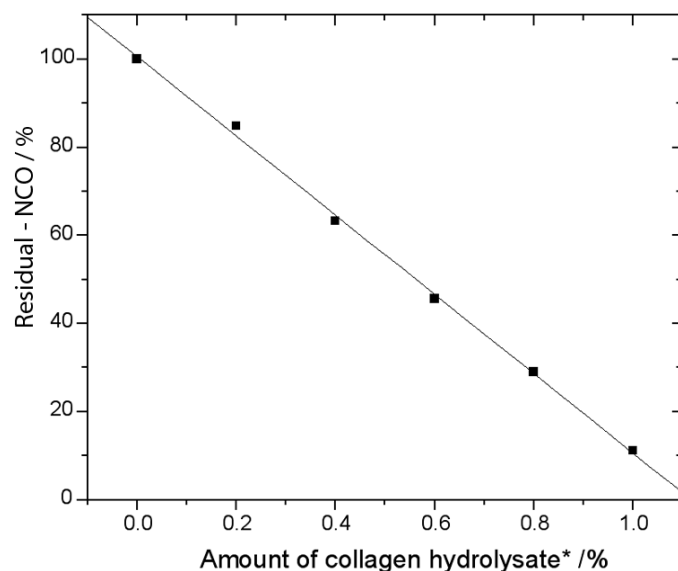


Figure 1. – Residual –NCO in the system vs. reaction time at different temperatures.



* percent of IPDI in weight

Figure 2. – Effects of collagen amount on residual –NCO.

TABLE I
Effect of temperature on reaction

Reaction temperature °C	60	70	80	90
Appearance	Stable reaction; residual collagen can still be found after 5h of reaction	Stable reaction; collagen disappeared, white	Stable reaction; collagen disappeared, white	agglomeration after 0.5h of reaction

From Table 1 and Figure 1, we know that the reaction rate is too low at 60°C, while the reaction rate is too speedy to control the reaction process at 90°C. At 70°C and 80°C, the reaction is stable and may be controlled successfully. Compared with the reaction at 80°C, the reaction rate at 70°C is still lower. Reaction equilibrium was reached at 80°C at a reaction time of 2.5 hours, while more than 4.0 hours was needed to reach equilibrium at 70°C. A reaction temperature of 80°C and reaction time of 2.5 hours were chosen in the preparation of collagen hydrolysate modified polyurethane finishing agent.

Collagen hydrolysate amount

The -NCO groups in IPDI may react with the reactive groups in collagen hydrolysate. When DMPA was 5.0% of the total monomers in weight at 80°C, the quantitative relationship between IPDI and collagen hydrolysate was calculated. With a fixed amount of IPDI, but different amounts of collagen hydrolysate, the mixture was allowed to react for 2.5 hours to yield Figure 2. Figure 2 shows a negative linear relationship between residual -NCO groups and the amount of collagen hydrolysate used in the experiment. By increasing the amount of collagen hydrolysate, the amount of residual 2NCO groups in the system decreases, indicating that the 2NCO groups were consumed by reaction with collagen hydrolysate.

DMPA amount

When the collagen hydrolysate was 0.8% of IPDI in weight, but different amount of DMPA, the mixture was allowed to react at 80°C for 2.5 hours. The properties of the collagen hydrolysate modified polyurethane emulsion are shown in Table 2.

From Table 2, when DMPA was less than 2.0%, the emulsion was not stable. With increasing DMPA concentration, a stable emulsion was obtained. A light blue emulsion was obtained when the DMPA was more than 6.0% of the total monomers in weight. When the amount of DMPA was more than 7.0%, water absorption was high, indicating a poor water resistance. With everything being considered, the amount of DMPA should be chosen at 5.0% of the total monomers in weight.

Properties of the product

Effect of collagen hydrolysate amount on the mechanical properties of the PU films

The influence of collagen hydrolysate amount on the mechanical properties of the modified polyurethane films was studied with collagen hydrolysate amounts of 0.2%, 0.4%, 0.6%, 0.8%, 1.0%, 1.2%, 1.5%, and 2.0% of IPDI in weight. It was found that the water absorption of the film was very poor and it was difficult to obtain a film when the

TABLE II
Effects of DMPA concentration on the reaction

DMPA Amount(wt%)*	Emulsion appearance	Solid content/wt%	Water absorption/%
2.0	Cannot form stable emulsion		
3.0	Milky emulsion	19.62	10.12
4.0	Milky emulsion	20.31	11.91
5.0	Milky emulsion	21.06	12.38
6.0	Light blue emulsion	22.21	12.93
7.0	Light blue emulsion	20.62	87.48

*Note: the percent of the total monomer in weight.

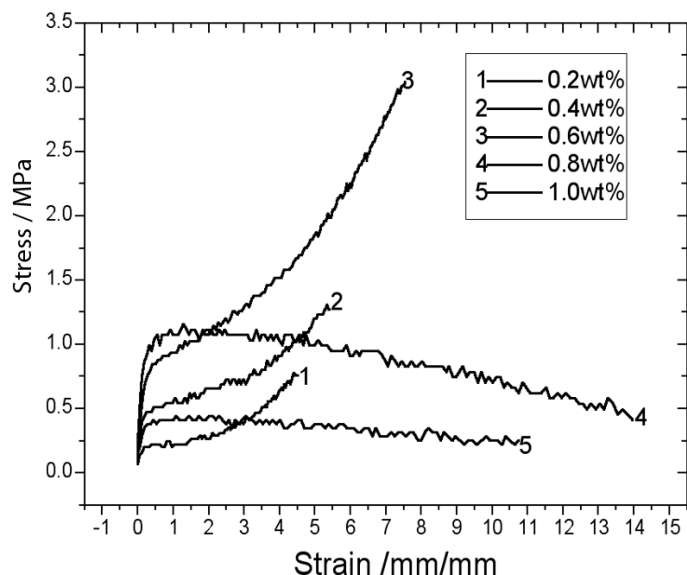


Figure 3. – Stress-strain curves of modified PU films with different collagen hydrolysate amount.

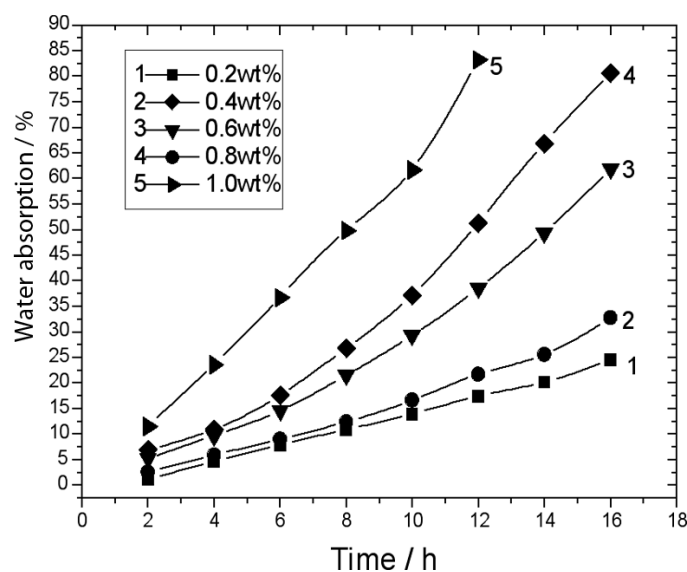


Figure 4. – Effects of collagen hydrolysate amount on the water absorption of modified PU films.

collagen hydrolysate amount was more than 1.2% of IPDI in weight. The polyurethane finishing agent with high collagen hydrolysate content was poor in water resistance. The stress-strain curves of polyurethane films modified with different amounts of collagen hydrolysate are shown in Figure 3.

From Figure 3, it was found that mechanical properties such as tensile strength, breaking strength, and elongation at break first increases and then decreases. The breaking strength reached a maximum value when the collagen hydrolysate was 0.6% of IPDI in weight, while the elongation at break reached a maximum value when the collagen hydrolysate was 0.8% of IPDI in weight. Both chain-extension and cross-

linking might take place in the modification of polyurethane emulsion by collagen hydrolysate. The strength of the PU films was small at low collagen hydrolysate content. Too much collagen hydrolysate will result in an unstable emulsion, with poor film formation, and a small elongation at break. A film of pure collagen hydrolysate is usually brittle. When the amount of collagen hydrolysate was more than 0.8% of IPDI in weight, the breaking strength was lower than the tensile strength. The amount of collagen hydrolysate should be 0.6-0.8% of IPDI in weight. When the collagen hydrolysate is 0.6% of IPDI in weight, the modified polyurethane finishing agent is strong in strength, and may be used in base or top finishing. When the collagen hydrolysate is 0.8% of IPDI in weight, the modified polyurethane finishing agent has a good elongation at break and extensibility, indicating a potential application in sealing finishing.

Effect of collagen hydrolysate modification on the water vapor permeability of finished leathers

The crust leather samples were finished with polyurethane finishing agent (PU), collagen hydrolysate modified polyurethane finishing agent (Modified PU), and pure collagen hydrolysate solution (Collagen). The water vapor permeability of the finished samples and the control sample (Unfinished) were obtained as shown in Table 3.

From Table 3, the crust sample is the best in water vapor permeability. Water vapor permeability was decreased by finishing. The water vapor permeability of the samples varied with different finishing agents, and the collagen hydrolysate directly finished sample was the best. The one finished with unmodified polyurethane finishing agent was the worst, with nearly half the water permeability of unfinished one. Collagen hydrolysate modified polyurethane finishing agent yielded much better water vapor permeability compared with that of the unmodified one, indicating that collagen hydrolysate modification improved the water vapor permeability of the finishing agent to meet the need for good water vapor permeability of leathers. The water vapor permeability of samples finished with the polyurethane finishing agent modified with different amount of collagen hydrolysate was determined as shown in Table 4. Table 4 indicates that increasing the collagen hydrolysate amount will result in an increase in water permeability of the finished samples. The introduction of collagen hydrolysate in the finishing agent improves the water vapor permeability of finished leathers.

Effect of collagen hydrolysate on the water absorption of the polyurethane films

With DMPA 3% of the total monomers in weight, the influence of the amount of collagen hydrolysate on water absorption of the PU films was obtained as shown in Figure 4. With increasing amounts of collagen hydrolysate in the

TABLE III
WVTR of leathers finished by different finishing agents

Samples finished by	Unfinished	Unmodified PU	Modified PU	Pure Collagen Hydrolysate
WVTRmg/10cm ² .24h	608.6	328.0	457.1	582.4

TABLE IV
WVTR of leathers finished with PU finishing agents modified with different amounts of collagen hydrolysate

Collagen hydrolysate amount *(%)	0.2	0.4	0.6	0.8	1.0
WVTRmg/10cm ² .24h	348.2	381.5	454.2	470.9	487.1

*Note: the percent of IPDI in weight.

PU films, the water absorption of the PU films increased remarkably. Collagen hydrolysate may play a role in the emulsification process of emulsifier to improve the emulsion stability and the water absorption of the modified polyurethane films. When the amount of collagen hydrolysate reached 0.8% of IPDI in weight, the water absorption increased rapidly, and the film was partly dissolved after 12 hours of water soaking.

Verification of the modification

-NCO content in the reaction mixture

From the changes in residual -NCO content in the reaction mixture shown in Figure 5, the residual -NCO content decreases with reaction time. Equilibrium was reached after 2 hours of reaction. When collagen hydrolysate was added after 4 hours of reaction, the residual -NCO content decreased rapidly again, indicating that the reaction between the reactive groups in collagen hydrolysate with the -NCO groups in the reaction mixture consumes the -NCO groups. Another 30 minutes were needed to reach a new equilibrium.

FTIR characterization

The FTIR spectrum of the collagen hydrolysate modified polyurethane film was shown in Figure 6. In Figure 6, the peak in 1711 cm⁻¹ is due to the C=O stretching vibration and the peak in 3388 cm⁻¹ is from the free -NH stretching vibration. Both are characteristic vibration modes of polyurethane. The peak in 1653 cm⁻¹ belongs to the urea-based C=O stretching vibration. The urea-based C=O was formed by the reaction between -NCO in the polyurethane and the amino groups in collagen hydrolysate. The weakness of the 2260 cm⁻¹ peak indicates little or no 2NCO groups in the product, an implication that the reaction was completely finished.

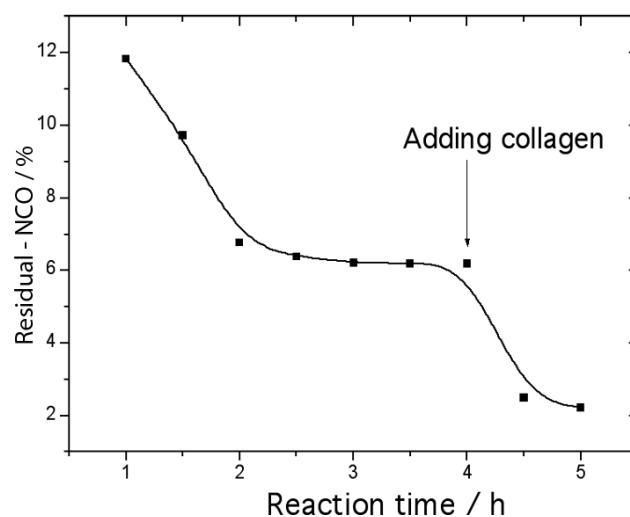


Figure 5. – Effect of collagen hydrolysate on residual -NCO in the system.

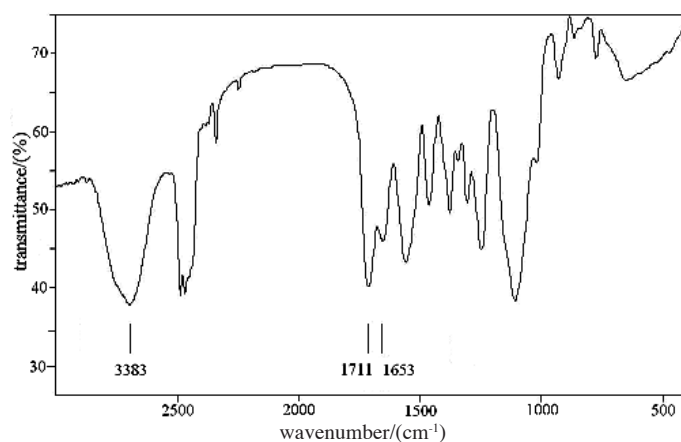


Figure 6. – FTIR spectrum of the PU film modified with collagen hydrolysate.

CONCLUSIONS

Collagen hydrolysate was successfully used to modify a polyurethane finishing agent. The optimum collagen-modifying condition for the polyurethane finishing agent is: DMPA is 5% of the monomers in weight, the reaction temperature is 80°C, and the reaction time is 2.5 hours. The collagen hydrolysate should be 0.6-0.8% of IPDI in weight to get a good modified product. When collagen hydrolysate is 0.6% of IPDI in weight, the modified polyurethane finishing agent has high strength and may be used in base or top finishing. When the collagen hydrolysate is 0.8% of IPDI in weight, the modified polyurethane finishing agent has a good elongation at break and extensibility, indicating a potential application in sealing finishing.

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