ELSEVIER

International Journal of Adhesion & Adhesives 25 (2005) 442–449

International Journal of Adhesion & Adhesives

www.elsevier.com/locate/ijadhadh

Adhesion enhancement of chromium tanned heavy-duty leather (Salz leather) under extreme conditions using photoreagents as surface primers

Catalin Fotea[a], Claudius D'Silva[b,*]

[a]LBSA, School of Pharmacy, University of Nottingham
[b]Department of Chemistry and Materials, The Manchester Metropolitan University, John Dalton Building, Chester Street, Manchester M1 5GD, UK

Accepted 18 December 2002

Abstract

The work described investigates the development of photoreagents as surface primers for the enhancement of adhesion with heavy-duty leather surfaces (Salz). Several reagents were investigated which included 4-azidophenol (**1**), 3-azidophenol (**2**), 4-(2,2′-iminodiethanol)-3-nitrophenylazide (**4**) and 4-azido-(2,2′-iminodiethanol)benzamide (**6**) and used as an intimate mixture with commercial polyurethane adhesive (Solibond PU39) to enhance the adhesion of Salz leather surfaces. The photoreagents upon UV irradiation covalently attach to the leather surface enriching it with new functionalities to provide sites for bonding with the adhesive layer. The adhesion strength of photo primer treated leather samples were tested using the T-peel test against abraded leather surfaces under dry and wet conditions. Compounds **4** and **6** on T-peel testing were found to enhance adhesion strength by 99% under dry conditions and 163% and 157%, respectively, under wet conditions. The observed failure type was cohesive within the substrate when photoreagents were used, suggesting covalent bonds formation at the interface in addition to the usual van der Waals forces and hydrogen bonds affecting adhesion.

Keywords: Coupling agents; Surface treatment; Destructive testing; Chromium tanned leather

1. Introduction

Leather is a naturally occurring material containing collagen as its major protein constituent. The characteristic properties of leather result after re-tanning, colouring, fat-liquoring and finishing [1]. The above treatments irremediably alter leather's chemistry (surface and bulk), with many groups on the peptide backbone being appreciably affected by the tanning process, making adhesion a problem. In an attempt to improve adhesion, we recently reported a method of bonding based on increasing the degree of molecular contact between adhesive and the leather surface by enhancing adsorption [2]. In this approach an IPN (Interpenetrating Polymer Network) was created by polymerisation of monomers of the structure X_3–Si–R–Y to form a cross-linked polysiloxane network which chemisorbed onto the leather surface via H-bonds or van der Waals interactions whilst the Y group reacted with an isocyanate reagent to increase the overall hydrophobicity and adherence of the resultant IPN [2].

Although the joints formed using an IPN based on 3-(2-aminoethylamino) propyltriethoxysilane (AEAPES) showed an increased total joint strength, of 96.9 N under dry and 51.2 N under wet conditions [2], further improvements in the joint under wet conditions were

---

[*] Corresponding author. Tel.: +44 161 247 1416; fax: +44 161 247 6357.

E-mail addresses: Catalin.Fotea@Nottingham.ac.uk (C. Fotea), C.DSilva@mmu.ac.uk (C. D'Silva).

URL: http://web:www.chem-mats.mmu.ac.uk/staffflist.html.

0143-7496/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ijadhadh.2002.12.001

considered necessary to meet the stringent requirements for use of this technology to heavy-duty leather boots. Chemisorbed bonds weaken under wet conditions therefore an ideal solution would involve the formation of a covalent bond between the adhesive and leather. The tanning process together with the waterproof treatments applied on the skin side make it chemically inert. Therefore surface enrichment with active chemical groups was sought to enhance adhesion and to produce strong, durable joint assemblies.

1.1. Surface primers

Aryl azides belong to a group of compounds capable of generating reactive electron deficient species (nitrenes) on irradiation with a UV light. Nitrenes are reagents of electrophilic character sharing chemical similarities with other electrophilic nitrogen reagent [3,4], but posseses four non-bonded electrons which can accept electrons from electron rich species [5], to form covalent bonds (see Fig. 1).

The thermal stability of azides are critically dependent on the nitrogen substituent, whilst aryl azides have high thermostability, alkyl or acyl structures are unstable and can decompose violently on exposure to heat, mechanical shocks or aggressive chemical reagents.

Aryl azides have been used to investigate the binding site of macromolecules and to bond polymers to glass [6]. In the latter approach a photoreactive siloxane primer of the structure N_3–R–Si(OR′)$_3$ was used to react with functional groups (OH) present on the glass surface via the siloxane function. On photoactivation of the aryl azide group a nitrene species is generated which bonds covalently to the backbone of the polymer film. In the approach proposed to functionalise leather we considered the preparation of a variety of hydroxyl functionalised aryl azides which on photoactivation could covalently bond to the leather surface and introduce hydroxyl groups to facilitate covalent bond formation with the adhesive (see Fig. 2). In this paper we report on the synthesis of two hydroxyl and two new dihydroxyl photoprimers (see Fig. 3) and their evaluation in the enhancement of adhesion to leather surfaces under dry and wet conditions.

2. Experimentation

2.1. Chemicals

Phloroglucinol.2H_2O, 4-hydroxylaniline and 2,4-dinitrobenzene were from Avocado, UK; diethanolamine (2,2′-iminodiethanol), sodium azide and 4-aminobenzoic acid were from Aldrich Chemical Co. Ltd. (UK). Preparative silica gel plates Analtech (12 × 12 cm; 2 mm) were obtained from Alltech. Chem. Co. The adhesive used was Solibond PU39 (Crispin-Adhesives Ltd) an opaque one component polyurethane polymer solution which hardened on solvent release. Manufacturer's specification: d 0.86–0.88 g cm^{-3}, drying time at 20 °C: 10 to 30 min. Solvents: acetone, EtOAc. Melting points were uncorrected. ATR and FT-IR spectra were analysed with Spectrum Lite software (Perkin–Elmer). ^{1}H and ^{13}C NMR spectra were recorded at 270.05 and 67.80 MHz, respectively, using TMS as an internal standard. MS were recorded at 70 eV and ESIMS at 3.5 or −3.0 kV, 70 °C, in a H_2O/MeOH (1:1) matrix.

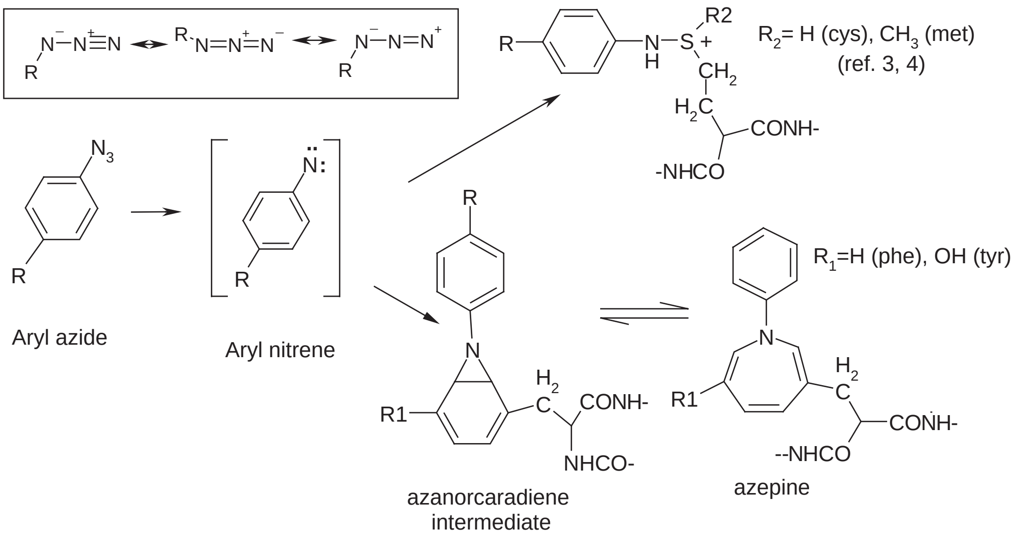

Fig. 1. Decomposition pathways of aryl azides with the amino acid residues of proteins. Inset: 1, 3-Dipolar nature of azides.