Phosphorus-nitrogen Flame Retardant Waterborne Polyurethane/Graphene Nanocomposite for Leather Retanning

by

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Abstract

We demonstrate a facile and green approach to prepare phosphorus-nitrogen containing waterborne polyurethane/ graphene nanocomposite (PN/G-WPU) as flame-retardant retanning agent for leather. The PN/G-WPU was synthesized by covalently embedding phosphoramidate-based diol into polyurethane chain, followed by emulsification with graphene oxide (GO) aqueous solution and *in-situ* reduced with hydrazine hydrate. The structure and emulsion stability of prepared PN/G-WPU were characterized, and the physical mechanical properties as well as the flammability of resulting leathers were investigated. The results indicate the good dispersion and strong interfacial interaction of graphene with polyurethane matrix, which facilitates the PN/G-WPU penetrating into leather fibers. The PN/G-WPU retanning agent can effectively improve the comprehensive performance of resultant leather such as hydrothermal stability, physical-mechanical properties, flame retardancy and smoke suppression performance. Accordingly, our method might provide an alternative strategy for manufacturing high-performance leather.

Introduction

Leather as a kind of natural polymer has been extensively used in upholstery, furniture, garments, automobiles and other fields.¹ However, the utilization of flammable organic compounds during manufacturing processes significantly reduces the flameretardancy of leather.^{1,2} Moreover, the flameless combustion time of leather is long and accompanied with the generation of smoke particulates and nasty smell during combustion. Under this consideration, it is of paramount importance to improve the fire-safety performance of leather.

Up until now, various flame retardants have been adopted to reduce the flammability of leather in the tanning, fatliquoring, dyeing and finishing processes.²⁻⁶ Among the available

alternatives, the phosphorus-nitrogen (P-N) flame retardants have triggered tremendous research interest due to their advantageous features such as non-halogen, low-toxicity and synergistic fire-resistance effect.^{6,7} Despite considerable research, the poor compatibility and weak interaction of most P-N flame retardants with leather fiber remain effectively unsolved.² Another problem facing such traditional fire retardants is that a relatively high loading is usually required to impart leather with satisfactory flame retardancy, which has negative effect on physical-chemical properties of leather.

With the development of nanotechnology, graphene is considered as a promising substitute to traditional flame retardants owing to its unique 2D layered structure.8 Actually, the lamellae blocking effect and high thermal stability give graphene outstanding flame-retarded efficiency, especially when used in conjunction with P-N fire retardants.8-10 It is commonly recognized that homogeneous dispersion and strong interfacial interactions are two prerequisites to fully exert graphene's exceptional properties in target matrices. However, graphene is prone to agglomerate and restack seriously in polymeric hosts due to the strong π - π stacking and van der Waals force among platelets.¹¹ From this point, many researchers have demonstrated the feasibility of grafting flame retardants onto backbone of graphene from graphene oxide (GO), which act as efficient synergistic flame retardant nanomaterials.9,10,12 Since the excessive oxygen-containing functional groups make the GO with poor intumescent ability, which is detrimental to the flameretarding efficiency.¹³ Thus, reduction is necessary to restore the sp² carbon structure of graphene, fully exerting its barrier properties to polymer composites. Unfortunately, a main deficiency encountered with these functionalized strategies is the large consumption of organic solvents in modification and separation steps.

Waterborne polyurethane (WPU) retanning agent, which disperses in aqueous media, is one of the environmentally friendly leather chemicals in leather industry. However, pure

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WPU is highly flammable, which has negative effects on the flame retardancy of resultant leather after retanning treatment. Considering the aforementioned inadequacies and taking full advantage of the hydrophilic characteristic of GO,¹⁴ we herein presented the fabrication of a novel P-N-containing WPU/ graphene nanocomposite (PN/G-WPU) by covalently conjugating P-N flame retardant in the prepolymerization process, which was emulsified with GO aqueous solution, followed by an *in-situ* reduction process. The resultant PN/G-WPU was used as retanning agent to reduce the fire hazards of leather. To the best of our knowledge, this is the first attempt of graphene or its derivatives as flame retardant for leather.

Experimental

Materials

 $2-(5,5-dimethyl-2-oxo-2\lambda^5-1,3,2-dioxaphosphinan-2-ylamino)-2$ methyl-propane-1,3-diol (PNMPD) was synthesized according to

H-O-CH-CH

PPC

-C-CH2-OH COOH

O-CH

O-CH-CH2+

č

our previous work.¹⁵ Chorme-tanned cattle skins (thickness: 1.5 mm) were purchased from Sichuan Lishen Leather Co. Ltd (Chengdu, China). Graphene oxide was provided by Ashine Technology Development Co., Ltd. (Shanghai, China). Poly(propylene glycol) (PPG, 600 g/mol), toluene 2,4-diisocyanate (TDI), dimethylol propionic acid (DMPA), triethylamine (TEA), formic acid, sodium formate, sodium bicarbonate, hydrazine hydrate (HHA) and acetone were supplied by Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China). PPG and DMPA were vacuum-dried at 120°C for 4 h, while acetone was treated with 4 Å molecular sieves for 48 h before use. DOWELLAN FG-B (Dowell Inc., China) and PELGRASSOL MB (Zschimmer & Schwarz Co., Germany) were used as received.

Synthesis of PN/G-WPU Dispersion

CH.

NCO

2,4-TDI

PNMPD

0

C-0-

GO aqueous dispersion

NCO

CH₃

C-CH3-

COOH

40 g of PPG and 30 g of TDI were charged into a three-neck flask and stirred for 2 h at 75°C under N_2 atmosphere. Subsequently, 6 g of PNMPD and 4 g of DMPA dissolved in acetone were fed into the mixture and implemented at 75°C until the NCO content



reached the theoretical value. When the NCO-terminated prepolymer was cooled down to 45°C, the carboxylic groups of DMPA were neutralized with TEA (DMPA equiv., 3 g) for 30 min. Then the intermediate was emulsified with proper GO aqueous dispersion under vigorous stirring. After agitation at room temperature for 2 h, HHA (3 folds of GO) was added and heated to 60°C for another 4 h. The PN/G-WPU emulsion was finally obtained after removal of acetone by rotary vacuum evaporation. Herein the mass fraction of PNMPD and GO was 7.5 wt% and 0.5 wt%, respectively. The synthesis route of PN/G-WPU dispersion is presented in Scheme 1.

Following this procedure, the parallel samples without PNMPD or GO, and with 7.5 wt% PNMPD or 0.5 wt% GO were prepared and respectively labeled as WPU, PN-WPU and G-WPU.

Retanning Process

The PN/G-WPU was utilized as flame retardant retanning agent to treat the shaved cattle spilt in accordance with the processing

technology shown in Table I. Meanwhile, the WPU, PN-WPU and G-WPU retanning agents were also used to handle the leathers with the same process. The retanned leathers herein were respectively abbreviated as $\rm L_{WPU}, \rm L_{PN-WPU}, \rm L_{G-WPU}$ and $\rm L_{PN/G-WPU}.$

Characterization and Performance Tests FTIR Analysis

Fourier transform infrared spectra (FTIR) of the retaining agents were scanned by a Nicolet IS10 FTIR spectrometer (Nicolet, USA) using KBr pellets over the wavenumber of 400–4000 cm⁻¹.

Emulsion Stability

The centrifugal stability of synthesized dispersions was determined by centrifuging at 1500 rpm for 10 min in a Shuke TD-420 centrifuge (Shuke, China). The zeta potential values were measured on a Malvern ZEN3600 Zetasizer (Malvern, USA) at a temperature of 25°C.

Procedures	Chemicals	T (°C)	Dosage (%)	t (min)	Remark
Weighting					
Washing	Water	35	200		
	DOWELLAN FG-B		0.3	60	Drain
Washing	Water	35	200	10	Drain
Neutralizing	Water	35	200		
	HCOONa		2	30	
	NaHCO ₃		0.8	60	pH = 5.5, Drain
Washing	Water	35	200	10	Drain
Retanning	Water	40	150		
	PN/G-WPU		8	60	
Fatliquoring	Water	50	100		
	PELGRASSOL MB		10	30	
	НСООН		1.5	30	pH = 3.8-4.0, Drain
Washing	Water	25	200	10	Twice, Drain
Drying					

Table IRetanning process for cattle hides.

XRD Analysis

X-ray diffraction (XRD) patterns were monitored by X-ray diffractometer (D8 advance, Bruker, Germany) equipped with graphite monochromatized high-intensity Cu Ka radiation ($\lambda =$ 0.1542 nm).

Hydrothermal Stability

The shrinkage temperature (T_s) of leathers was evaluated by reference to ASTM method D 6076-97 on a MSW-YD4 apparatus (China) under the bath of glycerin (75%).

Flammability Tests

The limiting oxygen index (LOI) values of leathers were examined using a HC-2C oxygen index analyzer (Jiangning Analysis Instrument Co., China) according to ASTM D 2863-77 standard. The UL-94 vertical burning levels were conducted by a CZF-3 tester (Jiangning, China) in terms of ALCA Method E 50 standard. All leathers were repeated in quintuple and average values were reported. Cone calorimeter test was conducted on a cone calorimeter device (FTT, UK) in accordance with ISO 5660-1 standard, samples were horizontally irradiated by heat flux of 35 kW/m².

SEM Observation

The morphologies of cross-section of leather and char residues after LOI test were observed by a J SM-7500F (JEOL, Japan) scanning electron microscope (SEM) at an accelerating voltage of 15 kV. The surfaces of all samples were gold-sputtered before examination.

Mechanical Properties

All leathers were conditioned at 20°C and 65% relative humidity (RH) complying with ASTM D1610-0l standard before tests. The tensile strength and elongation at break were determined on a GT-U55 functional testing machine (Gotech, Taiwan) according to ASTM D4704, while the tear strength was tested following ASTM D2209 standard method.





Results and Discussion

Characterization of Retanning Agents

The chemical structures of retanning agents were characterized by FTIR spectroscopy. As shown in Figure 1a, the characteristic absorption bands corresponding to polyurethane are detected at 3300 cm⁻¹ (N–H stretching vibrations), 1722 cm⁻¹ (C=O groups), 1536 cm⁻¹ (N–H deformation) and 1104 cm⁻¹ (C–O–C) for all retanning agents. For comparison, a new peak appears at 968 cm⁻¹ in the FTIR spectra of PN-WPU and PN/G-WPU, which is attributable to the P–O–C bending vibration in PNMPD. This suggests the reaction between PNMPD and isocyanateterminated polyurethane prepolymer.

The dispersion stability was monitored by zeta potential, and their values are recorded in Figure 1b. The zeta potential values for retanning agents are around -37.5 to -68.5 mV, which is believed to be sufficient mutual repulsion for maintaining stable emulsions.¹⁶ In Figure 1c, the dispersions appearance of all retanning agents remain visually stable without precipitates after centrifugation, again indicating that the synthesized retanning agents exhibit long-term stability.

XRD analysis is used to determine the exfoliation of graphene sheets in the nanocomposites. As plotted in Figure 1d, all retanning agents, regardless of whether or not GO is added, display similar diffraction patterns with a broad diffraction hump centered at $2\theta = 19.8^{\circ}$, demonstrating an amorphous structure of polyurethane. However, the characteristic diffraction peaks of graphene are undetectable in the diffractograms, manifesting that graphene sheets are fully exfoliated and dispersed homogeneously in the polyurethane matrix.¹⁷

Herein, PN/G-WPU nanocomposite was prepared by emulsifying the prepolymer with GO aqueous solution, which was then *in-situ* reduced with hydrazine hydrate. Figure 2 shows the possible interactions of graphene with polyurethane matrix. We rationally speculate that the hydroxyl groups on GO surface may react with isocyanates to form urethane bonds through bridge, loop or tail linkages. Meanwhile, the non-covalent forces are achieved by H-bonding between unreduced oxygen-bearing moieties of graphene (carboxyl, hydroxyl and ester groups) and urethane or phosphamide in polyurethane chains as well as the π - π conjugate interactions from the basal plane of graphene and aromatic nucleus of TDI molecules. Thus, the strong interfacial bonding contributes to the homogeneous dispersion of graphene in polyurethane matrix. In fact, recent studies also revealed that WPU particles with hydrophobic and negatively charged surface could be adsorbed onto the surface of GO, enhancing the colloidal stability.18

Absorption of Wet Blue to Retanning Agents

To determine whether the prepared retanning agents were absorbed by wet blue, the bath liquid and the retanned leathers were photographed. As can be seen from Figure 3a, the waste liquor of all samples is almost transparent with blue light after retanning process, which suggests the combination of wet blue with retanning agents. Meanwhile, it is evident from Figure 3b that G-WPU and PN/G-WPU retanned leathers show deepercolored surface for both grain and flesh sides than control samples. Furthermore, the elemental mapping of PN/G-WPU treated leather (Figure 3c) reveals the uniform distribution of carbon, nitrogen, oxygen, phosphorus and chromium atoms on the cross section of collagen fibers. This clearly indicates that PN/G-WPU nanocomposite can penetrate into the collagen fibers to form strong binding force, principally through the complexation reaction of carboxyl groups on PN/G-WPU and Cr(III) on chrome-tanned leather.19

Flammability of Leather

The flame retardancy of retanned leather was evaluated by LOI values and vertical burning tests, and the corresponding results are tabulated in Table II. Compared with control, the LOI values of leather retanned with PN-WPU, G-WPU and PN/G-WPU are positively improved. Typically, the $L_{PN/G-WPU}$ has a LOI value of 26.3%, increased by 1.0% over that of L_{WPU} , the amplification of which is more than the total discrepancies between L_{WPU} and those merely treated by PN-WPU or G-WPU (growth by 0.7%), unambiguously proving the synergistic flame-resistance effect in PNMPD and graphene. Likewise, the flaming and glowing combustion time decrease effectively when retanned by PN-WPU, G-WPU and PN/G-WPU. Interestingly, the flameless combustion time for $L_{PN/G-WPU}$ is shortened to 17 s from minutes for other leathers, which denotes the enhanced flame retardancy

In what follows, we lay particular emphasis on the heat release and smoke production of L_{WPU} and $L_{PN/G-WPU}$. Figure 4 displays the heat release rate (HRR), total heat release (THR), smoke production rate (SPR) and total smoke production (TSP) profiles



Figure 2. Possible interactions between graphene and polyurethane matrix.



Figure 3. (a) Photographs for the bath liquid before and after retanning process; (b) digital images of the grain and flesh surface of retanned leathers; (c) SEM images of cross section of PN/G-WPU retanned leather and its corresponding EDX element mapping.

of $L_{_{\rm WPU}}$ and $L_{_{\rm PN/G-WPU}}$ as a function of time, and related data are recorded in Table III. The WPU treated leather has a peak heat release rate (PHRR) of 197.2 kW/m² and releases a THR of 23.3 MJ/m². For comparison, the PHRR and THR of L_{PN/G-WPI1} decrease to 169.8 kW/m² and 21.1 MJ/m², representing a reduction of 13.9% and 9.4%, respectively. Based on the HRR curves, the fire performance index (FPI) and fire growth rate (FIGRA), which defined as the proportion of time to ignition (TTI) to PHRR and PHRR divided by time to PHRR (TTPHRR),²⁰ are proposed for overall fire hazards considerations. Qualitatively, higher FPI and lower FIGRA indicate better flame retardant performances. As listed in Table III, the FPI value shows an increase from 0.208 m²s/kW for L_{WPII} to 0.218 m²s/kW for $L_{PN/G-WPU}$, while FIGRA decreases from 2.465 kW/m²s to 1.974 kW/m²s, further confirming the improved fire safety.

Apart from reducing the heat release, it is of crucial importance to suppress the smoke production of leather considering that dense smoke during fire is the chief culprits for fatalities. As depicted in Figure 4c and d, the peak smoke production release (PSPR) of $L_{PN/G-WPU}$ is 0.012 m²/s, accounting for 57.1% over that of L_{WPU} (0.021 m²/s). Moreover, the TSR reduces from 0.95 m² (L_{WPU}) to 0.70 m² ($L_{PN/G-WPU}$), declined by 26.3%, which illustrates the positive role in smoke suppression.

Table II					
LOI values and detailed vertical					
burning test data of leathers.					

Sample	LOI (%)	Flaming combustion time (s)	Glowing combustion time (s)	Char length (cm)	
$L_{\rm WPU}$	25.3 ± 0.2	55 ± 5	> 180	6.0 ± 0.4	
L _{pn-wpu}	25.6 ± 0.1	40 ± 5	> 120	4.5 ± 0.3	
L _{g-wpu}	25.7 ± 0.2	43 ± 4	> 120	4.6 ± 0.4	
L _{PN/G-WPU}	26.3 ± 0.1	23 ± 2	17 ± 1	2.7 ± 0.2	

Char Morphology Analysis

SEM micrographs of the residual char of leather samples after cone calorimetry test were pictured and demonstrated in Figure 5. The WPU treated leather shows a fragile and scattered char structures with many obvious voids and flaws on the surface (Figure 5a). Differently, an integral, compact and denser carbonized layer is observed on the residue of PN/G-WPU retanned leather (Figure 5b), which effectively obstructs the heat and oxygen transfer between flaming zone and unburned fibers, thus enhancing the fire performance of leather.



Figure 4. (a) Heat release rate, (b) total heat release, (c) smoke production rate and (d) total smoke production curves of leathers.

Table IIICone calorimetric data for leathers.

Sample	TTI (s)	PHRR (kW/m ²)	TTPHRR (s)	THR (MJ/m ²)	PSPR (m ² /s)	TSP (m ²)	FPI (m ² s/kW)	FIGRA (kW/m²s)
$L_{\rm WPU}$	41	197.2	80	23.3	0.021	0.95	0.208	2.465
L _{pn/g-wpu}	37	169.8	86	21.1	0.012	0.70	0.218	1.974

Table IV Mechanical properties, thickness increment and shrinkage temperature of leather.								
Sample	Tensile strength (N/mm²)	Tear strength (N/mm)	Elongation at break (%)	Thickness increment (%)	T _s (°C)			
L _{wpu}	13.65	50.53	61.20	20.8	104.3			
L _{pn-wpu}	13.44	50.80	63.0	21.5	106.2			
L _{g-wpu}	14.11	51.12	62.81	24.2	104.9			
L _{PN/G-WPU}	16.13	51.40	65.13	26.1	107.1			



Figure 5. SEM micrographs of residues of leathers obtained from cone calorimetry tests. (a) WPU and (b) PN/G-WPU retanned leathers.

Physical Properties and Hydrothermal Stability of Leather

The physical and mechanical properties of the retanned leathers are listed in Table IV. Qualitatively speaking, the tensile properties, elongation at break, tear strength and thickness increment of L_{G-WPU} and $L_{PN/G-WPU}$ are simultaneously improved compared to those of L_{WPU} . Such anomalous enhancements can primarily be ascribed to the strong interfacial interactions and good compatibility between graphene and polyurethane matrix, as mentioned in Figure 2, which facilitates the graphene penetrating among leather fibers. After permeating into the inside of the leather, the graphene can form non-covalent bonding with collagen fibers, thereby fulfilling the nanoreinforcing effect of graphene. That is to say, the PN/G-WPU retanning agent can introduce more crosslinking between collagen chains. This assumption is confirmed by the higher shrinkage temperature of $L_{PN/G-WPU}$ than other samples.

Conclusion

In this work, we developed a feasible and green approach to prepare phosphorus-nitrogen containing waterborne polyurethane/graphene nanocomposite (PN/G-WPU) with longterm stability, which was used as retanning agent and exhibited multifunctional efficacies on enhancing the overall performance of the resultant leather. For PN/G-WPU retanned leather, the LOI value increases to 26.3% and the flameless combustion time is significantly shortened to 17 s, while the PHRR, THR, PSPR and TSP are respectively decreased by 13.9%, 9.4%, 42.9% and 26.3% over those of WPU treated leather, suggesting the enhanced flame retardance and ameliorated smoke suppression. Meanwhile, the tensile strength, elongation at break, tear strength and hydrothermal stability are also improved, highlighting its potential practical applications. Thus, this strategy described herein offers an effective yet promising paradigm to achieve flame retardant leather with excellent combination properties.

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