Preparation and Properties of Polyurethane Finishing Agent using Butylamine as Chain-extension Agent

by

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Abstract

With isophorone diisocyanate (IPDI), polytetrahydrofuran (PTMG), and dimethylolpropanoic acid (DMPA) as monomers, aqueous polyurethane finishing agents were synthesized. Butylamine, ethylene glycol and ethylene diamine were used as chain-extension agents. The aqueous polyurethane finishing agents were dried to yield polyurethane films (PU films). Mechanical properties of the films were studied. Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and water absorption were employed to characterize the structure and behaviors of the polyurethane films. Properties of the films obtained by different chain-extension agents were compared. Results show that the properties of the butylamine chain-extended film are better than those of the films chain-extended by either ethylene glycol or ethylene diamine. The elongation at break was the highest, 1454%. The glass transition temperature (Tg) reached -82°C and the water resistance was also better.

Resumen

Con diisocianato de isoforona (IPDI), politetrahidrofurán (PTMG) y ácido dimetíl propanóico (DMPA) como monómeros, agentes de acabados acuosos de poliuretano fueron sintetizados. Butil amina, etilenglicol, etilen diamina, fueron utilizados como agentes de extensión de las cadenas moleculares. Los agentes de acabados de poliuretanos acuosos fueron secados para producir películas de poliuretanos (PU films). Las propiedades mecánicas de las películas obtenidas fueron estudiadas. Espectroscopía infrarroja por medio de transformaciones de Fourier (FTIR), calorimetría diferencial por barrido (DSC), y absorción de agua fueron utilizados para caracterizar la estructura y comportamiento de las películas de poliuretano. Las propiedades de las películas obtenidas por el uso de los diferentes agentes de extensión molecular de cadenas fueron comparadas. Los resultados demostraron que las propiedades de la película obtenida por medio de butil amina como agente de extensión molecular de cadena, fueron superiores a las de las películas obtenidas con los otros extendedores de cadena, ya sea por etilenglicol o por etilen diamina. La elongación al instante de rotura [en el primer caso] fue la más alta, 1454%. La temperatura de transición cristalina (Tg) alcanzó -82°C y la resistencia al agua también fue mejor.

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Introduction

Aqueous polyurethane is widely used in leather making as a finishing agent. However, the properties of presently exploited aqueous polyurethanes cannot reach the level of solvent-based polyurethanes. Many attempts have been made in recent years to modify the aqueous polyurethanes (PU). [1-3]

Diamines and diols were usually employed as chain-extension agents. [4-6] It was not easy to control the cross-linking degree of the product because of the four active hydrogen atoms existing on diamine molecule. Too large a cross-linking degree may result in low elongation at break for these materials. When diols were used as chain-extension agent, sufficient micro phase separation cannot be obtained because of the large diol molecules. Neither the thermal resistance nor the mechanical properties of the polyurethane is sufficient for finishing agent. On the other hand, monoamines have also been applied as chain-extension agent. By the use of monoamines, the cross-linking degree can be easily controlled by the two active hydrogen atoms on them. Besides, the degree of micro phase separation may be increased and the performance of the materials may be improved greatly because of the shorter rigid polyurethane chain. Monoamines have been successfully used in PU elastomers before. We now hope to use this strategy for aqueous polyurethane. [2, 3, 7]

In the present paper, isophorone diisocyanate (IPDI), polytetrahydrofuran glycol (PTMG), and dimethylolpropanoic acid (DMPA) were used as monomers and butylamine, ethylene glycol, and ethylene diamine were employed as chain-extension agents. Our goal was in order to obtain polyurethane finishing agents with good performances. Polyurethane films were prepared from these aqueous polyurethane finishing agents. The mechanical properties of these films were studied. Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and water absorption were employed to characterize the structure and behaviors of the polyurethane films. Properties of the films obtained by different chain-extension agents were compared. The results show that the film chain-extended by butylamine has superior properties than those of the films chain-extended by either ethylene glycol or ethylene diamine. Specifically, elongation at break is the highest at 1454%, the glass transition temperature (Tg) reached -82°C and the water resistance was also better.

Experimental

Materials and apparatus

Isophorone diisocyanate (IPDI), polytetrahydrofuran glycol (PTMG, Mw=2000), and dimethylolpropanoic acid (DMPA) were all industrial grade and purchased from Yantai Wanhua Synthetic Leather Co. Ltd. Triethylamine, acetone, butylamine, ethylene glycol, ethylene diamine, and dibutyltin dilaurate were all chemically pure and made in China. DSC 204C thermal analyzer was manufactured by Netzsch, Germany. A Fourier transformation infrared spectrometer, FTIR-8700, was made by Shimadzu Co. Ltd, Japan. A Computer controlled electronic universal testing machine, CMT6000, was from Sans Testing Machine Co. Ltd., Shenzhen, China.

Synthesis of aqueous polyurethane finishing agents

After being weighed accurately, IPDI, PTMG, DMPA, and dibutyltin dilaurate were put into a four-necked flask and heated to 80°C for pre-polymerization. After 3 hours of reaction, some acetone was added to decrease the viscosity if necessary. Triethylamine was added according to the stoichiometric amount of DMPA required for neutralization. Then, the mixture was cooled to approximately 25°C. A pre-polymer was thus obtained. According to the ratio of active hydrogen atoms on chain-extension agent to the dissociative diisocyanate (residual -NCO), different amounts of chain-extension agents were then added and the system was allowed to react for 5 mins at the resulting temperature. Next, the system was stirred in high speed, 500 rpm, and was dispersed with a substoichiometic amount of water. Finally, the system was heated to 90°C and the temperature was held for 1 hour. A light blue translucent polyurethane-water emulsion was obtained.

Preparation of polyurethane films

The polyurethane-water emulsion was put into a mould, prepared in our laboratory. After drying at 50°C for 72 hours, an additional 48 hours of drying was permitted at the room temperature.

Characterization

Mechanical behavior: After the different aqueous PU films were air-conditioned at 25°C and RH=65%, CMT6000 computer controlled electronic universal testing machine was employed to determine the mechanical properties. A standard dumbbell shape cutter was used to make the sample specimens. The specimens were then stretched at a speed of 500 mm/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.

Thermal analysis: The glass transition temperature (Tg) of the film was obtained by the DSC method, using indium as a calibrating external standard. Eleven milligrams of aqueous PU film was used and the heating rate was 10°C /min. The experiments were carried out from -100°C to 0°C, with nitrogen as an inert, protective atmosphere.

Water absorption: After vacuum-dried at 70°C and 0.09MPa for more than 5 hours to reach constant weights, the films were weighed, giving a mass m_1. Then, they were put in distilled 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:

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

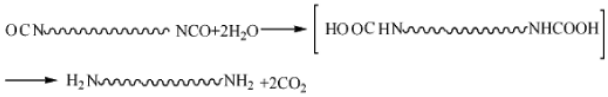
Water absorption ratios were then plotted against water soaking time, producing water absorption curves.

Results And Discussion

Mechanical properties of different PU films

In use, leathers inevitably endure such mechanical processes as stretching and bending. Therefore, leathers should have a good elongation at break. The finishing agents used in leather manufacture should also have a good elongation at break. Besides, the elongation (extensibility) of the finishing agent may also affect the softness of the finished leathers to some extent. Table 1 shows some mechanical properties of the aqueous PU films chain-extended by different chain-extension agents, various amounts of chain-extension agents and different ratios of -NCO/-OH. From Table 1, we see that the tensile strength of the PU films decreases somewhat with increasing the elongation at break. What's more, the tensile strength of our samples is better than that of the commercial product. This indicates that the series of experimental samples may be competitive with regard to tensile strength.

Figure 1 shows the relationship between elongation at break and the amount of chain-extension agents in the finishing agents. Here, the amount of the chain-extension agent is the percent of the amount required to make a 100%, or fully-chain-extended product. As Figure 1 indicates, with increasing the amount of chain-extension agent, the elongation at break of the PU films increases first and then decreases. The PU film chain-extended with butylamine is the best in elongation at break in all the samples, which indicates that butylamine is the best of all the three chain-extension agents studied. Butylamine may also contribute to the flexibility of the PU films. The elongation at break begins to decrease when the amount of chain-extension agent exceeds 70%. This is probably due to the by-product reaction with water. When the chain-extension agent is stoichiometrically sufficient, IPDI will react with the chain-extension agent completely. However, when the amount of the chain-extension agent decreases, the extent of by-product reaction may increase and affects the results greatly. With an excess amount of chain-extension agent, hard segments in the films will be reduced, the interactions among molecules will be reduced, the flexibility of the samples will be increased, and the elongation at break will decrease as a result. In the case with sufficient chain-extension agent, the isophorone diisocyanate will react completely. If we reduce the amount of chain-extension agent, more and more residual isophorone diisocyanate will exist, which may react with water as by-product reaction. The by-product reaction was proposed by Liu and his co-workers as follows:[6]



(2)

The molecular chain of the intermediary product is quite long. It will react with the residual isophorone diisocyanate (IPDI) to form a product, most similar to the two phase structures of pure polyurethane. [5] The hydrogen bonding among the molecules is strong, resulting in the increase in tensile strength and the decrease in elongation at break. Figure1 also shows that the elongation at break of the film chain-extended with butylamine is greater than those of films with ethylene glycol or ethylene diamine as chain-extension agents. This is probably due to the different size of the hard segments. The more the chain-extension agent in the material, the more hard segments will exist in the system and the poorer the flexibility of the film. The smaller the molecule of the chain-extension agent, the smaller the hard segments, the interaction among molecules will be less, the molecular chains will be more flexible, and elongation at break will be greater. By controlling the molecular length of the chain-extension agent, we can control the percent of hard segments and the degree of micro phase separation. The hard segment composed by the reaction of butylamine and IPDI is smaller than that formed by ethylene glycol and IPDI or ethylene diamine and IPDI. The interaction of PU molecules is reduced with decreasing the size of the hard segments. Therefore, the elongation at break of the sample chain-extended by butylamine is greater.

TABLE I

Mechanical behavior of chain-extended polyurethane films

Sample	-NCO/-OH	Chain-extension Agent	Amount of Chain-extension Agent * (%)	Elongation at break (%)	Tensile Strength (MPa)
1	1.1:1	Ethylene glycol	25.0	1011	0.11
2	1.1:1	Ethylene glycol	50.0	1060	0.13
3	1.1:1	Ethylene glycol	70.0	1305	0.06
4	1.1:1	Ethylene glycol	100	1157	0.06
5	1.1:1	Ethylene diamine	40.0	638	0.66
6	1.1:1	Ethylene diamine	70.0	864	0.29
7	1.1:1	Ethylene diamine	100	730	0.17
8	1.1:1	butylamine	0.00	634	0.44
9	1.1:1	butylamine	10.0	755	0.40
10	1.1:1	butylamine	33.3	1075	0.13
11	1.1:1	butylamine	66.7	1454	0.02
12	1.1:1	butylamine	100	1405	0.02
13	1.2:1	butylamine	100	1124	0.04
14	1.5:1	butylamine	100	787	0.08
15	2.0:1	butylamine	100	192	0.35
16	PU67**		------	1640	0.02

The amount of chain-extension agents is the molar ratio of chain-extension agents to the diisocyanate left in the system after pre-polymerization.
** A finishing agent from Clariant Corporation.

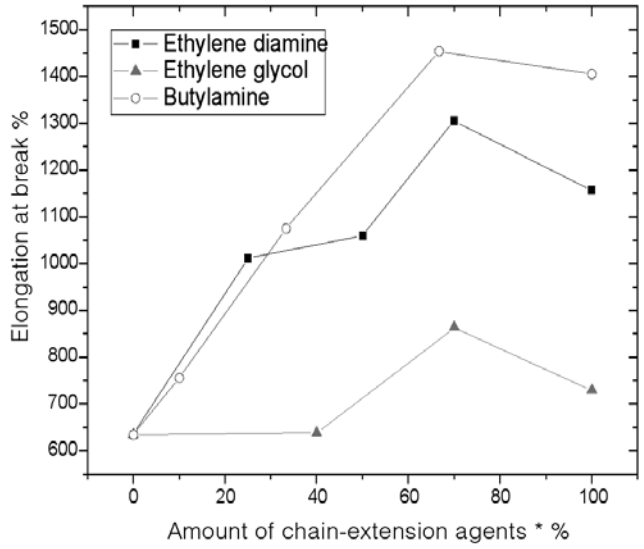


Figure 1. – Elongation at break of polyurethane films vs. amount of chain-extension agents

*The amount of chain-extension agents is the molar ratio of chain-extension agents to the residual diisocyanate in the system after pre-polymerization.

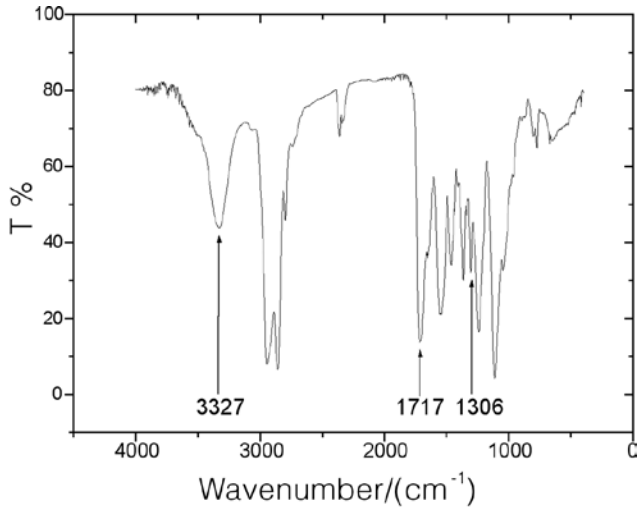
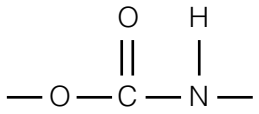


Figure 2. – FTIR spectrum of the PU film chain-extended with butylamine.

FTIR analysis

Figure 2 shows the FTIR spectrum of the polyurethane film chain-extended by butylamine. A non-hydrogen bonded N-H stretching peak usually appears at 3340 cm^{-1}. Participation in hydrogen bonding may decrease the frequency of the N-H vibration. [7] The N-H stretching band at 3327 cm^{-1} should be hydrogen-bonded. The N-H flexural band of butylamine at 1650-1590 cm^{-1} is weak. This indicates that butylamine has almost been consumed completely in the polymerization. Therefore, butylamine does not serve as a plasticizing agent in the system, but plays the role as a chain-extension agent. The absorption peak at 2270 cm^{-1} is very weak. This indicates that IPDI has been almost completely consumed. The absorption peak at 1241 cm^{-1} and the C=O stretching peak at 1717 cm^{-1} belongs to the group:



Usually, the C=O stretching band is at the range from 1730cm^{-1} to 1745cm^{-1}. The sharp peaks and frequencies for both N-H (3327 cm^{-1}) and C=O (1717 cm^{-1}) show that most of the urethane groups are hydrogen-bonded [7]. The peak at 1717 cm^{-1} indicates that there may be urea bands and biuret groups. The C-N flexural band at 1306 cm^{-1} suggests the formation of urea-like groups. Besides, the C-O-C stretching band at 1113cm^{-1} is observed. In short, then, it can be concluded that, with butylamine as the chain-extension agent, molecules were obtained with urea as hard segments and polyether binary alcohol connected with urethane as soft segments.

Glass transition temperature (Tg) of the PU film

Weathering resistance is important for finishing agents in leather-making and the glass transition temperature (Tg) of a finishing agent will determine whether the coating film behaves elastically or plastically when being used. Polyether dihydroxy alcohol (PTMG) and polyester dihydroxy alcohol (ODX218) were employed as monomers for pre-polymerization, respectively, and butylamine was chosen as the chain-extension agent to get a fully chain-extended product. After drying, two kinds of PU films were obtained, which were subsequently analyzed by DSC. From Figure 3, we see that the Tg of the PU film with polyether dihydroxy alcohol is lower than that with polyester dihydroxy alcohol. Using diamine as the chain-extension agent, Fu and co-workers found that the Tg of PU film with polyether dihydroxyl alcohol (PTMG) as the raw material was about -75°C, while that with polyester dihydroxy alcohol as raw material was approximately -40°C. [4] In our present study, with butylamine as the chain-extension agent, the Tg of the PU film using polyether dihydroxy alcohol as the raw material is -82°C, and that made with polyester dihydroxy alcohol as raw material is -55°C. Thus, using butylamine as chain-extension agent, we see that the Tg has decreased, not increased. The finishing agent has a good resistance to low temperature and may be used in cold environments.

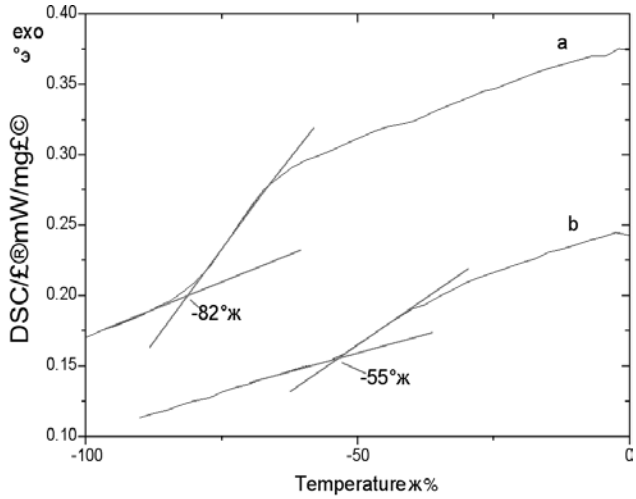


Figure 3. – DSC curves of different films synthesized using (a) Polyether dihydroxy alcohol, and (b) Polyester dihydroxy alcohol as monomer.

Water absorption of the PU films

Water resistance is necessary for polyurethane to be used as a finishing agent. The greater the water absorption of the finishing agent is, the poorer the wet rubbing resistance is, and the lower the water resistance is. By measuring water absorption ratios of the PU films at different water soaking times, we determined the water absorption curves as shown in Figure 4, and Figure 5. Figure 4 shows the extent of water absorption for PU films comprising different chain-extension agents, i.e., ethylene glycol, ethylene diamine, and butylamine, at constant DMPA content, 8% of the system in weight. The water absorption ratio of the PU film increases with increasing the water soaking time. Using ethylene glycol as chain-extension agent, equilibrium was reached at about 3.5 hours. The water absorption ratio for this system is the highest in all the samples. Regarding the ethylene diamine chain-extended PU film, the water absorption ratio is lower than that of the ethylene glycol chain-extended PU film at the same water soaking time. After 4.5 hours of water soaking, the film tends to be dissolved and/or hydrolyzed, indicating a very poor water resistance. With butylamine as the chain-extension agent, however, the water absorption gradually increases with increasing the water-soaking time. After water soaking for 6 hours no weight loss was detected, indicating a good water resistance. Here, the water absorption is the lowest of all the experimental chain-extended PU film samples.

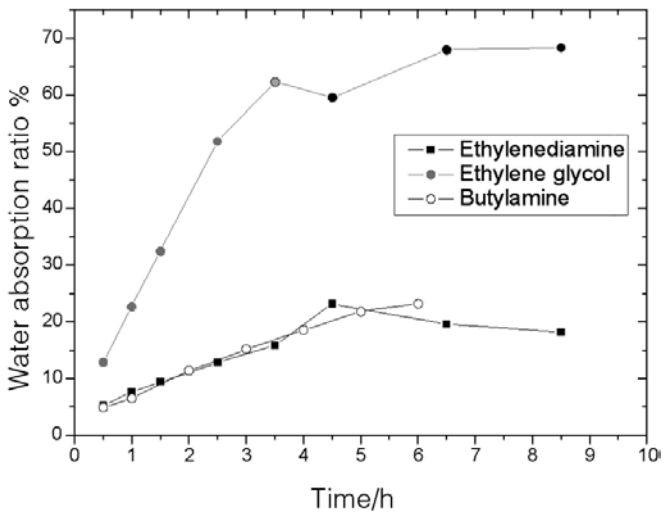


Figure 4. – Water absorption ratios of the films vs. water soaking time.

With the same amount of DMPA, but a different amount of butylamine chain-extension agent, a series of PU films were obtained. Their water absorption ratios were shown in Figure 5. In all these samples, the water absorption ratios also gradually increase with increasing the water-soaking time. Increasing the amount of chain-extension agents, the water absorption ratio decreases. In the sample that has not been chain-extended, however, the water absorption of the sample is the poorest. The water absorption ratio of the film is the highest when the mole ratio of the active hydrogen atoms on monoamine to the residual diisocyanate is 10%. Decreasing the amount of chain-extension agent will reduce the number of urea groups. On the other hand, the amount of carboxylic groups and C-O-C groups were not changed. Therefore, the water affinity increased. In the trial without chain-extension agent, the polyurethane molecules will arrange neatly to form a uniform structure. The interaction force among the molecules will be greater, and fewer polar groups will be exposed on the surface of the film. This might be the reason why the water absorption ratio was so low if the film had not been chain-extended by butylamine.

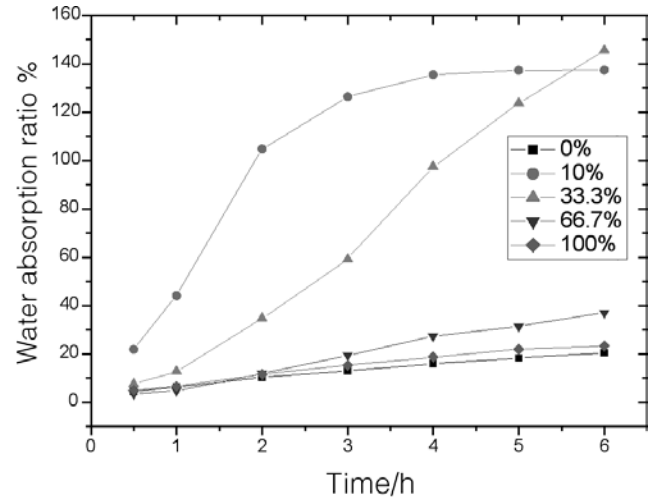


Figure 5. – Water absorption ratios of the films vs. water soaking time.

Fully chain-extended film samples were prepared when the condition of equal number of carboxylic groups, but different ratios of -NCO/-OH (Molar ratio, R) was achieved. After water soaking for 24 hours, the data shown in Figure 6 were obtained. Figure 6 shows the relationship between water absorption and R. We see that the water absorption ratios decrease with the increase of R. From the viewpoint of structure, with increasing R, the amount of such hydrophobic segments as benzene, carbamoyl bond, and urea bond increase, whilst the hydrophilic groups, carboxylic groups decrease. The water absorption will decrease and the water resistance will be increased as a result. Both Figure 5 and Figure 6 indicate that it does well to increase the water resistance of PU film by increasing the amount of hard segments in the system.

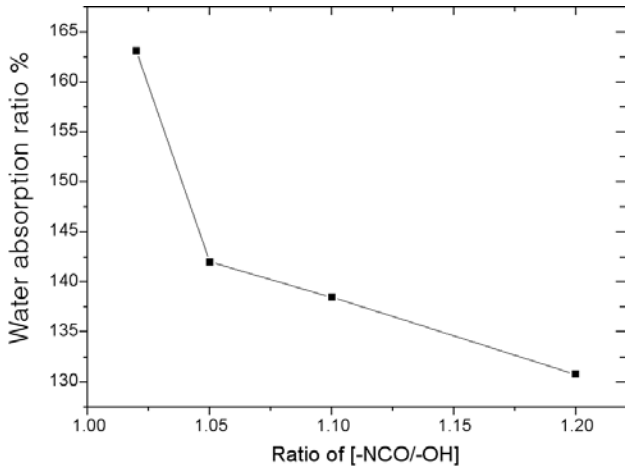


Figure 6. – Water absorption ratios of the films vs. ratio of –NCO/ -OH.

CONCLUSIONS

The mechanical behavior of PU films chain-extended with butylamine is better than those with ethylene diamine or ethylene glycol as chain-extension agents. Through proper choice of the chain-extension agent molecule, the hard segment size may be adjusted, and the elongation at break of the PU films may be increased. Using butylamine as chain-extension agent enhanced mechanical performance and cold resistance may be achieved for polyurethane finishing materials. Hard segments of smaller size in the polyurethane can improve the elongation at break of PU films. Water resistance of the butylamine chain-extended film is better than that of the films chain-extended by ethylene glycol or ethylene diamine.

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