Hyperbranched Polyurethanes with Flammability Resistance for Leather Retanning

by

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Abstract

In this study, diethyl bis(2-hydroxyethyl) aminomethyl phosphonate was modified by hexamethylene diisocyanate, and then was utilized to partly replace the isocyanates to prepare hyperbranched polyurethanes (HPU-DPAs). The hyperbranched polyurethanes were then employed in the retanning process of wet blue. The shrinkage temperature, average thickness as well as mechanical properties of leather before and after retanning were acquired. The flammability of retanned leather was measured by cone calorimeter test. The morphologies of wet blue and leather after retanning by HPU-DAP were obtained using a scanning electron microscope. Results showed that the average thickness, tensile strength and elongation at break of leather were all improved after retanning. Retanning by HPU-DAPs can effectively increase flame retardancy of final leather.

Introduction

Nowadays, leather products have been widely used in our daily life, such as furniture, clothing, shoes and bag.[1] However, the inflammability of leather greatly limits its further application in more fields. When leather burns, high concentrations of hazardous gases (such as HCN, HNCO, CO, NO, NO_2, etc.) are released,[2,3] severely causing health problems. As a result, it is crucial to improve the fire resistance of leather. Great efforts have been made to prepare leather with flammability resistance. For instance, Lyu and coworkers[4] utilized zanthoxylum bungeanum seed oil and aqueous miscible organic solvent treatment modified layered double hydroxide to prepare flame retardant leather. The flame retardant property of leather was demonstrated to be improved owing to the formed continuous dense char layer.

The retanning process is considered as one of the important steps in leather manufacturing processing, which can improve the shrinkage temperature, assist the dyeing process, and endow some functional properties to the final leather, such as fire-retardancy, water-proof, antifouling, antimicrobial and so on.[5-7] For example, our group previously prepared a fluorescent waterborne polyurethane retanning agent through chemical incorporation of fluorescer into polyurethane backbone as a chain extender.[8] The resultant leather after retanning exhibited a magic fluorescence effect under a UV lamp.[9] In another research, a chromotropic acid grafted amphoteric polyurethane was synthesized and then applied in the retanning process of aldehyde tanned leather. The reaction between chromotropic acid and formaldehyde occurred between two naphthalene rings, effectively reducing the content of free formaldehyde in leather.

Among the retanning agents, hyperbranched polymers, which are highly branched macromolecules with three-dimensional architecture, have been paid considerable attention because of their novel structures, unique properties, and potential application prospects.[10] On the one hand, hyperbranched polymers have a large number of active groups (such as hydroxyl, carboxylic, amino, etc.), which can not only form hydrogen bonds with hydroxyl, amino and carboxyl groups of leather collagen fibers, but also coordinate with chromium in wet blue.[11] Consequently, the collagen fibers can be cross-linked, thereby increasing the shrinkage temperature, physical and mechanical properties of leather. More specifically, the structure of hyperbranched polyurethane can be tailored during the preparation process, by changing the types and contents of raw materials accordingly, to achieve satisfactory performance.[12] Hence, flame retardant hyperbranched polyurethanes can be achieved by covalently incorporating flame retardant moieties into hyperbranched chains during the synthesis process. Particularly, phosphorus-based flame retardants play an important role in flame retardant additives and change the decomposition as well as combustion characteristics of leather.[13] At elevated temperatures, the chemical interactions in the condensed phase could result in changes in the decomposition pathway of the leather and formation of carbonaceous char residues on the surface of decomposing leather, thus preventing further oxidation. Besides, the volatilized compounds could interact with the combustion intermediates in the gas phase as inhibitors. Such interactions usually cause recombination of the H and OH radicals and prevent oxidation. However, to the best of our knowledge, no research has been done on preparing hyperbranched polyurethane with flammability for leather retanning. Therefore, the flame retardant moieties can be covalently conjugated into the chains of hyperbranched polyurethane.

In this study, hyperbranched polyurethanes were prepared by chemically incorporating phosphorous units into branched chains. Then they were applied as retanning agents in the

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by HPU -DAP-6 after burn. For the wet blue, the fiber structures were heavily damaged, and the surface was covered by powder after combustion. On the contrary, although small cracks were found on the surface of the fiber, the fiber structure of leather retanned by HPU-DPA-6 was clearly retained.

Conclusion

In this study, hyperbranched polyurethane leather retanning agents with flammability were synthesized. A phosphorous compound was modified by hexamethylene diisocyanate, and then was used to partly replace the isocyanates to prepare hyperbranched polyurethanes. After retanning, the average thickness, tensile strength and elongation at break of leather were all improved. When the content of DAP increased, PHRR, TPHRR, THR, SPR, PTSR and TTI of leather retanned by HPU-DAPs decreased and the TPHRR was advanced. For the wet blue, the fiber structures were heavily damaged after combustion. On the contrary, the fiber structure of leather retanned by HPU-DPA was clearly retained. All these results suggested the potential application of HPU-DAPs as flame retarded retanning agents for leather manufacturing.

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