Waterborne Dimethylolpropionic Acid-diisocyanate Adducts with Alkali-deblockable Isocyanate Groups as Pretanning Agent for Chrome Tanning

by

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Abstract

Diisocyanates qualify as tanning agent by virtue of their strong tendency to crosslink collagen molecules by reacting with amino groups. However, due to their sensitivity to water, these compounds cannot be used directly in aqueous environment, which is the basis for leather processing. To address this problem, waterborne dimethylolpropionic acid-diisocyanate adducts (WDDAs) with temporarily-blocked isocyanate terminals were prepared in the present paper by using $NaHSO_3$ as blocking agent, and further evaluated as a pretanning agent for chrome tanning. Fourier transform infrared (FTIR) spectra revealed that the isocyanate terminals in WDDAs were successfully blocked by $NaHSO_3$. The blocked isocyanates were stable under ambient temperature, but prone to deblocking under alkaline condition. The regenerated isocyanates were found still capable of crosslinking collagen molecules to impart hydrothermal stability. In leather tanning, a high shrinkage temperature (Ts>110°C) was achieved by successively treating goat skin with 5 wt% WDDAs and 4 wt% chrome powder. Stereomicroscope and SEM observation further indicated that the WDDA-chrome tanned leather exhibited tight grain surface and well opened up fiber structure in comparison with semi-chrome tanned leather. Due to the presence of carboxyl group in dimethylolpropionic acid, it was also found that WDDAs enhanced the absorption of chromium in the resultant leathers (% chrome uptake> 90%), resulting in significantly less Cr residual in the tanning wastewater. In addition, it is important to note that the usage of salt in pickling process was avoided owing to previous crosslinking of amino groups, which is very helpful for overcoming the problem of total dissolved solid (TDS) related to neutral salts. The tanning effect of WDDAs and their auxiliary function for chrome tanning allow them to be applicable as a pretanning agent, which efficiently alleviates the environmental impact of traditional chrome tanning for sustainability.

Introduction

Leather tanning is without a doubt one of the oldest human activities. Since the Stone Age 2.5 million years ago, when cavemen only used raw hides or skins for protection, man has mastered the complicated leather tanning techniques, to produce high-quality leather shoes, garments, furniture and other necessities.[1] According to modern tanning theory, the stabilization of skins against degradation by microorganisms, wet heat and thermo-mechanical stress is achieved by tanning agents, which introduce crosslink between collagen chains to permanently alter their structure so that they can be preserved and irreversibly converted into useful leather. The most popular tanning agent in leather industry so far is still chromium salts,[2,3] which coordinate with ionized carboxyl groups offered by aspartic and glutamic residues in collagen to impart excellent hydrothermal stability. However, despite many technical advantages associated with this tanning method, traditional chrome tanning is under continuous pressure currently from various perspectives. For example, over 90% of the world's chromite reserves and resources are located in South Africa and Zimbabwe.[4] This uneven geographical distribution results in high and still-rising price of chrome tanning agent. In addition, the mole ratios of aspartic and glutamic residues to all amino acids in collagen molecules are as low as 42/1000 and 73/1000, respectively.[5] As a result, the combination sites in raw skins for chrome tanning agent are usually low, leading to high chromium discharge in the effluent. In most Chinese tanneries, conventional chrome tanning system usually generates industrial effluent containing about 2000-fold more chromium than the norm (1.5 ppm) specified by China's environmental regulatory agency, arousing much public concern nowadays.[6] Furthermore, although Cr(III) is commonly considered harmless and even used as nutritional supplements (such as

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chromium picolinate, [$Cr(pic)_3$]) for diabetic people, some researches have correlated Cr(III) complexes with genotoxic side-effects[7] and apoptosis.[8] In particular, it has been recognized that Cr(III) may be oxidized to carcinogenic Cr(VI) in the natural environment. Over the past decades therefore, there has been a huge surge of interests in seeking alternative tanning agents that are environmentally-friendly while achieving comparable tanning effect to chromium salts. However, despite many encouraging progresses achieved in this field, none of the candidates, mostly aluminium, vegetable tanning, aldehyde, oil, synthetic organics, or even nanomaterials, can reproduce the great hydrothermal stability and retain the versatility of chromium(III). Thus, some researchers argue that chrome tanning is actually irreplaceable under current technology levels, and will still remain the most important tanning system at least in the short term. In such circumstances, how to minimize the environmental impact of chrome tanning, by manipulating the parameters of the process, or using carboxyl-containing auxiliaries, like hydroxyethyl acrylate,[9] aldehyde-acid,[10] oxazolidine derivative[11] and WDDA present in this paper, seems another promising alternative for sustainability of leather industry.

Diisocyanates, a kind of bifunctional organic compounds, have been of great interest to academia and industry, especially as a covalent crosslinking agent. Since isocyanates are prone to react with compounds containing active hydrogen such as amines, some researchers attempted to use them to tan leather. Half a century ago, Robert C. Putnam *et al*. described a new tanning agent, aliphatic diisocyanates with 6-18 carbon atoms in their patent.[12] According to their invention, skins or hides were first immersed in organic solvents for dehydration, and then aliphatic diisocyanates were introduced for crosslinking. Obviously, this tanning process can not be widely applied in the industry technically or commercially because it is carried out in non-aqueous medium that is incompatible with conventional leather processing. Therefore, how to convert isocyanates into water-soluble derivatives and retain their reactivity is considered a key issue for their successful application in crosslinking of collagen.[13,14] Based on this concept, Brian Milligan *et al*. prepared a water-soluble dicarbamoylsulfonate by additive reaction between bisulfite and diisocyanates monomer (tolylene diisocyanate, hexamethylene diisocyanate, and isophorone diisocyanate).[15] This dicarbamoylsulfonate, like the parent diisocyanates, could react with amines in aqueous medium to give ureides. In this way, stable crosslinks between amino-terminated side-chains of collagen were introduced, which avoided the usage of organic solvent as a medium. This investigation is stimulating ever greater interest, because it proposes a feasible way to utilize the reactivity of diisocyanates for leather tanning. However, when used as a primary tanning agent, it was found that the shrinkage temperature of the tanned leather was only in the range of 69-88°C, depending on the parent diisocyanates monomer used. If applied as a retanning agent for chrome tanned leather, the dicarbamoylsulfonates caused only a few-degree temperature rise. This was probably because the reaction between dicarbamoylsulfonates and amines in collagen required a high pH, which might cause de-tanning of chrome tanned leather.

In the present paper, additive reaction was carried out between dimethylolpropionic acid and twofold mole ratio of diisocyanates (toluene diisocyanate, isophorone diisocyanate, or methylene-bis(4-cyclohexylisocyanate)) to design a new pretanning agent for chrome tanning. $NaHSO_3$ was employed to temporarily block the isocyanate terminals of adducts. Such product was water-soluble due to the presence of carboxyl and carbamoylsulfonate (-CS) groups. Under alkaline condition, the blocked isocyanate groups were prone to deblocking, regenerating intermediate -NCO which remained reactivity towards amino groups in collagen. When the skins were successively treated with such adduct and 4% chrome tanning agent, a shrinkage temperature >110°C was achieved. Moreover, the TDS load was reduced accordingly for the salt-free pickling process prior to chrome tanning, and the percentage chrome uptake was significantly promoted due to the presence of carboxyl groups in adducts. Organoleptic properties and fiber structure of the tanned leathers were further evaluated, employing WDDA-chrome tanned or chrome tanned leather as control. The aim of this paper is to provide an efficient pretanning agent, which not only displayed tanning effect itself but also promoted adsorption of Cr(III) in the resultant leather. The new pretanning agent displays great potential to alleviate the environmental impact of traditional chrome tanning, which may not be environmentally sound but is deemed irreplaceable currently in leather industry.

EXPERIMENTAL PROCEDURES

Materials

Toluene 2,4-diisocyanate (TDI), isophorone diisocyanate (IPDI), methylene-bis(4-cyclohexylisocyanate) ($H_{12}MDI$) used in this study were supplied by Mistui Takeda Chemicals, Inc. (Tokyo, Japan). Dimethylolpropionic acid (DMPA), triethylamine (TEA), N, N-dimethylformamide (DMF), sodium bisulfite, sodium sulfite, isopropyl alcohol, iodine, potassium iodide, gelatin powder of laboratory grade were obtained from Kelong Chemical Engineering Co. Ltd. (Chengdu, China). Pickled goat skins used in this study were made in-house. KMC chromium powder (chemical grade) with 33% basicity was purchased from Sichuan Tingjiang New Material, Inc. (Shifang, China).

Synthesis of WDDA

Isocyanate (0.2 mol) was charged into a four-necked flask, equipped with a PTFE stirrer, a thermometer, a dropping funnel and a pressure equalizing funnel under nitrogen atmosphere at 40°C. The solution of dimethylolpropionic acid

(DMPA, 0.1 mol) in DMF was added dropwise to the isocyanate. Then the mixture was stirred and heated to 50°C for 1h and successively to 65°C. The reaction mixture was allowed to react at 65°C until the theoretical -NCO content was reached. The change in the -NCO value during the reaction was determined with the standard di-*n*-butylamin back-titration method.[16] After cooling to 40°C, the viscosity of mixture was adjusted by adding 5 ml DMF, and 0.1 mol triethylamine was added to neutralize the carboxyl groups of the NCO-terminated prepolymer. After neutralization for 20 min, flask was placed in an ice-water bath to cool to 5°C, and 10 ml isopropyl alcohol was added to reduce the viscosity. A mixed aqueous solution of $NaHSO_3/Na_2SO_3$ (1:0.2, n/n) at 4°C upon the theoretical residual -NCO value was added with intense stirring for 40 min, and the reaction continued until the -NCO peak (around 2270cm^{-1}) in the IR spectrum completely disappeared. Cold deionized water was added to the resulting solution to achieve a solid content of 40%, followed by 6 hours of static defoaming. Finally, the waterborne dimethylolpropionic acid-diisocyanate adduct (WDDA) was obtained. The schematic reaction sequence is given in scheme 1.

Characterization of WDDA

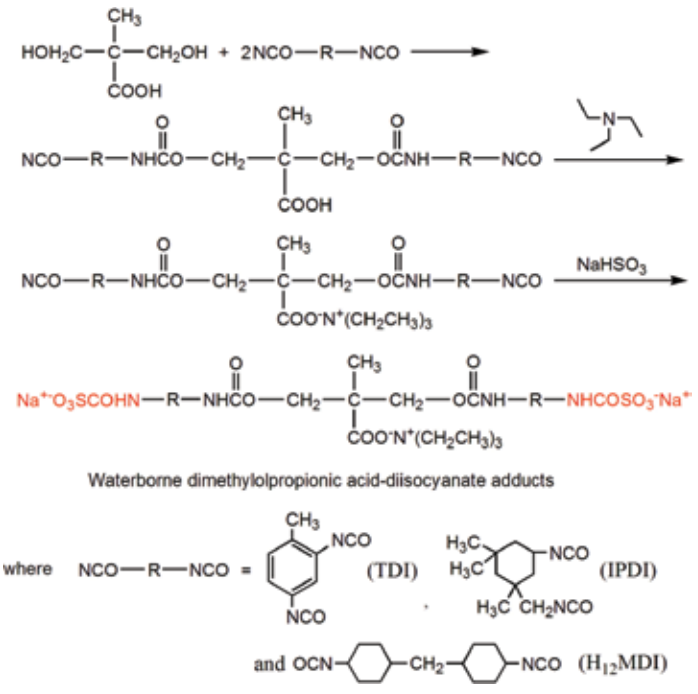
Iodimetric Analysis

The blocking degree of -NCO was determined by the method of Dalton *et al*. with some modification.[17] Approximately 2g of WDDA was dissolved in the mixture of water/isopropanol (20/30 ml) and titrated with 0.5 M iodine solution to the pale yellow end-point V_1, indicating the unreacted HSO_3^- or SO_3^{2-}; then 7.5 M NaOH (10 ml) was added, followed after *ca*. 1 min by addition of 1% phenolphthalein (1 drop). Ten minutes later the solution was titrated with 2.5 M H_2SO_4 until the red color disappeared, then supernumerary H_2SO_4 solution (3 drop) was added to ensure a weakly acidic medium; the solution was again immediately titrated with iodine to the new end-point V_2, which was equivalent to HSO_3^- liberated by the carbamoylsulfonate ion. The conversion rate of -NCO to carbamoylsulfonate ion was calculated as follows:

$$C_s\,(\%) = \frac{V_2}{V_1 + V_2}$$

$$C_i\,(\%) = f_n \times C_s$$

Where C_s is the $NaHSO_3$-based conversion ratio, C_i is the conversion ratio using -NCO as reference, and f_n is the molar ratio of ($HSO_3^- + SO_3^{2-}$) to -NCO.



Scheme 1. Synthesis of WDDAs.

FTIR Analysis

Lyophilized WDDA samples were equilibrated in a desiccator containing silica gel for 3 days at 25°C before testing. Subsequently, sample (*ca*. 2 mg) was triturated with 200 mg KBr and prepared as pellets. The FTIR spectra were obtained using a Nicolet iS10 spectrometer (Thermo Fisher Scientific, United States) at 4 cm^{-1} resolution, over a wavenumber range from 500 cm^{-1} to 4000 cm^{-1}, and the spectra plots represented the average of 32 scans.

DSC Measurement

To examine the deblocking temperature of the WDDA, DSC measurement was conducted on a differential scanning calorimeter (DSC) from NETZSCH Instrument Company (PC200-DSC, German). The lyophilized sample (*ca*. 3 mg) was sealed in an aluminum pan with an empty aluminum pan as the reference and heated at a constant rate of 10°C/min from 30°C to 140°C under a nitrogen flow.

Preparation of Gelatin Modified by WDDA

Gelatin was used as a model for collagen, and the reaction mechanism of collagen with WDDA under weakly alkaline condition was investigated. In a 250 ml beaker, gelatin was dissolved overnight in deionized water with a concentration of 40g/L. Thereafter, WDDA at an amount of 10% w/w on gelatin was added in several portions. After the solution was homogeneously stirred, the pH of the reaction mixture was gently brought to 8-9 through the dropwise addition of 1M Na_2CO_3 at 45°C with magnetic stirring for 2h. Finally, the pH= 5.5 was reached with 1M hydrochloric acid. The modified gelatin solution was collected by centrifugation (2000 r/min, 15 min), in order to remove the hydrolysis products in the case of non-exhausted WDDA. Then, the resultant gelatin was precipitated in ethanol rinse bath, washed three times with deionized water. Before analysis, the modified gelatin was dried at 25°C under vacuum condition until a constant mass was obtained.

Characterization of Gelatin Modified by WDDA

TOC Analysis

Gelatin and gelatin modified by WDDA were hydrolyzed and dissolved in 1M NaOH solution at 40°C for 5h and diluted into a concentration of 0.15g/L with deionized water, respectively. The total organic carbon contents (TOC) of the solutions were measured by a TOC analyzer (Tekmar Dohrmann Apollo9000, United States).

TGA Measurement

Thermogravimetric analysis (TGA) was carried out in a NETZSCH TG 209 F1 analyzer equipped with a TASC 414/3 thermal analysis controller. The gelatin sample (*ca*. 5mg) was loaded in a tared Al_2O_3 pan and heated from 40 to 600°C with a heating rate of 10°C/min under N_2 atmosphere. The 5 wt% weight loss temperature of each sample was calculated by the Proteus software connected to the analyzer.

Tanning Trial

Tanning trials were carried out on pickled goat skin with WDDA and KMC chromium powder employing conventional tanning procedures.[18] The amounts of materials used for tanning process are expressed as percentages of the original pickled goat skin weight and the detailed process is given in Table I.

Assessment of Properties of Tanned Leathers

The shrinkage temperature of strips of wet leather was measured by a MSW-YD4 shrinkage meter from Yangguang Research Institute of Shanxi University of Science Technology according to Chinese Industrial Standard (QB/T 2713-2005). A known weight (*ca*. 1 g) of the sample was treated by dry digestion and the measurement of the amount of Cr_2O_3 was followed by Chinese Industrial Standard (QB/T 3812.15-1999). The wet blue leathers were assessed for color, grain tightness, grain smoothness, strength, and fullness by hand and visual examination of experienced tanners.

Stereomicroscope and Scanning Electron Microscope (SEM) Observation

Samples were cut with fresh stainless steel blades from the official sampling position, washed, dehydrated slowly in acetone and dried at 45°C in an oven for 12h. The grain surface of leathers was analyzed using an Olympus SZX12

TABLE I
Tanning process with WDDA and KMC chromium powder.

Process	%	Chemical	Temp. °C	Time (min)	pH	Remark
De-pickle	50	Water	22			
	4	NaCl				
	0.5-1	$NaHCO_3$		60	4-5	Drain
WDDA tannage	50	Water				
	5/7.5	WDDA		120		
Basification	0.6-1	$NaHCO_3$	45	3×10 + 90	7	
	1.5-2	MgO		3×20 + 120	8-9	Drain and stand overnight
Wash	300	Water	20	60		
Pickle	50	Water				
	1.5-2	HCOOH		40	3	
Chromium tannage	4/5	KMC		180		
	1-1.2	$NaHCO_3$		3×20	4	
	150	Water	45	120		Stand overnight

stereomicroscope (Olympus, Tokyo) at 50× magnification with a digital camera. Subsequently, sample pieces were mounted on aluminium specimen stubs using double-sided adhesive tape and then directly introduced into the specimen chamber of Phenom™ Pro Scanning Electron Microscope (Phenom-World Company, The Netherlands) without coating with gold. The micrographs for cross section were obtained by operating the SEM at low vacuum with an accelerating voltage of 5 kV and at magnifications of 250× and 500×.

Determination of Total Chromium in Tanning Wastewater

The spent tanning liquors were collected and analyzed for chromium content by an inductively coupled plasma-atomic emission spectrometry (2100 DV ICP-AES, from PE Company, USA), and then the percentage exhaustion of chromium was calculated. Briefly speaking, the sample (5 ml) was suffered from atmospheric digestion with HNO_3-H_2O_2-HCl and diluted to 50 ml with deionized water.[19] Afterward, the analyte was vaporized and introduced into plasma ion source through the port to the torch. The concentration of element chromium was determined according to the intensity of characteristic spectral lines.

Results and Discussion

Chemical Structure of WDDAs

Scheme 1 illustrates the synthetic route of WDDAs. DMPA reacted with isocyanate (NCO/OH mole ratio, R=2) to get NCO-terminated adduct with pendant COOH group. Adducts were later masked with excess blocking agents ($NaHSO_3$/NCO 1.2:1, n/n) to get WDDAs. The FTIR spectra of WDDAs are displayed in Figure 1.

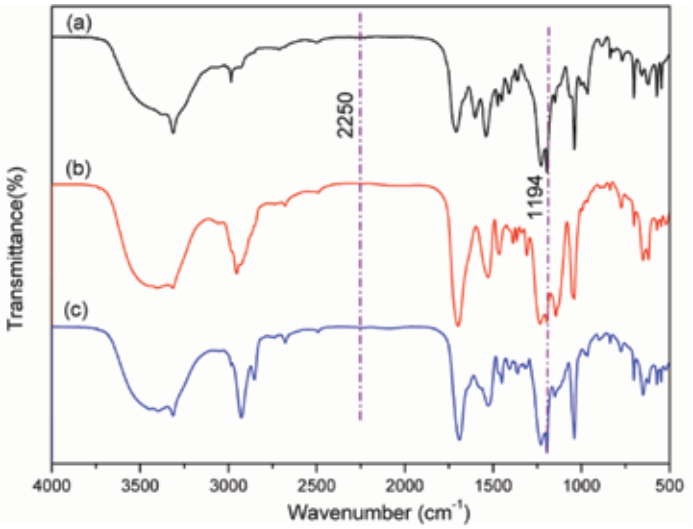


Figure 1. FTIR spectra of (a) TDI-WDDA, (b) IPDI-WDDA, and (c) H_{12}MDI- WDDA.

In general, -NCO groups exhibit a strong FTIR absorption band in the range of 2250-2270 cm^{-1}, corresponding to the asymmetric stretching vibration. According to Figure 1, FTIR spectra of WDDAs are similar and show no absorption in the 2250-2270 cm^{-1} range, which indicates that the -NCO groups of the diisocyanates are completely masked by the blocking agent.[20,21] The absorption at 1194 cm^{-1} corresponds to the characteristic peak of $-SO_3^-$.[22] The peak at 1600 cm^{-1} can be assigned to C=C stretching vibration of the aromatic ring (Figure 1a). The NHCOO structure is demonstrated by the absorptions around 3315 cm^{-1} (N-H stretching), 1700 cm^{-1} (C=O stretching of urethane and carboxylic groups), 1530 cm^{-1} (C-N stretching, combined with N-H out of plane bending), and 1235 cm^{-1} (the stretching vibration of the C=O of urea combined with the N-H group).[23,24] All these results confirm the formation of WDDAs.

Storage Stability of WDDAs

Besides bisulfate, numerous commercial agents can be used to block isocyanates, such as phenols, alcohols, oximes, 3,5-dimethylpyrazole (DMP) and diethyl malonate.[25,26] As far as the choice of blocking agents, it is critical that the deblocking temperature should be suitable for their application. In particular, the storage stability of polymeric articles is susceptible to hydrolytic precipitation. For example, the insoluble polyurea will be produced from the reaction of released -NCO with water during storage and transport if the deblocking temperature is too low.

In this study, sodium bisulfite is selected to block the NCO-terminated prepolymers because the resultant products are easy to return to the -NCO group and bisulfite in a condition of alkaline solution or at elevated temperature.[26,27] It is well known that the leather manufacturing process needs to be conducted in mild and gentle environment due to inherent vulnerability of skin collagen. Consequently, the wet

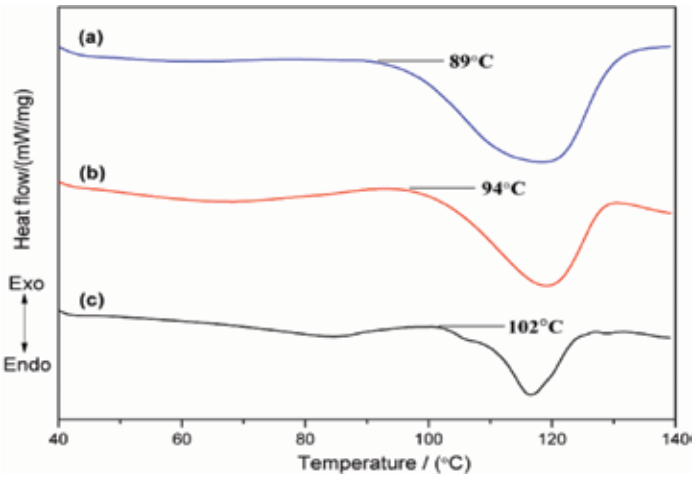


Figure 2. DSC curves of (a) TDI-WDDA, (b) IPDI-WDDA, (c) H_{12}MDI-WDDA.

processing of leather normally takes place in aqueous baths, the pH values of which generally range between maximum of 12 (liming) and minimum of 2 (pickling) without dramatic changes;[28] and the operating temperature does not exceed 60°C that is also the approximate shrinkage temperature of most animal skins.[29] Carbamoylsulfonate ion is stable in neutral and acidic solution but easy to deblock in alkaline condition (pH≥ 8) at ambient temperature. In other words, adjusting the pH value can induce the occurrence of deblocking, which provides much convenience and possibility for leather tanning.

The deblocking is an endothermic process and can be determined by DSC analysis, so that an endothermic peak on DSC curve is usually associated with the deblocking reaction.[20,26] The deblocking temperatures for different WDDAs are depicted in Figure 2.

As shown in Figure 2, the deblocking temperatures of three kinds of WDDAs are all above 80°C, indicating that the WDDAs are able to provide long-term storage stability under ambient conditions. In addition, the order of deblocking temperatures of three WDDAs is H_{12}MDI-WDDA (102°C) > IPDI-WDDA (94°C) > TDI-WDDA (89°C). In general, the onset temperature of deblocking reaction mainly depends on the chemical structure of analyte at the same testing condition. TDI-WDDA exhibits the lowest deblocking temperature as compared with aliphatic WDDA. This could be ascribed to the electron-withdrawing effect of aromatic ring. For aliphatic WDDAs, IPDI-WDDA instead of H_{12}MDI-WDDA shows lower deblocking temperature, which may be related to the steric hindrance of cyclohexyl ring.

Conversion Ratio

The conversion ratio of -NCO to carbamoylsulfonate ion is listed in Table II.

It is noticed that, compared with other types of WDDAs, TDI-WDDA shows relatively lower conversion ratio or blocking degree (only *ca*. 74.4%). Owing to the electron-withdrawing effect of aromatic ring, -NCO group of TDI is susceptible to nucleophilic attack and exhibits higher reactivity to water or alcohol than that of other aliphatic (or alicyclic) isocyanates. Competitive reaction among -NCO, water (or alcohol) and HSO_3^- results in a lower conversion ratio.

The difference in conversion ratio between H_{12}MDI-based and IPDI-based prepolymers may be attributed to the steric hindrance effect. H_{12}MDI has a more regular and symmetrical structure. Hence, less steric hindrance of H_{12}MDI imparts the -NCO group of prepolymer higher activity to HSO_3^- and lower side-reaction to water (or alcohol), which consequently leads to a slight increase of blocking degree as compared with IPDI-based prepolymer.

Reaction Between WDDA and Collagen

Possible Reaction Mechanism

WDDA synthesized here, just like its parent isocyanate, is able to react with amino groups of collagen under suitable deblocking condition. A possible reaction mechanism is presented in Figure 3.[30-32]

Just as mentioned above, the WDDAs can be cleaved to release -NCO group under heating (≥ 80°C) or weak alkaline condition (pH≥ 8). The released or intermediate existent -NCO groups react quickly with non-protonated amino groups of collagen at a slightly alkaline pH as described in Figure 3, which is expected to contribute to the skin-tanning effect. Although the released -NCO group has a tendency to react with water or alcohol, the reaction rate is too slow, about 50 times lower than that of -NCO with aromatic amines, moreover, 1000 times lower than that of -NCO with aliphatic amines, to form a competition with lateral amino groups of collagen.[30] Clearly the reaction between the released -NCO and primary amines of collagen is the predominant reaction with a minimal risk of hydrolysis. Similarly, even if these amino groups are

TABLE II
Conversion of -NCO to carbamoylsufonate.

Conversion ratio (%)	Blocked WDDAs		
	TDI-WDDA	IPDI-WDDA	H_{12}MDI-WDDA
C_s	51.7	63.5	65.1
C_i	74.4	91.5	93.7

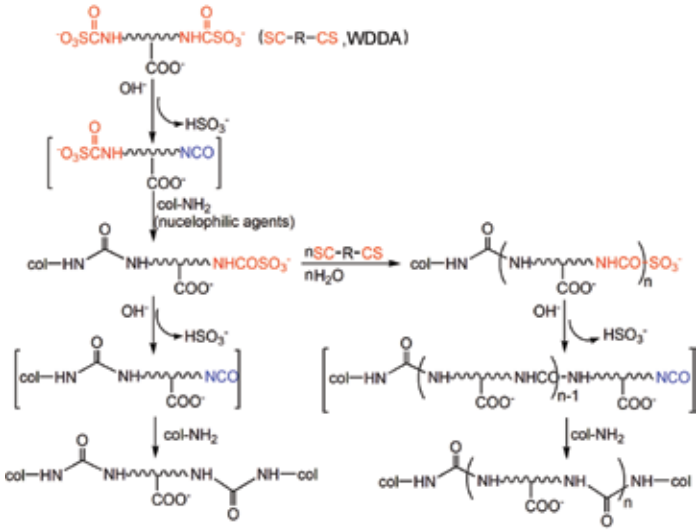


Figure 3. Reaction mechanism between WDDA and collagen.

unavailable, perhaps -NCO will react with ureas and amides; nevertheless, this reaction is also slow (ureas and amides react at almost the same reaction rate as water).

Deblocking of WDDA Under Alkaline Condition

In order to verify whether the deblocking of WDDA takes place under alkali-catalyzed condition, gelatin was used as a model for skin collagen, and the experiments were carried out in a pH range of 8 to 9. After modification by WDDA, the change of total organic carbon content (TOC) in gelatin was measured and shown in Figure 4.

It can be found that TOC of gelatin increases after modification, which reveals that the deblocking reaction of WDDA occurs under basic condition. The released -NCO groups react with the amino groups of gelatin to form urea bonds, thereby introducing new carbon chains and resulting in an increase of TOC. The improvement of TOC follows the order of TDI-WDDA < IPDI-WDDA < H_{12}MDI-WDDA, indicating that the reaction extent between the amino groups of gelatin and WDDA is greater for aliphatic WDDA than for aromatic TDI-WDDA. It can probably be attributed to the conversion ratio of -NCO as discussed above, where aliphatic-based WDDA shows a higher conversion ratio of -NCO to carbamoylsulfonate ion. Besides, the increasing carbon content of WDDAs in mentioned above order may be another factor causing this variability.

Thermal Stability of Modified Gelatin

The thermal stability of samples can be determined by TGA analysis. The curves of weight loss and first derivate related to the rate of weight loss (DTG) for pristine gelatin and modified gelatin are compared in Figure 5 (a) and (b), respectively.

Two weight-loss steps can be distinguished on TGA curves for pristine gelatin and modified gelatin samples. The first one from 40 to 160°C is related to the breakage of inter- and intra-molecular hydrogen bonds accompanied by gradual loss of water.[33,34] In fact, 5% weight loss temperature occurs at 104°C, 115°C, 137°C, 140°C for pristine gelatin and TDI-WDDA, IPDI-WDDA, H_{12}MDI-WDDA modified gelatin, respectively, which reveals that the thermal stability of gelatin is enhanced through this treatment. The second step in the range of 230-500°C is associated with the decomposition of the polypeptide chains in gelatin.[33] As shown in TGA curves, the maximum decomposition temperature for pristine gelatin is at 313°C, however, the maximum of the peak for modified gelatin is shifted to higher temperature, namely 320°C, 328°C and 330°C for TDI-WDDA, IPDI-WDDA, H_{12}MDI-WDDA, respectively. In addition, the residual weights of modified gelatin are also higher than that of the pristine gelatin. These results all suggest that the thermal decomposition of protein is hindered by the chemical crosslinking of WDDA. This conclusion is in good consistent with other's work in the literature for collagen modification by cross-linkers.[33-35]

Tanning and Tanning Wastewater Analysis

WDDAs prepared above can react with collagen and have good water solubility as well as storage stability, providing a possibility for leather tanning. In practice, WDDAs can be used both as an organic pretanning agent and a semi-chromium tanning auxiliary agent. Additionally, it is worth mentioning that no salt was added to the float before adding the acid as shown in Table I. Therefore, the total dissolved solids (TDS) load in the effluent was effectively reduced. As well-known in tanning industry, commonly used acids in pickling process such as H_2SO_4 and HCOOH will result in the swelling of pelts, which is not conducive to the penetration of the chrome tanning agent. Thus the salt (e.g., NaCl) should be previously added to restrict the swelling of the collagen in the acidic medium. According to the previous study, the swelling was mainly due to electrostatic repulsion of protonated amino groups of collagen at low pH. For this reason, selectively blocking the amino group is an effective way to solve this problem.[36] Since the mechanism of WDDA pretanning is to

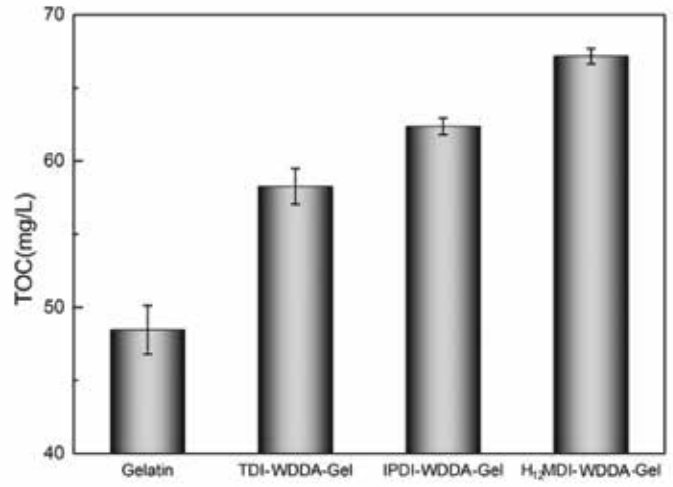


Figure 4. TOC of gelatin modified by WDDA.

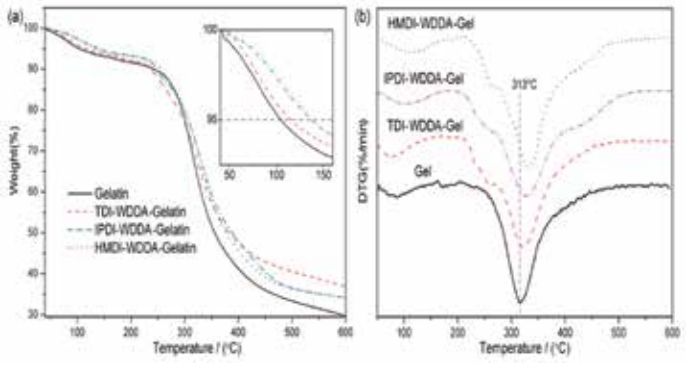


Figure 5. (a) TG curves of pristine and modified gelatin; (b) TGA curves of pristine and modified gelatin.

covalently crosslink the amino groups of collagen, there is no need to add salt into the pickling bath. In fact, in practice the swelling of pelts was not observed. Table III further gives the values for the tanning characteristics of WDDAs such as shrinkage temperature and the percentage chromium uptake.

As can be seen from Table III, in the case of the same amount (7.5 wt%), the shrinkage temperatures of skin tanned directly by WDDA is up to 80°C for H_{12}MDI-WDDA, 78°C for IPDI-WDDA and 74°C for TDI-WDDA, exhibiting the same order of magnitude as their blocking degrees of -NCO. When they were used for semi-chromium tanning auxiliary agent, it was found that after pretreated with WDDA firstly then followed a 4 wt% semi-chromium tannage, the shrinkage temperatures of resultant leather increased from 96°C to above 110°C. In comparison with traditional chromium tannage (7 wt% chromium powder), 42.8% chromium was saved. Meanwhile, the chromium exhaustion is significantly improved for WDDA-KMC combination tannage which provides increased uptake of chromium in the range of 90–94%. For instance, the percentage chrome uptake increases from 70.3% to 94.1% (5 wt% H_{12}MDI-WDDA), showing a synergistic effect of combination tannage and high chromium absorption. It is also evident from the lower amounts of chromium present in the spent chrome liquor as compared to the control (4% or 5% KMC tanning). The reason for high chromium exhaustion is believed to be related to the introduction of additional carboxyl groups, which provides more sites available for chromium(III) complex and leads to formation of the single or multi-point binding between collagen fibers.[5,37,38] This means that pretanning with WDDA helps chromium to exhibit a high degree of complexation with collagen. A possible model of WDDA-chromium(III) synergy reaction is further described in Figure 6.

Organoleptic Properties of the Tanned Leather

Assessment of organoleptic properties of wet blue leather developed in this study is given in Table IV. It is seen that the color, grain tightness and smoothness of the WDDA-chrome tanned leathers are comparable to/better than those of semi-

TABLE III
The effect of WDDA in tanning and chromium absorption.

WDDA	%	pH	T_S (°C)	KMC %	T_S (°C)	Chromium in the waste bath (mg/L)	% Chromium uptake
-	0	-	59±1	4	96±2	992.8±7.99	70.3
				5	107±1	1240.1±19.02	69.4
TDI-	5	9	74±1	4	112±1	234.2±2.05	92.5
				5	115±1	388.0±12.89	90.1
	7.5		74±1	4	113±1	210.2±0.42	93.2
				5	116±1	320.4±4.15	91.8
IPDI-	5	9	75±1	4	113±1	203.6±0.84	93.5
				5	115±1	297.6±1.63	92.4
	7.5		78±1	4	117±2	195.8±0.30	94.0
				5	118±1	248.4±2.45	93.5
H_{12}MDI-	5	9	79±1	4	115±1	200.7±0.58	94.1
				5	117±1	269.9±3.01	93.1
	7.5		80±1	4	119±1	186.8±1.06	95.3
				5	119±2	241.1±1.33	93.9

chrome tanned leathers. The presence of WDDA improved the tightness and fullness of the experimental wet blue leathers as displayed in Table IV. The amounts of Cr_2O_3 in the wet blue leathers tanned with chromium and WDDA-chromium are respectively given in Table V. Obviously the chromium content in the experimental wet blue goat leathers is higher than that in the control wet blue leathers, indicating the improved uptake of the chrome due to WDDAs.

Morphologies of Grain Surface and Fibers of the Tanned Leather

To further study the influence of the WDDA on the tanned leathers, stereomicroscope and SEM were employed to observe the grain surface and fiber structure, respectively. Photomicrographs showing the grain surface of the leathers in a magnification of 50× are shown in Figure 7. It can be seen that the grain surface of the wet blue leather tanned using 5% H_{12}MDI-WDDA and 4% KMC (Figure 7 b) seems to be slightly tight without any wrinkles than the one tanned with 4% KMC (Figure 7 a), which is in agreement with the wet blue assessment data. This could be attributed to more chromium-binding sites existing in the grain surface due to the introduced additional carboxyl groups as well as the tanning effect of WDDA. Both the samples exhibit a clearly grained surface, indicating there is no physical deposition of chromium. The SEM analyses of tanned leather samples showing cross section in a magnification of 250× and 500× respectively are depicted in Figure 8. The fiber bundles seem to be less dispersed (separation of fibers) in the KMC tanned sample (Figure 8 a) compared to a WDDA-KMC tanned sample (Figure 8 b). It is because that WDDA pretanned leather has a higher binding capacity for chromium(III), which disperses the collagen fibers more effectively. Since the combination tanned sample exhibits better opened up fiber structure, it also shows increased fullness together with softness.

CONCLUSIONS

$NaHSO_3$ blocked waterborne dimethylolpropionic acid-diisocyanate adducts (WDDAs) with good storage stability are resistant to decomposition under ambient condition, but can be deblocked by heating or in aqueous alkaline medium. After modification with WDDAs, the growing TOC and enhanced thermal stability of gelatin confirmed that these WDDAs were able to chemically bond to the collagen in a pH 8-9 environment. Compared with aromatic WDDA, aliphatic or alicyclic WDDA exhibited a higher blocking degree (>90%) and a more desired tanning effect. The additional carboxyl groups introduced by WDDAs together with intrinsic carboxyl groups of collagen fibers coordinated with the chromium. This, as well as urea bonds created by the crosslinking reaction of carbamoylsulfonates with amino groups, contributed to the high hydrothermal stability of resultant leathers (>110°C), the improved percentage chrome uptake (>90%) and the low chromium powder consumption (4% or 5% KMC). In pickling-chrome tanning process, the addition of salt was deliberately omitted owing to the previous crosslinking, accordingly reducing the TDS load in tanning effluents. The wet blue leathers obtained using WDDA-chrome tanning showed tight grain surface, excellent fullness and color, as well as completely opened up fiber structure. These comprehensive properties further proved that WDDA with controllable reactivity and good synergistic effect has potential to be a promising high-chromium absorption and semi-chromium tanning auxiliary agent for it's environment-friendly characteristic and combination tanning effect.

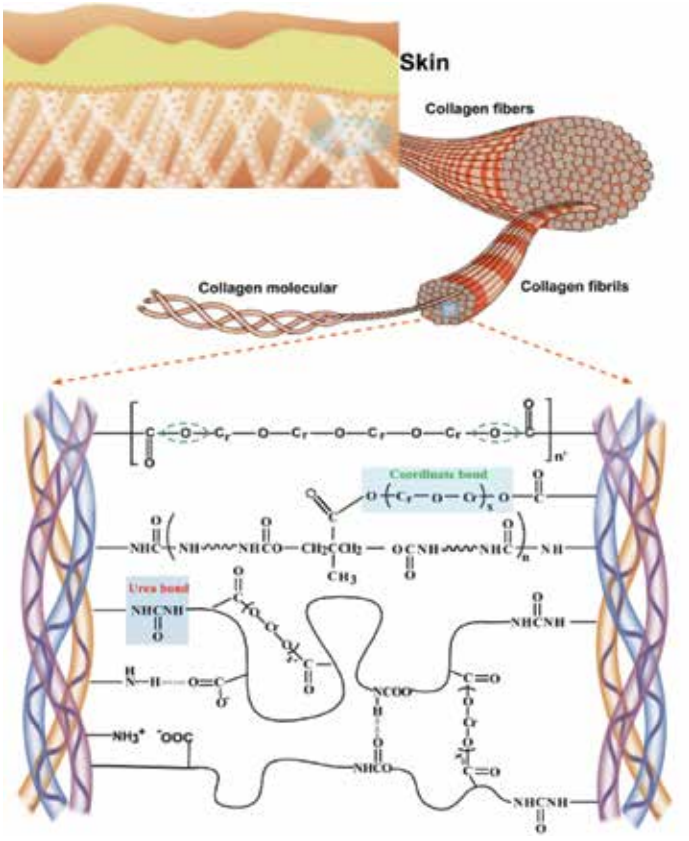


Figure 6. Model of WDDA-chromium(III)-collagen combination tannage.

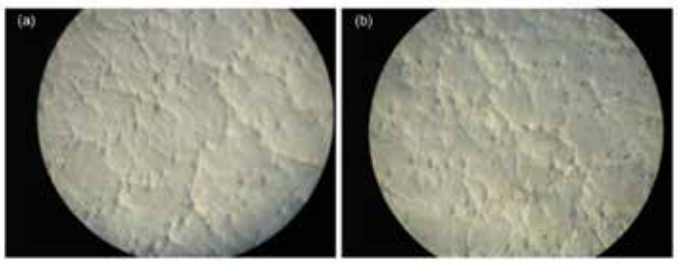


Figure 7. Photomicrographs (50×) showing the grain surface of the tanned leather; (a) tanned with 4% KMC; (b) tanned with 5% H_{12}MDI-WDDA and 4% KMC.

TABLE IV
Assessment date of the tanned leathers.

Parameter	Control (KMC tannage)	Experiment (WDDA -KMC combination tannage)
Color	Good	Excellent
Grain tightness	Fair	Good
Grain smoothness	Good	Slightly rough
Strength	Good	Good
Fullness	Fair	Fuller

TABLE V
Chromium content in leathers tanned using semi- and WDDA-chrome tannage.

Sample		% Cr_2O_3 in the wet blue(dry basis)
Control	(4% KMC)	3.12±0.11
	(5% KMC)	3.80±0.08
Experiment	(5%H_{12}MDI-WDDA+4% KMC)	4.01±0.14
	(5%H_{12}MDI-WDDA+5% KMC)	4.57±0.05

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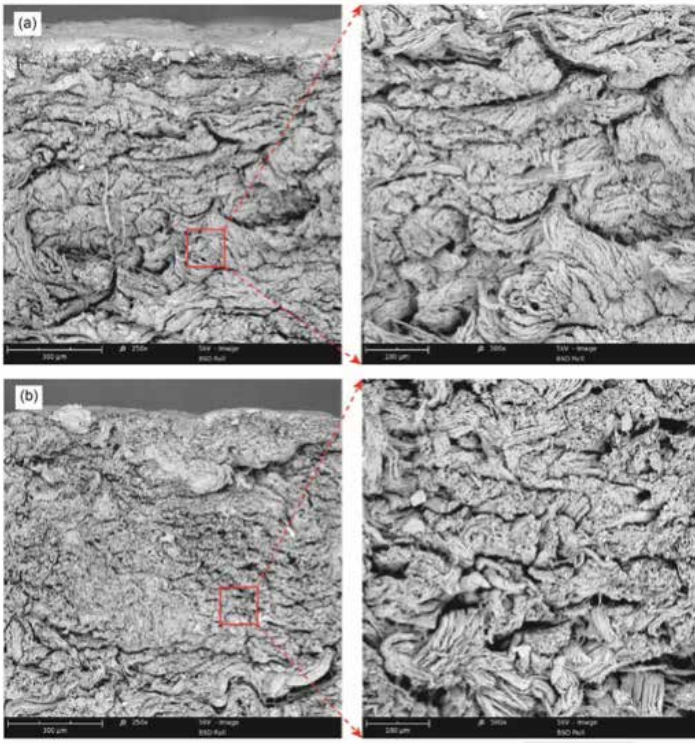

Figure 8. Scanning electron micrographs showing the cross section (250× and 500×) of the tanned leather; (a) tanned with 4% KMC; (b) tanned with 5% H_{12}MDI-WDDA and 4% KMC.

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