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Biotransformations in synthetic fibres

CARLA SILVA & ARTUR CAVACO-PAULO

University of Minho, Textile Engineering Department, Guimarães, Portugal

Abstract

Recent studies clearly indicate that the modification of synthetic polymers with enzymes is an environmentally friendly alternative to traditional chemical methods requiring harsh conditions. Some work already performed on polyamide 6.6 (nylon 6.6), polyethyleneterephthalate (PET) and polyacrylonitrile (PAN) revealed that surface functionalization of these materials is a key requirement for an extensive range of applications, such as textiles, electronics, biomedical field and others. Research performed on PET with lipases, cutinases and other esterases has previously been reported, whilst enzymatic treatment of PAN with nitrilases and cutinase has also been the subject of study. However, at present, few studies have been done on nylon fabrics, mainly with esterases and proteases. This work is intended as a brief review of research in the area of biocatalytic functionalization of synthetic fibres, with a special focus on work recently performed by our research group with cutinase from *Fusarium solani pisi*.

Keywords: *Cutinase, polyamide 6.6 (nylon 6.6), polyacrylonitrile (PAN), polyethyleneterephthalate (PET).*

Introduction

Natural fibres are true substrates in enzymatic processes. Synthetic fibres have been explored for their support properties in enzyme immobilization and for potential special applications, such as biosensors, electronics or membranes. All synthetic fibres are petroleum derivatives; they are designed in the chemical laboratory and created to achieve the most favourable properties at reasonable cost. With advances in polymer synthesis, recombinant technologies, engineering and fibre formation methods, more man-made fibres are expected to enter the market place (Cavaco-Paulo & Guebitz 2003).

Polyamide (PA), polyethyleneterephthalate (PET) and polyacrylonitrile (PAN) fibres have high crystallinity and low moisture regain. They exhibit excellent physical properties of strength, flexibility, toughness, stiffness, wear and abrasion resistance. Beside these properties, they also demonstrate good dyeing ability, low friction coefficient, low creep and good chemical resistance. However, the poor wet-ability and hydrophilicity make it difficult to apply finishing compounds, colouring agents, and to

couple flame retardants or covalently immobilize proteins (Vertommen et al. 2005; Jia et al. 2006).

The classical chemical modification of synthetic polymers, using strong alkaline or acid agents, requires high amounts of energy and chemicals (binders, coupling agents, etc.), which are partially discharged to the environment. Furthermore, some of the substances used, due to their weak bonding, are released from the end-products, presenting potential health risks and reducing the technical lifetime of the products. Although alkaline products render synthetic fibres more hydrophilic, they also lead to the deterioration of other properties causing irreversible yellowing and loss of resistance (Guebitz & Cavaco-Paulo 2003).

In order to reduce the use of such chemicals and their environmental impact, new technologies have been developed to replace classical methodologies. Two technologies suitable for this purpose are plasma technology, where hydrophilic groups are generated at the surface, and the grafting of specific groups at the surface of the synthetic fibres (McCord et al. 2002; Tobiesen & Michielsen 2002; Grace &

Gerenser 2003; Pappas et al. 2006; Shalaby et al. 2006).

Surface modification with enzymes has been considered a valuable tool to improve the quality and the processing properties of synthetic fibres. A bio-catalytic method would have the advantage of being performed under mild and environmentally friendly process conditions. Moreover, no complicated machinery would be required, as in the case of plasma treatment, and little or no additional chemicals would be needed. Furthermore, direct control on the extent of specific group formation may be difficult to achieve using physical techniques. Due to the selectivity of enzymes and their presence only at the surface of fibres, enzymatic hydrolysis is desirable when compared with traditional chemical methods.

Advances in enzymology, genetic engineering and industrial enzyme production make existing technologies using enzymes for fibre processing more attractive and open up new possibilities, such as the improvement of synthetic fibres with higher added value and material functionalization hence improving environmental aspects of textile processing (Guebitz & Cavaco-Paulo 2003, Guebitz et al. 2004).

The enzymatic modification of synthetic materials has immense potential both in the functionalization of bulk materials, such as polyamide, polyacrylonitrile or polyester, and in the production of polymers for special applications, such as medical devices and electronics (Deguchi et al. 1998; Tauber et al. 2000; Yoon et al. 2002; Silva et al. 2005).

Polyamide 6.6 fibres

Polyamide 6.6 (nylon) is a semi-crystalline material that has a combination of strength, flexibility, toughness and abrasion resistance. It is also known for its dye-ability, low coefficient of friction, low creep, and resistance to solvents, oils, bases, fungi and body fluids (Jia et al. 2006). The applications of nylon 6.6 include textile fibres, membranes, tapes, food packaging, electronics and automotive parts. To further improve performance it is necessary to generate specific functional groups at the surface of the fibres. Amine-enriched surfaces can play an important role in processes, such as the removal of heavy metal ions from aqueous solutions, bio-fouling prevention, as well as the removal of dyes from wastewater and also for the covalent immobilization of proteins.

Nylon surfaces have been modified by physical and chemical methods. The first category includes activation of the surfaces through treatment with UV radiation (Shearer et al. 2000), plasma activation

(Foerch & Hunter 1992) or plasma deposition (Tobiesen & Michielsen 2002). While these methods are inherently clean, the disadvantages are that chemically well-defined surfaces cannot be designed and prepared, and, often, functionalization is accompanied by surface destruction. As mentioned, a biocatalytic method would be a valuable tool for surface modification of nylon.

Few studies on functionalization of nylon fabrics with enzymes have been reported. Some demonstrated that manganese peroxidase was able to modify the surface of PA 6.6 and PA 6 without reducing the fibre diameter (Deguchi et al. 1997, 1998; Friedrich et al. 2007). Heumann and co-workers demonstrated that polyamide substrates can be efficiently functionalized with esterase, cutinase or proteases. A model substrate (adipic acid bis-hexyl-amide) was developed for screening polyamidase activity of a given enzyme. A protease from *Beauveria* sp., an amidase from *Nocardia* sp. and a cutinase from *Fusarium solani* were used to hydrolyse this model substrate (Heumann et al. 2006). Laccases in combination with a mediator have been claimed to increase the hydrophilicity of PA 6.6 fabrics (Miettinen-Oinonen et al. 2002). Nylon degradation with the laccase-mediator system has also been investigated (Fujisawa et al. 2001). Partial hydrolysis of PA fibres and PA oligomers has been demonstrated with proteases (Kakudo et al. 1993; Fischer-Colbrie et al. 2004). Other authors showed the biodegradation of nylon oligomers by micro-organisms, such as *Flavobacterium* sp. and *Pseudomonas* sp. (Negoro 2000; Prijambada et al. 1995). Oxidases from lignolytic fungi have been used to depolymerise polyamides (Klun et al. 2003).

The use of enzymes for the improvement of nylon performance has only been studied recently, with the first investigations of surface modification of nylon fabrics using cutinases being performed by our research group.

Polyester fibres

In the last 50 years, the production of synthetic fibres has been growing rapidly and polyester represents the most widely used man-made fibre (Taylor 1999). Polyester fibres made of polyethylene terephthalate (PET) have very good strength properties. They are resistant to a wide range of chemicals and also withstand abrasion, stretching, shrinking and wrinkling. However, these fibres also exhibit a number of undesirable features affecting the wearing comfort of PET textiles. These include a low flexibility and high hydrophobicity, the tendency to pilling, static charges and resistance to the removal of oil stains. Chemical treatments would improve

their hydrophilicity but at the same time reduce the quality of the fibres causing loss of resistance (Shukla et al. 1997; Zeronian & Collins 1989). A biocatalytic method for polyester finishing would be performed under mild and environmentally friendly conditions. Compared with chemical hydrolysis, enzymatic hydrolysis has the advantage of maintaining mechanical stability, as well as the natural colour of the polymer. Despite the fact that aromatic polyesters like PET have previously been considered as resistant to hydrolytic action (Müller et al. 2001) some authors had observed changes in the physical properties of PET fibres and films after enzymatic action of *Cladosporium cladosporioides* (Sato 1983).

The enzymatic controlled surface hydrolysis of PET facilitates the attachment of cationic compounds (e.g. dyes) or the direct application of coatings for the production of technical fabrics with reduced consumption of coupling agents.

The hydrophilicity of polyesters can be increased by hydrolysis of ester bonds (Genencor int 2001; Khoddami et al. 2001; Yoon et al. 2002).

Treatment of PET with several lipases has been shown to improve wettability and absorbent properties of PET fabrics, while strength properties were retained (Hasan et al. 2006; Hsieh & Cram 1998). Polyester hydrolysing bacterial and fungal esterases have been claimed to reduce the pilling properties of PET fabrics (Andersen et al. 1999). Other authors have claimed improved stain resistance, wetting and/or dyeing abilities of PET fabrics treated with so-called polyesterases (lipases, esterases or cutinases; Yoon et al. 2002; Alish et al. 2004; Fischer-Colbrie et al. 2004; O'Neill & Cavaco-Paulo 2004; Vertommen et al. 2005). The ability of cutinase to hydrolyse PET cyclic oligomers was demonstrated by Hooker and co-workers (Hooker et al. 2003).

Besides esterases and lipases, enzymes acting on natural polyesters such as cutinases or polyhydroxyalkanoate depolymerases have the potential to modify the surface of PET fibres (Calado et al. 2004; O'Neill & Cavaco-Paulo 2004; Alish-Mark et al. 2006; Nimchua et al. 2006). Enzymatic treatment with these enzymes enhanced the hydrophilicity, wettability and cationic dye binding ability of the PET fibres. Additionally, the fibres showed improved pilling and oil stain removal properties.

Oxidative enzymes, such as laccases, have also been claimed to modify the PET surface (Miettinen-Oinonen et al. 2002). However, there is no detailed mechanism or application related data available yet.

McCloskey and Jump demonstrated that 100% polyester fabric can be treated with a cutinase to impart a biopolished finish (McCloskey & Jump 2005).

Acrylic fibres

Polyacrylonitrile (PAN) fibres have a combination of desirable properties such as high resistance to outdoor exposure and chemicals, excellent elasticity, natural-like aesthetic properties and colour fastness. However, due to its hydrophobic nature, PAN fibres also exhibit undesirable properties such as uncomfortable hand and static charge accumulation (Matamá et al. 2007). The quality and properties of acrylic fibres can be improved by chemical means, using co-monomers, additives and polymer blends, or by physical means (carried out at the polymerisation, dope preparation and spinning stages) (Burkinshaw 1995).

A few studies on the modification of acrylic fibre with enzymes have been done, mainly using nitrile hydratases (Battistel et al. 2001; Banerjee et al. 2002; Tauber & Cavaco-Paulo 2000). The modification of nitrile surface groups into amide groups was accomplished by the action of nitrile hydratase from *Rhodococcus rhodochrous* (Tauber & Cavaco-Paulo 2000), from *Brevibacterium imperiale* (Battistel et al. 2001) and from *Arthrobacter* sp. ECU1101 (Wang et al. 2004). Recently, it has been shown that *Micrococcus luteus* could degrade PAN fibres and the products of hydrolysis were detected by NMR analysis (Fischer-Colbrie et al. 2007). The direct modification of nitrile groups into carboxylic groups was performed by a nitrilase (Matamá et al. 2007). Some of the carboxylic groups were released into the treatment solution as polyacrylic acid depending on the time of treatment. The affinity towards a basic dye was also highest after enzymatic treatment.

Surface modification of synthetic fibres with cutinases

Recent studies by our research group revealed that cutinase from *Fusarium solani pisi* (EC 3.1.1.74), which is an α/β hydrolase able to degrade cutin from higher plants, was able to efficiently modify the surface of polyester and also, to a lesser extent, acrylic fibres by hydrolysis of the ester linkages with the formation of carboxylic and hydroxyl groups (O'Neill & Cavaco-Paulo 2004; Matamá et al. 2006). In the case of polyamide fibres, the hydrolysis occurs by breakage of amide linkages with the formation of carboxylic and amino groups on the surface of the treated materials (Silva & Cavaco-Paulo 2004). The hydrolysis products can be found in the treatment solution as monomers and soluble oligomers, as well as on the fibres surfaces as end group chains. Methodologies to monitor the formation of these groups were also described

(O'Neill and Cavaco-Paulo 2004; Silva & Cavaco-Paulo 2004; Matamá et al. 2006).

Since enzymes are large molecules, diffusion inside the fibre core is not possible. The implication of this is that the reaction is site selective, involving only modification at the fibre surface. This has the advantage of avoiding loss of strength of the treated materials (O'Neill & Cavaco-Paulo 2004; Silva & Cavaco-Paulo 2004; Matamá et al. 2006). In order to reduce treatment time and improve enzyme efficiency, treatments with cutinase in the presence of organic solvents were performed. This revealed that cutinase activity is preserved in the presence of low amounts of benzyl alcohol and dimethylacetamide. The acrylic and polyamide fibre structure became more open providing more access to cutinase, when organic solvents were present in the system (Matamá et al. 2006; Silva et al. 2005).

Site-directed mutagenesis was also described as an efficient tool to develop cutinase in order to obtain a higher specific activity towards insoluble substrates, such as polyester and polyamide 6.6. Cutinase from *Fusarium solani pisi* was genetically modified near the active site. Five mutations (L81A, N84A, L182A, V184A and L189A) were obtained by substitution of residues with smaller ones such as alanine, allowing better accommodation of the synthetic substrates (see Figure 1). Modelling studies were also performed and have shown enhanced free energy stabilization of the model substrate tetrahedral intermediate (TI) bound at the enzyme active site for all enzyme mutants. L182A showed the highest

activity towards polyester and polyamide 6.6 substrates (see Figure 1). L81A and L182A showed enhanced activity towards polyester fibres, while L182A had improved activity against polyamide. (Araújo et al. 2007).

The technical and mechanistic complexity of the enzymatic process is high, since cutinase has not evolved to interact with insoluble fibres. Furthermore, the compacted fibre structure of synthetic materials severely restricts accessibility of the enzyme at the fibre surface. The process of enzyme adsorption is of major importance to the enzymatic hydrolysis of synthetic fibres. Different studies have revealed that adsorption of proteins follows different steps and that mechanical agitation plays an important role in all of them (Cavaco-Paulo & Almeida 1996; Maldonado-Valderrama et al. 2005).

The synergism between mechanical agitation and enzyme activity was investigated using polyester, acrylic and polyamide 6.6 fibres. The incubations took place in apparatus with different types of agitation and higher levels of mechanical work were obtained by including stainless steel discs in the system (Silva et al. 2007a–c; O'Neill et al. 2007; Matamá et al. 2006). With polyester and polyamide fibres, lower levels of mechanical agitation gave slower, enzymatic reaction, but reached more satisfactory results in terms of fabric functionalization. However, in the case of acrylic, surface modification was only obtained when a high level of mechanical agitation was used in the presence of stainless steel

Figure 1. Detail of the active site X-ray structure of cutinase with the energy minimized structure of the TI of 1,2-ethanodiol dibenzoate (PET model substrate) (A) and PA 6.6 (B). The catalytic histidine (H188) and oxanion-hole (OX) are shown. Residues mutated in this study are labelled as: L81A, N84A, L182A, V184A and L189 (Silva et al. 2007b).

Figure 2. Possible cross-linking reactions between glutaraldehyde, spacer and protein, on immobilization procedure (Silva et al. 2007a).

discs, reflecting the low amount of the hydrolysable co-monomer.

The amine-enriched surfaces obtained by enzymatic action of cutinases or proteases were used to immobilize laccase from *Trametes hirsuta* using glutaraldehyde as the cross-linking agent with the inclusion of a spacer (1,6-hexanediamine) in some cases (see Figure 2). The application of a heterogeneous biocatalyst via immobilization can lead to reduction downstream processing costs and enables biocatalyst reuse. Laccase immobilization onto nylon matrices seems to be a promising system for bioremediation of contaminated soils, wastewater treatment, wine and other beverage stabilization, and even biosensor applications (Silva et al. 2007a–c).

Future strategies

The functionalization of synthetic fibres with enzymes has a lot of potential to be explored. Site-directed mutagenesis seems to be an excellent tool for the development of enzymes creating catalysts with improved ability to modify the surface of these materials. The possibility of including enzymes in several steps of fibre processing is also a possible approach to obtain value-added and highly functionalized materials. Continuing research is required in order to achieve the best processing conditions for future industrial applications.

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