SYNTHESIS, APPLICATION AND COMPARISON OF AQUEOUS POLYURETHANE

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ABSTRACT

A series of aromatic and aliphatic cationic aqueous polyurethane dispersions were successfully prepared with polypropylene glycol, polypropylene polyol, toluene diisocyanate(TDI), and isophorone diisocyanate(IPDI) as raw materials. The structure and properties of the synthesized aqueous polyurethane dispersions were characterized with FTIR, UV spectra, TEM, DSC, TGA, electronic tensile machine, and the aliphatic and aromatic cationic aqueous polyurethane were compared. Both the aliphatic and the aromatic cationic aqueous polyurethanes are all two phase structure systems. Their two glass transitions took place in the range of -100°C to +220 °C, respectively corresponding to the glass transitions of soft segments and hard segments. Their thermal decomposition also exhibited two stages, respectively corresponding to thermal decompositions of hard segments and soft segments. The strong π-π^* transition absorption peaks took place when λ was in the vicinity of 220nm. With the increasing of isocyanate (NCO) group content, the tensile strengths of the films increased and their elongations at break decreased. The particle morphologies of aromatic and aliphatic dispersions both are spherical. They both could be used as the base sealing of pig leather. They also could be used in the sandwich finishing system for pig garment leathers. Compared to the aromatic cationic aqueous polyurethane, the aliphatic series is lower at the glass transition of hard segments, better at photo-resistance; greater in the elongation at break, and lower in tensile strength. The aliphatic cationic aqueous polyurethane can be used as the finishing system of shallow color pig leather or white pig leather, and its UV spectra did not show a characteristic B absorption peak.

RESUMEN

Una serie de dispersiones catiónicas acuosas de poliuretanos aromáticos y alifáticos fue preparada con éxito con polipropilenglicol, el poliol del polipropileno, el di-isocianato (TDI) del tolueno, y el di-isocianato (IPDI) de la isoforona como materias primas. La estructura y las propiedades de las dispersiones acuosas del poliuretano sintetizadas fueron caracterizadas con FTIR, espectros UV, TEM, DSC, TGA, máquina extensible electrónica, y los poliuretanos acuosos catiónicos alifáticos y aromáticos fueron comparados. Los poliuretanos acuosos catiónicos alifáticos y aromáticos son todos sistemas de estructura de dos fases. Sus dos transiciones cristalinas ocurrieron en la gama de -100°C a +220°C, correspondiendo respectivamente a las transiciones de cristales de segmentos blandos y de segmentos duros. Su descomposición térmica también exhibió dos etapas, correspondiendo respectivamente a la descomposición térmica de segmentos duros y de segmentos blandos. El pico fuerte de la absorción de la transición π-π^* ocurrió cuando λ estaba en la vecindad de los 220nm. Con el aumento del contenido del grupo del isocianato (NCO), las fuerzas extensibles de las películas aumentaron y sus elongaciones a la rotura disminuyeron. Las morfologías de la partícula de las dispersiones aromáticas y alifáticas son esféricas. Ambas podrían ser utilizadas como una base sellante para cuero de cerdo. También podían ser utilizadas en el sistema sándwich de acabado de cueros de cerdo para vestimenta. Comparado al poliuretano acuoso catiónico aromático, la serie alifática inferior en cuanto en la transición cristalina de segmentos duros, superior en fotoresistencia; mejor en el alargamiento en la rotura, y más baja en resistencia a la tracción. El poliuretano acuoso catiónico alifático se puede utilizar en el sistema de acabado de cueros de cerdo en colores claros o en cuero blanco de cerdo, y su espectro UV no mostró el pico de absorción B característico.

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INTRODUCTION

The aqueous polyurethane is environmentally friendly material. The hydrophilic group is usually introduced in the aqueous polyurethane prepolymer molecules to get stable aqueous polyurethane. The aqueous polyurethane can be divided into anionic, cationic, non-ionic, amphoteric classes in terms of the charge of the hydrophilic groups. Although at the present time, there have been many research reports about the anionic aqueous polyurethane, but the reports about the cationic aqueous polyurethane have been lesser, especially the reports about the aliphatic cationic aqueous polyurethane have been much lesser. Because the most of cationic aqueous polyurethane belong to quaternary ammonium salt type, and the production technologies of quaternary ammonium salt derivatives using the prepolymer are more complicated, the costs are higher, sometimes the emulsification products are not stable, the industrialized productions are more difficult. But there are cationic ions in framework of cationic aqueous polyurethane which make the cationic polyurethane hold unique properties and are well used for leather, coating, paper, textile finishes, and other applications.[1] So the market foreground of developing cationic polyurethanes which have excellent properties is very wide.

In this paper, not only the aromatic cationic aqueous polyurethane dispersions were successfully synthesized, but also the aliphatic cationic aqueous polyurethane dispersions were successfully synthesized. For the first time, the structures and properties of the synthesized aromatic cationic aqueous polyurethane dispersions and the aliphatic cationic aqueous polyurethane dispersions were characterized and compared more systematically. And the base sealing application experiments in pig leathers as well as the experiments in sandwich finishing systems for pig garment leathers were also done.

EXPERIMENTAL

Materials

Toluene diisocyanate(TDI, CAS number 26471-62-5) was chemical grade and was supplied by Peking Xizhong Chemical Plant, isophorone diisocyanate(IPDI, CAS number 4098-71-9) was supplied by Hues AG Company in Germany, polypropylene glycol (PPG-1000, CAS number 25322-69-4),polypropylene polyol (PPG-3000, CAS number 25322-68-3) was supplied by the 3th Petrochemical Plant of Tijian, their average functional degrees were separately 2 and 3. Dibutyltin diaurate(T-12, CAS number 77587), dioctyl phthalate(DOP, CAS number 117-81-7), acetone(CAS number 67-64-1), N-methyldiethanolamine(N-MDEA, CAS number 105-59-9), ice acetic acid(AA, CAS number 64-19-7) were analytically pure grade, were used as received, and were purchased from Peking Chemical Reagent Company. The water was deionized and distilled, the conductivity of which was below 1μs /cm.

Preparation of the cationic aqueous polyurethane dispersions

The synthesis of the cationic aqueous polyurethane dispersions were carried out in a four-neck glass reactor equipped with a mechanical stirrer, a thermometer, a nitrogen inlet. First, TDI (or IPDI), PPG and few of drops T-12 of DOP solution were poured into the reactor, the reactor mixture was kept 90 °C for about 3 h, until the NCO% dropped below theoretical values, the reactor was cooled down to 50°C, freshly dried acetone was added into it in order to bring down the viscosity of these polyurethane prepolymer. The N-MDEA was added and temperature remained constant for another 1 h. Then, the polyurethane dispersion was obtained from a high shear rate mixing of this polyurethane prepolymer with aqueous solution of acetic acid. The final aromatic cationic aqueous polyurethane dispersions had 20% solid contents with a pH value of 8.5 after acetone were removed by vacuum. In the process of experiment, the NCO/OH ratios were 1.125, 1.25, 1.375, 1.5, respectively, while the other conditions were the same; the numbers of the different samples were A, B, C, M for aromatic polyurethane, D, E, F, N for aliphatic polyurethane, correspondingly. The recipes are summarized in Table I.

Characterization

FTIR Analysis

Fourier transform infrared spectra(FTIR) were acquired with a Fourier transform infrared spectrometer (Bruker Equinox55). For each sample, 16 scans at a 4-cm^{-1} resolution were collected in absorption group mode.

TABLE I
The Mole Ratios of the Polyurethane Dispersion Recipes

Reagents	PPG-1000	PPG-3000	N-MDEA	TDI	IPDI	AA
A	0.048	0.0023	0.0827	0.15		0.0827
B	0.035	0.0023	0.0827	0.15		0.0827
C	0.024	0.0023	0.0827	0.15		0.0827
M	0.015	0.0023	0.0827	0.15		0.0827
D	0.048	0.0023	0.0827		0.15	0.0827
E	0.035	0.0023	0.0827		0.15	0.0827
F	0.024	0.0023	0.0827		0.15	0.0827
N	0.015	0.0023	0.0827		0.15	0.0827

TABLE II
Base Sealing Recipes of Pig Leather for Making Garments

Scheme	Aromatic cationic aqueous PU (Sample B)	Aliphatic cationic aqueous PU (Sample E)	Anionic base sealing agent used in production	Water
1	200			100
2		200		100
3			200	100

TABLE III
Sealing Coat Formulation Used For Pig Garment Leathers

Scheme	1	2	3
Aromatic cationic PU dispersion (sample B)	3.5		
Aliphatic cationic PU dispersion (sample E)		3.5	
Anionic PU dispersion			3.5
Water	6.5	6.5	6.5

TABLE IV
Basecoat Formulation of Pig Garment Leathers for Scheme 1, 2, 3

Component	Parts of component
Water	3
Black pigment	2
Anionic polyurethane dispersion PUC-321	2.5
Anionic polyurethane dispersion PUC-322	1.5
Anionic or non ion wax emulsion	0.2
Acrylic binder XG-461	0.5

Ultraviolet Spectra Analysis

The different aqueous polyurethane dispersions were separately diluted to 10^{-3}-10^{-4}g/l concentration, the UV spectra were measured by the double-beam ultraviolet-visible light spectrophotometer of Beijing Purkinje General Instrument Limited Company.

Transmission Electron Microscopy (TEM) Observation

The particle morphology of the cationic aqueous polyurethane dispersion was observed with a Hitachi H-800, transmission electron microscopy.

Differential Scanning Calorimetric Analysis

DSC analysis of different samples was conducted by using Perkin-Elmer Pyrisl DSC instrument. Indium was taken as internal standard for analysis. The samples were first heated to 100°C, equilibrated at that temperature for 3 min, then the samples were quickly cooled to -100°C ,equilibrated at that temperature for another 3 min, and then heated to +220°C at a scanning rate of 20°C /min under N_2 atmosphere. The weights of the samples were 5-8mg. The samples for DSC analysis were cut from the polymer films that were prepared by casting the cationic aqueous polyurethane dispersions on the glass and were dried at 50°C for 1 week.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was performed in an analyzer Model Perkin-Elmer TGA-7 calibrated with an aluminum standard, under a nitrogen flow, at a heating rate of 10°C /min and temperature range from 25°C to 600°C. The weights of the samples were 5-8 mg.

Static Mechanical Properties

A model WD-3000 electronic testing machine (Changchun, China) was employed for the tensile test. The specimens for the tensile test were dumbbell cut from sample films, which were prepared by casting the dispersions on the glass plates and dried at 50°C for 1 week, and carried out at a crosshead speed of 100mm/min according to standard of ASTM-D638. A 20-mm benchmark and the original cross-sectional area were utilized to calculate their tensile properties. The tensile strength and elongation at break were automatically calculated by the computer connected to the machine. The average of at least five measurements for each sample was reported, the experimental error is 10%.

Application experiments in the base sealing coat of pig leather

There are large numbers of pigskins in china, the technology using pigskin make leather in china is better. But the application of cationic finishing agent in pig leather is less. Pigskins are essentially porous, so the sealing is more difficult than cattlehide, sheepskin and goatskin. In the process of finishing pig leather, the finishing agent is easy to penetrate into the porous hole as well as between the grain layer and reticular layer, the softness and fullness of leather is affected because of this, so the good sealing for pig leather is very important.

The application experiments were carried out using the synthesized aliphatic and aromatic aqueous polyurethane in the Yi Yuan Leather Factory, The base sealing recipes are listed in Table II, the other recipes and working procedures were the same with the production.

Application experiments in the sandwich finishing system

The aqueous polyurethane dispersions are widely used in the leather finishing system, but most of the aqueous polyurethane used in leather finishing is anionic type. The final finished leathers have excellent properties, but also have some disadvantages. One of them is that the anionic dispersions can easily be absorbed by the leather inside, so the fullness and hand of the leather is not very good. Another disadvantage is that there are some hydrophilic groups such as carboxyl group in the molecule chains, so the wet rub resistance of the finished leather is lower. A new technology of "sandwich" type leather coating can solve these problems.[7]

TABLE V
Topcoat Formulation of Pig Garment Leathers for Scheme 1, 2, 3

Component	Parts of component
Water	3.5
Black pigment	2
Anionic polyurethane dispersion PUC-321	2.0
Anionic polyurethane dispersion PUC-322	2.0
Anionic Wax emulsion	0.2

Formulation and procedures of the sandwich finishing experiments

In our work, based on the synthesized cationic polyurethane dispersions, the "sandwich" finishing technique is used alternately the anionic and cationic dispersions for scheme 1 and scheme 2, the regular anionic finishing system scheme 3 is also used for contrast. The sealing coat, basecoat, topcoat, gloss coat formulations are showed in Table III, Table IV , Table V, Table VI respectively. The base coat and the topcoat formulations are not only for scheme 1, scheme 2, but also for scheme 3. The finishing conditions and finishing procedures were the same to the regular production. All materials in leather finishing application experiments except to the synthesized cationic polyurethane dispersions are from Yi Yuan Leather Factory in China.

Properties of the finished leathers

Wet rub fastness

Wet rub fastness was conducted using a rub fastness tester GJ9G1. A felt rubbing pad was saturated with water and placed on the equipment rubbing head, the leather swatch was inserted into the rub fastness tester, the water saturated felt pad was applied to the finished surface and 100 rubbing cycles were completed. The color difference between the felt pads was assessed using a grayscale chart.

Flex resistance

A swatch of the finished leather was attached to a flexometer (GJ9C-1) and subjected to 50000 flexing cycles at ambient temperature. After flexing, the leather was evaluated using a stereoscope to assess damage to the finish (cracking or white crazing).

Finish feel

A subjective assessment of the finished leather was conducted by feeling the leather in multiple ways. To assess the touch (or hand) of the finished leather, the leather surface was evaluated by rubbing the surface and measuring level of smoothness and softness, fullness. The finished leather was also rubbed surface to surface to determine the level of grip of the finishing agent.

TABLE VI
Gloss Coat Formulation Used for Pig Garment Leathers

Scheme	1	2	3
Cationic aromatic PU dispersion (sample B)	0.5		
Cationic aromatic PU dispersion (sample M)	2		
Cationic aliphatic PU dispersion (sample E)		0.5	
Cationic aliphatic PU dispersion (sample N)		2	
Aliphatic PU dispersion PUC-501			0.5
Aliphatic PU dispersion PUC-502			2
Cationic wax emulsion	0.5	0.5	
Anionic wax emulsion			0.5
Cationic (or non ion) silicon-bearing agent	0.7	0.7	
Anionic silicon-bearing agent			0.7
Water	6.3	6.3	6.3

RESULTS AND DISCUSSION

FTIR Analysis of Cationic Aqueous Polyurethane

Figure 1 demonstrates the typical FTIR spectra of the dried film from the cationic aqueous polyurethane dispersions, B was aromatic, E was aliphatic. In the FTIR spectra of pure polypropylene glycol, the peak at 3528cm^{-1} is characteristic peak of hydroxyl group. In the FTIR spectra of pure IPDI and pure TDI, the peaks at 2270cm^{-1}~2280cm^{-1} are unsymmetrical vibration peaks of NCO group.

Whether the FTIR spectra of the aromatic cationic aqueous polyurethane or the FTIR spectra of the aliphatic cationic aqueous polyurethane, the characteristic peak of the hydroxyl group at 3528cm^{-1} and the NCO unsymmetrical vibration peaks at 2270cm^{-1}~2280cm^{-1} are both disappeared, the characteristic absorption peaks of N-H bond at 3321.5cm^{-1}~1536cm^{-1} are both appeared, this shows the reaction between isocyanate group and hydroxyl group have both taken place and have formed urethane group. The peak at 1703cm^{-1} belongs to amide I, the peak at 1615cm^{-1} belongs to amide II, the peak at 1104 cm^{-1} is the characteristic absorption peak of ether-oxygen bond[2].

Ultraviolet Spectra Analysis of Cationic Aqueous Polyurethane

The aromatic cationic aqueous polyurethane contains urethane group, tertiary amine, and phenyl group. Their molecules contain oxygen and nitrogen atom with unpaired electron, C=O double bond, conjugated pi bond, and will bring σ-σ^*, π-π^*,n-σ^*,n-π^* four kinds of transitions, there-into σ-σ^* transition is below 200nm.[3]

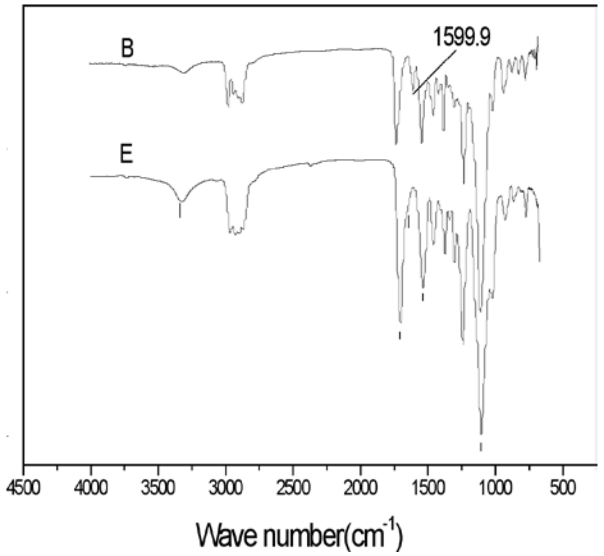

Figure 1: -FTIR spectrum of cationic polyurethane films

A, B, C in Figure 2 show the Ultraviolet Spectra of the aromatic cationic aqueous polyurethane dispersions based on different NCO/OH ratios. The strong absorption peak when λ is in the vicinity of 220 nm is K absorption peak produced by the π-π^* transition of conjugated double bond in phenyl group. The absorption peak when λ is in the vicinity of 245 nm is R absorption peak produced by the C=O double bond in ester group. It is produced by a looser n-electron which transit to the lowest unoccupied π^* orbit in carbonyl group, Because R peak is weak, so R peak in low concentration of polyurethane is easily concealed by strong absorption peak. The absorption peak when λ is in the range of 280-305 nm is the characteristic absorption peak-B absorption peak.[3] The λ position of B absorption peak in pure benzene is in the vicinity of 256 nm; when the hydrogen atom in benzene is substituted by methyl, alkyl or urethane group, B absorption peak will transit to red wave length. In the cationic aqueous polyurethane, the B absorption peak transit from pure benzene's 256 nm to the vicinity of 293nm, the transition amount is 38 nm. This is agreement with the reported 38.5 nm transition amounts of the substituent benzene if the substituent group is - NHCOCH$_3$ group.[4]

E in figure 2 exhibits UV spectra of the aliphatic cationic aqueous polyurethane dispersion in order to be convenient for comparison. The absorption peak when λ is in the vicinity of 200nm is π-π^* transition absorption peak of C=O bond in carboxyl group. This peak is the strongest. The absorption peak when λ is in the vicinity of 250 nm is the n-σ^* transition absorption peak of C=O double bond and C-N single bond in ester group. This peak is so weak that it can not be seen at low concentration.[4]

Compare the UV spectra of the aromatic and aliphatic cationic aqueous polyurethane dispersion, the prominent difference is that the aliphatic cationic aqueous polyurethane have no the characteristic absorption peak-B absorption peak in the range of 280-300nm. That is to say that the aromatic cationic aqueous polyurethane have larger absorption in the range of 280-300nm, the urethane group with benzene ring finally form large conjugated diazo coloring group by a series of light radiation reaction. The aliphatic cationic aqueous polyurethane hardly has absorption peak above 280 nm, it is better at photo resistance accordingly.

Figure 2 also shows that with the increase of NCO/OH ratios, the UV absorbance of the aromatic cationic aqueous polyurethane dispersion increase evidently. Just like the anionic aqueous polyurethane, the UV absorbance of polymer dispersion has to do with the size of emulsion particles, the larger the average diameter of dispersion particles is, the higher the UV absorbance is; on the contrary, the smaller the average diameter of dispersion particles is, the lower the UV absorbance is. The increase of the UV absorbance of the cationic aqueous polyurethane dispersion in Figure 2 shows that the average diameter of the cationic aqueous polyurethane dispersion particles increases with the increase of the mass percentage of the NCO group. This is agreement with the results of the diameter measured using the light scattering method.

TABLE VII
Mechanical Properties of Different kinds of Cationic PU Films

Types NCO/OH	Aromatic		Aliphatic	
	Tensile strength(Mpa)	Elongation at break(%)	Tensile strength (Mpa)	Elongation at break (%)
1.125	3.23	460	1.63	810
1.25	4.58	320	2.43	750
1.375	5.42	280	3.15	710
1.5	8.12	262	4.53	685

TABLE VIII
The Results of the Base Sealing Experiments

Scheme	Covering grain damage and mending properties	Uniformity and full of color	Astringency of coat	Softness and fullness of leather itself
1	better	better	weaker	good
2	better	better	weak	better
3	good	good	weaker	better

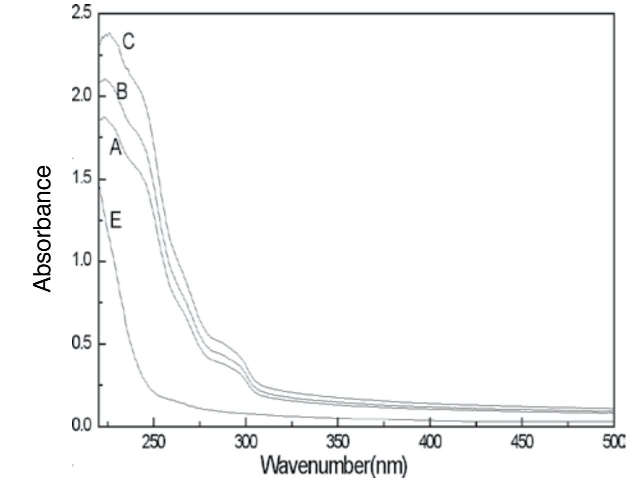

Figure 2: -UV spectra of the cationic aqueous polyurethane

TEM Analysis of the cationic aqueous polyurethane dispersions

The TEM photos of the particles of the aromatic and aliphatic cationic aqueous polyurethane dispersion are presented in Figure 3. B is aromatic, E is aliphatic. The particles morphology of the aromatic cationic aqueous polyurethane dispersions is spherical structure, the average diameter of its particles is about 100 nm; the particles morphology of the aliphatic cationic aqueous polyurethane dispersions is also spherical structure, the average diameter of its particles is about 105 nm according to a statistical calculation; its size is a little bigger than the aromatic aqueous polyurethane. This is because that in the same NCO/OH ratios, the mass percentage amounts of the hydrophilic agent in aliphatic polyurethane is a little less than in the aromatic polyurethane.[5]

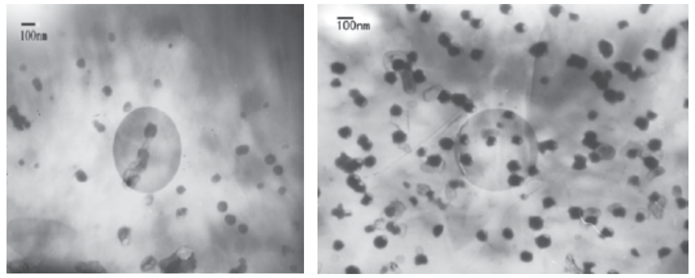

Figure 3: TEM of the cationic aqueous polyurethane dispersions

Static Mechanically Properties

Table VII shows the influence of NCO/OH ratios on the physical mechanic properties of the cationic aqueous polyurethane dispersions.

With increasing of the NCO/OH ratio, the placed stability of cationic aqueous polyurethane dispersions decreases, the tensile strength of cationic aqueous polyurethane films increases and the elongation at break of the films decreases. This is because with increasing of the NCO/OH ratios, on the one hand, the contents of the soft segments of polyurethane system decrease, the flexibility of the molecule chain decreases, the decreasing of flexibility is disadvantaged to emulsification and distribution, so the stability of the dispersion decreases; On the other hand, the contents of the hard segment of system increase, the polarity between molecules increases, the action of hydrogen bond, the physical crosslinked action become strong, so the tensile strength of cationic aqueous polyurethane films increases, the elasticity of the cationic aqueous polyurethane films decreases naturally.

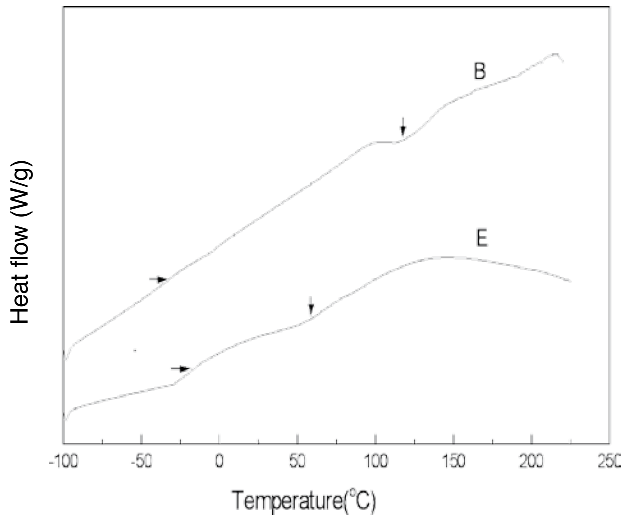

Figure 4: DSC curves of films casted from the cationic PU dispersions

Compared to the aromatic cationic aqueous polyurethane, at the same NCO/OH ratio, the aliphatic series is greater in the elongation at break, and lower in tensile strength. This is because that the aromatic cationic aqueous polyurethane include phenyl group, the rigidity of molecule chain is larger.

Differential Scanning Calorimetric Analysis

Figure 4 exhibits the DSC curves of the cationic aqueous polyurethane films; B is aromatic, E is aliphatic.

For the aromatic cationic aqueous polyurethane system, the two glass transitions take place in the range of -100°C — +220°C. One is in the vicinity of -20°C, one is in the vicinity of 100°C which respectively correspond to the micro-Brownian segmental motion of soft segment and hard segment of polyurethane, this shows the aromatic cationic aqueous polyurethane film has two phases.

For the aliphatic cationic aqueous polyurethane system, the two glass transitions also take place in the range of -100°C — +220°C. One is in the vicinity of -25°C, one is in the vicinity of 50°C which respectively correspond to the micro-Brownian segmental motion of soft segment and hard segment of polyurethane, this shows the aliphatic cationic aqueous polyurethane film also has two phases.

The glass transition temperature of soft segments of the aromatic cationic aqueous polyurethane is closer than that of the aliphatic cationic aqueous polyurethane. The glass transition temperature of hard segments of the aromatic cationic aqueous polyurethane is larger than that of the aliphatic cationic aqueous polyurethane. This is because that the aromatic cationic aqueous polyurethane include phenyl group, the rigidity of molecule chain is larger. In addition, the phase separation degree of two phases in the aromatic cationic aqueous polyurethane is larger than that in the aliphatic cationic aqueous polyurethane.

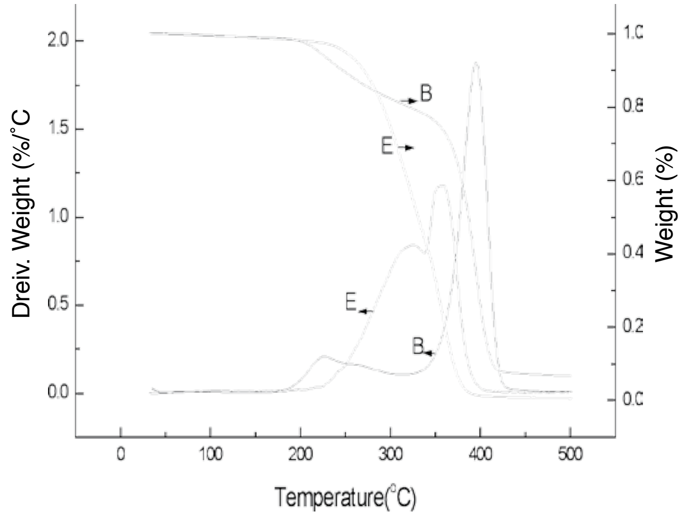

Figure 5: TGA curve of film cast from cationic aqueous PU

Thermogravimetric Analysis

The thermal stability of the cationic aqueous polyurethane is an important target to evaluate its good and bad application properties[6], so the thermogravimetric analysis of the aromatic and aliphatic cationic aqueous polyurethane film was done, the integral and differential curves of the film are shown in Figure 5, B is aromatic, E is aliphatic.

The decomposition of the aromatic cationic aqueous polyurethane exhibits two stages as shown in figure 4. This is analogous to the thermal decomposition curves of the reported anionic aqueous polyurethane which is synthesized using 1,6-hexamethylenediisocyanate(HDI)as raw materials.[6] The thermal decomposition temperature range in first stage is between 204°C and 270°C, the weight loss is about 66.0%, and the fastest temperature is 229°C. The thermal decomposition temperature range in second stage is between 368°C and 415°C, the weight loss is about 28.0%, and the fastest temperature is 395°C. The residue after thermal decomposition is about 6-7%.

The decomposition of the aliphatic cationic aqueous polyurethane also exhibits two stages as shown in figure 4. The thermal decomposition temperature range in first stage is between 271°C and 337°C, the weight loss is about 61.2%, and the fastest temperature is 325°C. The thermal decomposition temperature range in second stage is between 337°C and 415°C, the weight loss is about 35.5%, and the fastest temperature is 355°C. The residue after thermal decomposition is about 4%.

Whether for the aromatic cationic aqueous polyurethane or for the aliphatic cationic aqueous polyurethane, the two stages of their thermal decomposition respectively belong to the decomposition of hard segment and soft segment. That is to say, the first stage belongs to the decomposition of the hard segment; the second stage belongs to the decomposition of soft segment.

TABLE IX
Properties of the Finished Leathers

Finishing system	Sandwich finishing system	Sandwich finishing system	Anionic finishing system
Scheme	1	2	3
Wet rub fastness	≥4.0	≥4.0	≥3.0
Flex resistance	No cracking or white crazing	No cracking or white crazing	No cracking or white crazing
Fullness	Better	Better	Good
Softness	Good	Better	Good
Feel of real leather	Stronger	Stronger	Strong

The calculated hard segment amounts of the aromatic cationic aqueous polyurethane are 66.3% according to the recipe of the aromatic cationic aqueous polyurethane. The calculated hard segment amounts of the aliphatic cationic aqueous polyurethane are 68.2% according to the recipe of the aliphatic cationic aqueous polyurethane. The calculated result is good agreement with the measured result using TGA.

Compare the TGA curves of the aromatic and aliphatic cationic aqueous polyurethane, the beginning decomposition temperature 204°C of the aromatic cationic aqueous polyurethane is much lower than the beginning decomposition temperature 270°C of the aliphatic cationic aqueous polyurethane. This shows that the thermal stability of the aliphatic cationic aqueous polyurethane is better than that of the aromatic polyurethane. In addition, the TGA curves show that the phase separation degree of the aromatic cationic aqueous polyurethane is larger than that of the aliphatic cationic aqueous polyurethane. This result is good agreement with the measured result using DSC.

Application in the Base Sealing Coat of Pig Leather

Contrast to the traditional anionic finishing agent used in production, the cationic aqueous polyurethane –the base sealing agents showed better covering grain damage and mending properties, better uniformity and full of color, good softness of leather itself, and have no astringency from table VIII. If excessive quantities of the synthesized cationic base sealing agents are used, and when they come into contact with the following anionic finishing agents, because of electric charges are opposite and attractive each other quickly, although the base sealing effect is good, but phenomenon of uneven finishing, colour out, uneven dyeing can be easily produced. It is necessary that the levelling agent or penetrating agent is added into the anionic finishing agents to improve this condition.

Application in the sandwich finishing system

The wet rub resistance of the finished leather using the sandwich system is better than using the anionic finishing system from table IX. This is probably because that the cationic and anionic dispersions are used alternatively, the chemical reactions take place between the anionic and cationic ions, the hydrophilic groups disappeared, the water resistance of the finished leather using sandwich finishing system increased.

From the overall point of view, the touch of the finished leather using sandwich system is better than using the anionic finishing system from table 5. As we know, there are a large number of anionic groups inside the leather fiber, when the cationic polyurethane dispersion are used for the sealing coat, the thinner, softer, cemented films are formed quickly, prevent the successive anionic dispersions from penetrating through the leather, avoiding the hardness and the astringency, and can keep leather crust soft, full. Furthermore, because of the adhesion force of anionic and cationic ions between different layers, make the finishing coat cement together firmly, result in the finishing leather denser, thinner, so the finished leather using sandwich system is of good feel of real leather.

In addition, the aliphatic cationic aqueous polyurethane film, the aromatic cationic aqueous polyurethane film, and the anionic aqueous polyurethane film used in production were exposed under UV light about 24 hours respectively, the aliphatic cationic aqueous polyurethane didn't change to yellow; the aromatic and the anionic aqueous polyurethane did change to yellow. This showed that the synthesized aliphatic cationic aqueous polyurethane can be used the finishing system of shallow color leather or white leather.

CONCLUSION

A series of aromatic and aliphatic cationic aqueous polyurethane dispersions were successfully prepared with toluene diisocyanate(TDI), and isophorone diisocyanate(IPDI) as raw materials. Both the aliphatic and the aromatic cationic aqueous polyurethane are all two phase structure systems. Their two glass transitions took place in the range of -100°C to+220°C, respectively corresponding to the glass transitions of soft segments and hard segments. Their thermal decomposition also exhibited two stages, respectively corresponding to thermal decompositions of hard segments and soft segments. The particle morphologies of aromatic and aliphatic dispersions both are spherical. The strong π-π^* transition absorption peaks took place when λ was in the vicinity of 220nm. With the increasing of NCO/OH ratios, the tensile strengths of the films increased and their elongations at break decreased.

Compared to the aromatic cationic aqueous polyurethane, the aliphatic series is lower at the glass transition of hard segments, better at photo-resistance; greater in the elongation at break, and lower in tensile strength. The UV spectra of the aliphatic cationic aqueous polyurethane did not show a characteristic B absorption peak, the aromatic cationic aqueous polyurethane have larger B absorption peak in the range of 280-300nm.

The synthesized aliphatic and cationic aqueous polyurethane can be used to the base sealing coat of pig leather, and showed very good sealing effect. Contrast to the traditional anionic finishing agent, the cationic base sealing agents showed better covering grain damage and mending properties, better uniformity and better full of color, good softness of leather itself, and have no astringency.

The wet rub resistance of the finished leather using the sandwich system is better than using the anionic finishing system. From the overall point of view, the touch of the finished leather using sandwich system is better than using the anionic finishing system.

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