Review

Enzymes go big: surface hydrolysis and functionalisation of synthetic polymers

Georg M. Guebitz[1] and Artur Cavaco-Paulo[2]

[1] Department of Environmental Biotechnology, Graz University of Technology, Petersgasse 12, 8010 Graz, Austria
[2] Department of Textile Engineering, University of Minho, 4800 Guimaraes, Portugal

Enzyme technology has progressed from the biotransformation of small substrates to biotransformation of synthetic polymers. Important breakthroughs have been the isolation and design of novel enzymes with enhanced activity on synthetic polymer substrates. These were made possible by efficient screening procedures and genetic engineering approaches based on an in-depth understanding of the mechanisms of enzymes on synthetic polymers. Enhancement of the hydrophilicity of synthetic polymers is a key requirement for many applications, ranging from electronics to functional textile production. This review focuses on enzymes that hydrolyse polyalkyleneterephthalates, polyamides or polyacrylonitriles, specifically on the polymer surface thereby replacing harsh chemical processes currently used for hydrophilisation.

Introduction

Biocatalytic processes are well established for synthetic biotransformation of small molecules. In 2004, economists predicted a 25-fold increase in turnover for polymers processed by biotechnological methods up till 2010, compared with only a seven-fold turnover increase for fine chemicals [1,2]. Recent launches of new commercial products, such as enzymes for processing polyester (Inotex Ltd; http://www.inotex.cz/) and patents by major industrial players (Genencor, http://www.genencor.com/; Novozymes, http://www.novozymes.com/en; CIBA, http://www.cibasc.com/; Henkel, http://www.henkel.com/; [3–6]) indicate that enzymes are going 'big' in terms of their substrates.

Limited surface hydrolysis of polyalkyleneterephthalates (PAT), polyamides (PA) and polyacrylonitriles (PAN) by enzymes increases their hydrophilicity, which is a key requirement for many applications, including gluing, painting, inking, anti-fogging, filtration, textile production, electronics and applications in the biomedical field (Box 1) [2,7–10].

Synthetic polymers are coated with bioactive compounds for many applications, including applications in textile manufacturing, microelectronics, bioprocessing and medical and food packaging. For example, biocoating of PET can lead to biocompatible and/or haemocompatible materials and antimicrobial surfaces, and is also used in tissue engineering [11]. Surface hydrophilisation is an important step in the biocoating process. PET is also used in cardiovascular implants such as artificial heart valve sewing-rings and artificial blood vessels. Enhanced hydrophilicity of PET (i.e. 15° lower contact angle) in these applications has led to reduced bacterial adhesion, thereby reducing the risk of infection [12]. PET shows excellent properties for use as a transparent cover layer in Flexible Electronic Devices (FEDs) (e.g. displays or photovoltaic cells), including mechanical stability and resistance to oxygen and water vapour. Again, the PET surface must be rendered more hydrophilic for increased adhesion of the subsequent functional layers, which have a major affect on the FED performance, efficiency and lifetime [9].

Ultrafiltration is used in many processes, including water purification and/or desalination, wastewater treatment and separations in the food, dairy, paper, textile, chemical and biochemical industries. Membrane fouling by proteins and other biomolecules increases the energy demand for filtration and requires cleaning with aggressive chemicals or replacement of the membrane. Ultrafiltration and reversed osmosis devices based on polyamide or polyacrylonitrile can be rendered more hydrophilic by grafting poly(ethylene glycol) (PEG) to the devices, or by polymerisation of acrylate monomers to the devices, which increases resistance to fouling [10,12–15].

Textile materials made of PA and PET are uncomfortable to wear because perspiration cannot penetrate the materials and evaporate. This poor water permeability is due to the hydrophobicity of synthetic polymers, which also leads to static cling and stain retention during laundering. A variety of different plasma treatments had been investigated to increase hydrophilicity for PET, PA and PAN fabrics and films [16–20]. Chemical finishers, for example those based on hydrophilic carboxyl-containing polymers, are widely used to increase hydrophilicity of synthetic textiles and are continuously being improved, as evidenced by numerous patents filed [21]. In addition to these benefits to potential users of the relevant products, increased hydrophilicity also makes polymer processing (e.g. dying) more efficient [7]. Alkaline treatment of polyester can improve texture and hydrophilicity, and reduce pilling. However, extremely high weight losses from 10–30% have been reported for this treatment [22]. Similarly, alkaline hydrogen peroxide or concentrated strong acid treatments for hydrolysing nitrile groups of PAN are difficult to control and have a negative impact on the environment [16]. By contrast, enzyme hydrolysis is targeted to the surface of the polymers while the bulk properties of the polymers remain un-changed.

Corresponding author: Guebitz, G.M. (guebitz@tugraz.at).

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Box 1. Synthetic fibres

About 90% of all synthetic fibres are made from either polyethylene terephtalate (PET), polyamides (PA) and polyacrylonitrile (PAN). Synthetic fibres already hold a 54% market share in the fibre market and >25 million tones (Mt) of PET, 5Mt PA and 2.6Mt PAN are produced annually [32]. PET alone is forecasted to account for almost 50% of all fibre materials in 2008 (see Journal for Asia on Textile and Apparel (ATA), http://www.adsale.com.hk/pub/en/ata_index.asp, issue 2006/06).

There is no doubt that synthetic polymers have unique properties, such as high uniformity, mechanical strength or resistance against chemicals or abrasion. However, high hydrophobicity, the build-up of static charges, not allowing 'breathing' and being difficult to finish are undesirable properties of synthetic materials [2,3,16,49]. In this article, we show how enzymes can be used to increase the hydrophilicity of synthetic polymers.

How to quantify success?

Enzymatic modification of PAT, PA and PAN materials involves limited hydrolysis of backbone esters, amide bonds, or of nitrile groups, respectively (Figure 1). The resulting changes of surface properties can easily be quantified with simple methods such as tensiometry or hydrophilicity measurements (e.g. contact angle) [23]. However, it is considerably more difficult to quantify the corresponding chemical changes on the polymer surface, for example the increase of carboxyl groups. If nitrile groups of PAN are converted to the corresponding acids, the concomitant release of ammonia can be used to quantify turnover of the biotransformation [24] (Figure 1). In the case of PA and PAT, hydrolysis would lead to the solubilisation of the resulting smaller fragments at a certain point, and this can be quantified by HPLC (high performance liquid chromatography) [2] and other methods [25]. However, it is not the aim of enzymatic surface treatment to liberate these soluble oligomers and thus 'degrade' the polymer. Instead, limited hydrolysis in the middle of the polymer chain is desired because it leads to the production of novel functional groups. Derivitisation of these functional groups (e.g. amino groups) is another possibility for quantifying surface hydrolysis based on colour changes using agents such as 2,4,6-trinitrobenzenesulfonic acid or α-bromoacrylamido reactive dyes [26].

X-ray photoelectron spectroscopy (XPS) has been proven to be a powerful tool for quantifying surface chemical changes created by enzymatic modification of PAN, PET and polypropylene [2,4,16,24,27,28]. In addition to XPS, attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) and scanning electron microscopy (SEM) have been used to analyse surface hydrolysis of polyacrylonitriles, and solid-state nuclear magnetic resonance (NMR) has been used to confirm enzymatic conversion of ^{13}C-labelled PAN into polyacrylic acid during bacterial growth on this substrate [29]. Angle-resolved

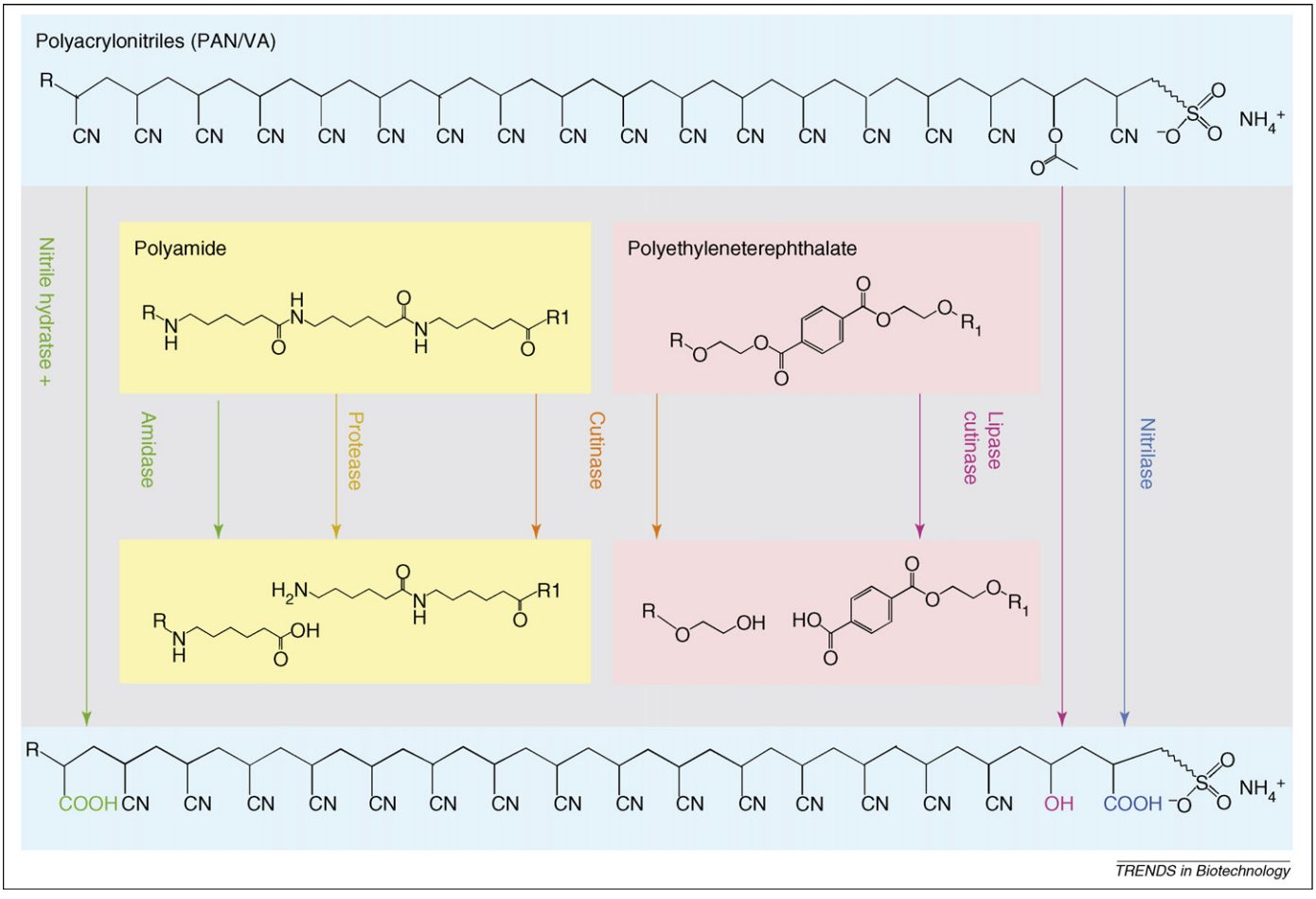

Figure 1. Enzymatic hydrolysis of synthetic polymers (amidase hydrolyses amides formed from PAN by nitrile hydratase; lipases and cutinases hydrolyse vinyl-acetate moieties in PAN).

XPS has been used to measure the thickness of protein (enzyme) layers on the PET surface, which often led to misinterpretation of results [2]. Thus, it is important to consider the contribution of protein adsorption during enzyme treatment on measured values of surface properties such as hydrophilicity. Most researchers use severe washing procedures with ultrasound or organic solvents and compare their results to controls run with inhibited enzymes [4].

Enzymatic hydrolysis of polyacrylonitrile

Polyacrylonitrile is a collective name for all polymers that consist of at least 85% acrylonitrile monomer. The typical PAN textile fibre consists of 89–95% acrylonitrile, 4–10% non-ionic co-monomer (e.g. vinyl acetate) and ~1% ionic co-monomer, containing a sulpho (SO_3H) or sulphonate (OSO_3H) group. Recently it has been shown that bacteria (a novel strain of *Micrococcus luteus*) can degrade PAN fibres. During this process, polyacrylic acid was released from PAN that was ^{13}C-labelled for NMR analysis [29]. The release of polyacrylic acid from PAN, together with the formation of ammonia, was also shown for commercial nitrilases [30].

Several researchers have shown that nitrile groups of PAN can be converted to the corresponding acids or amides by nitrilases or by an enzyme system consisting of nitrile hydratase and amidase, respectively, and major increases in hydrophilicity were found [16,27,29] (Table 1). These changes in surface properties corresponded to increases of the surface oxygen-to-carbon (O/C) ratio by up to 80% owing to enzymatic hydrolysis of the nitrile groups, as quantified with XPS [27,28].

Commercial PAN-based materials usually contain ~7% vinyl acetate to reduce rigidity of the polymer. The vinyl acetate moieties in PAN can be hydrolysed by cutinases and lipases, making this approach applicable to most commercially available PANs [31]. Factors that influence the enzymatic activity are crystallinity and accessibility of nitrile groups. High crystallinity of certain PAN materials has been shown to have a negative influence on susceptibility to enzymatic hydrolysis [29]. Although the accessibility of nitrile groups to enzymes can be increased by the presence of solvents such as dimethylacetamide or dimethylformamide, the use of organic solvent is not desirable owing to environmental and safety concerns [24,30].

Enzymatic hydrolysis of polyamides

The first important polyamide was Nylon 66, produced by the reaction of adipic acid and hexamethylene diamine. Several structural modifications with differing temperature capabilities have become commercially available, including Nylon 46, 610, 612, 6, 11, and so on. Polyamides have applications in many areas, the most important being in the production of fibre-based materials [32].

Enzymes that can hydrolyse polyamides are proteases, amidases and cutinases (Table 1). A model substrate (adipic acid bishexyl-amide) has been developed for screening polyamidase activity of a given enzyme. For a protease from *Beauveria* sp., an amidase from *Nocardia* sp. and a cutinase from *Fusarium solani,* activity on this model

Table 1. Enzymatic modification of synthetic polymers

Enzyme	Organism	Analysis method	Refs
Polyacrylonitrile (PAN)			
Nitrile hydratase	*Rhodococcus rhodochrous*	XPS, NH_3 formation, dye-binding assay	[24]
	Arthrobacter sp	XPS	[27]
	Brevibacterium imperiale; Corynebacterium nitrilophilus	XPS, dye-binding assay, contact angle	[16]
	Micrococcus luteus	NMR, NH_3 formation, dye-binding assay	[29]
Nitrilase	*Agrobacterium tumefaciens*	XPS, FTIR, SEM, dye-binding assay	[28]
	Commercial enzyme	NH_3 and polyacrylic acid formation, dye-binding assay	[30]
Cutinase[a]	*Fusarium solani*	X-ray diffraction, formation of acetic acid, dye-binding assay	[31]
Lipase[a]	*Thermomyces lanuginosus*		
Polyethyleneterephthalate (PET)			
Cutinase	*Thermobifida fusca*	Release of terephthalic acid, hydrophilicity	[48,57]
	Penicillium citrinum	Release of oligomers, hydrophilicity	[52]
	Fusarium oxysporum	Release of terephthalic acid, hydrophilicity	[50,57]
	Fusarium solani		
	Fusarium solani	XPS, Release of oligomers	[2]
Lipase	*Candida antarctica*		
	Humicola sp., Candida sp., Pseudomonas sp.	Depilling assay, Release of hydrolysis products, hydrophilicity	[5]
	Thermomyces lanuginosus	Release of oligomers, hydrophilicity	[23]
Serine esterase	*Pseudomonas spp.*	Release of terephthalic acid, dye-binding assay, hydrophilicity, depilling assay	[3,49]
Nitro-benzyl-esterases	*Bacillus* sp.	Hydrolysis of bis-(*p*-methylbenzoic acid)-ethylenglycol ester, dimethylterephtalate and diethylterephthalate, depilling	[6]
Polyamide (PA)			
Protease	*Bacillus subtilis*	Release of oligomers, reactive dye-binding assay, hydrophilicity	[33]
	Beauveria sp.	Release of oligomers, hydrophilicity	[23]
Cutinase	*Fusarium solani pisi*	Release of oligomers, reactive dye-binding assay, hydrophilicity hydrophilicity	[33] [23]
Amidase	*Nocardia sp.*	Release of oligomers, hydrophilicity	[23]
Hydrolase	*Arthrobacter sp.*	Release of hydrolysis products from 6-aminohexanoate-dimer	[37]

[a]PAN co-polymer with 7% vinyl acetate.

substrate correlated with hydrolysis activity in polyamide [23]. This cutinase has been genetically modified with the aim of achieving higher activity on synthetic polymers and the resulting L182A cutinase mutant showed increased PA-hydrolysing activity when compared with the native enzyme [33,34]. Similarly, the activity of a nylon-oligomer hydrolysing enzyme EII' from *Flavobactererium* sp. was increased 200-fold by genetic engineering [35]. In addition to genetic engineering, reaction engineering (i.e. influencing reaction mix, temperature and additives) seems to be an important factor and enzymatic hydrolysis of PA can be increased in the presence of solvents [36].

Linear and cyclic nylon oligomers are undesirable by-products in Nylon production that are released into the environment. Negoro and co-workers described the enzymatic degradation of these by-products by bacteria [37]. Several bacteria, including *Arthrobacter* sp., grow on the 6-aminohexanoate-cyclic dimer as the sole carbon and nitrogen source. Under these conditions 6-aminohexanoate hydrolases are produced. Similar to the penicillin-recognizing family of serine-reactive hydrolases, an oxyanion of the substrate is formed as a common intermediate, which is stabilised by the positively charged nitrogen at Ser112 and Ile345 in the case of the 6-aminohexanoate-dimer hydrolase [37].

In addition to hydrolytic enzymes, oxidases from lignolytic fungi have been shown to depolymerise polyamides [38–40]. Nylon-degrading peroxidases attack methylene groups adjacent to the nitrogen atoms and the reaction then proceeds in an auto-oxidative manner [40,41]. Nylon degradation capability of *Bjerkandera adusta* was ascribed to the activity of two manganese-peroxidases [39]. In general, degradation of polyamide with oxidative enzymes seems to be difficult to control and therefore has less potential for commercial applications of surface functionalisation.

Enzymatic hydrolysis of polyesters

Enzymes have shown potential both for synthesis of functional polyesters and for surface functionalisation and grafting. Lipases have been used for the synthesis of bifunctional polyesters [42], biocompatible sorbitol-containing polyesters [43] and for polyester coating of cellulose [44]. The enzymatic synthesis of chiral polyesters with high optical purity, which have applications as responsive materials in stereoselective reactions, is difficult to achieve using other approaches [45]. Attachment of novel side-chains (grafting) on poly(styrene-co-4-vinylbenzyl alcohol) was achieved by lipase-catalysed ring-opening polymerisation [46]. Recently, stereoselective grafting from polymers containing defined ratios of enantiomeric secondary alcohols was achieved [47].

PET is a polymer of ethylene glycol and terephthalic acid, produced from purified terephthalic acid (PTA) or alternatively, dimethyl terephthalate (DMT), and ethylene glycol. In addition to fibre production, a minor share of PET produced is used for packaging (30%) and other applications (5%). Enzymes are potential tools for PET recycling [48], for targeted surface hydrolysis of PAT-based materials and for depilling of PAT fabrics during washing processes [49].

PAT hydrolysing enzymes have been reported among cutinases, lipases and esterases (Table 1). PET was hydrolysed by cutinases from *F. solani* and *F. oxysporum* [2,34,50,51] and from *Pencillium citrinum* [52]. Based on the same activity on *p*-nitrophenyl butyrate, the *F. oxysporum* cutinase released more terephthalic acid from PET and increased the hydrophilicity to a greater extent than the *F. solani* enzyme [50]. Other PAT-hydrolysing enzymes, such as those from *Humicola* sp., *Candida* sp., *Pseudomonas* sp. and *Thermomyces lanuginosus,* are typical lipases [3,5,23,49].

Cutinases that hydrolyse PATs can also hydrolyse polyamides and vinyl acetate moieties of PAN (Figure 1). Hydrolysis activity of nylon oligomers by a 6-aminohexanoate-dimer hydrolase emerged in an enzyme with esterase activity [37]. Such catalytic promiscuity has been previously reported and exploited [53,54]. Structural elements (loops) of various hydrolases, including cutinase from *F. solani* and acetyl xylanesterase from *P. citrinum,* were engineered into the structure of the smallest known lipase (lipase A from *Bacillus subtilis*). These fragments still showed considerable activity, indicating that this might be a promising approach for developing novel enzymes for particular applications, including polymer surface hydrolysis [55,56].

A major parameter that can be improved by surface hydrolysis of aromatic polyesters is hydrophilicity [50,57–59]. However, in addition to enzymatic hydrolysis, the simple adsorption of enzyme protein to the polymer can also increase the hydrophilicity of PET owing to the hydrophilicity of the protein. Using XPS analysis an increase in nitrogen content of up to 7.2% owing to adsorption of a lipase to PET was measured, and angle-resolved XPS confirmed the presence of protein layers with thicknesses of 1.6–2.6 nm and 2.5–2.8 nm in PET treated with cutinase from *F. solani* and lipase from *C. antarctica*, respectively [2].

High crystallinity negatively affects the ability of the enzymes to hydrolyse PET, which has been shown for enzymes from *F. solani* and from *T. fusca*, as well as for an experimental polyesterase from Danisco (http://www.danisco.com/cms/connect/) [2,49,60].

Improving polymer-hydrolysing enzymes

Polymer-hydrolysing enzymes should be highly active on water-insoluble polymers. Only a few known and/or commercially used esterases and lipases were able to hydrolyse PET when dosed with the same activity on *p*-nitrophenyl butyrate [23,50]. To make screening procedures more efficient, easy-to-analyse oligomeric PET and PA model substrates have been developed and novel polyesterases and polyamidases identified [52]. In terms of surface functionalisation, these enzymes should be endo-acting. This means that bonds should preferentially be hydrolysed centrally in the polymer and not only on the chain ends. This would avoid the release of short-chain oligomers and furthermore provide evenly distributed increasing hydrophilicity [23]. The mode of action of enzymes on PET substrates can be modified with changes to reaction conditions. It has been reported that the ratio of the ethyleneglycolmono-ester of terephthalic acid to terephthalic

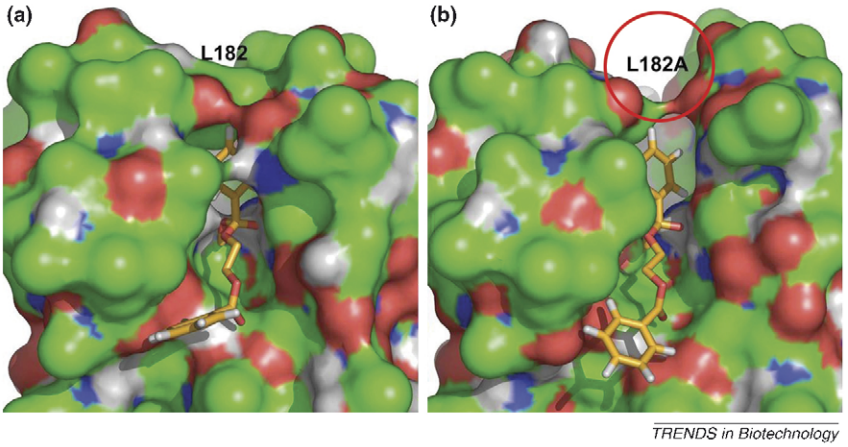

Figure 2. Single exchanges of amino acids of a cutinase from *F. solani* **(a)** leads to enlargement of the active site and better accommodation of a PET model substrate, shown by the red circle in **(b)**. L182A mutation is responsible for better stabilization of the 1,2-ethanodiol dibenzoate tetrahedral intermediate and for five-fold higher activity on PET [34].

acid detected in solution depends on the enzyme-(i.e. *F. solani* cutinase)-to-substrate ratio [2,61].

Only recently, the potential of genetic engineering to make polyesterases more 'fit' for their polymeric substrates was demonstrated (Figure 2). Site-directed mutagenesis of a cutinase from *F. solani* was carried out to enlarge the active site, which could then better accommodate polymeric substrates [34]. Single amino acid replacements were shown to better stabilise the PET model substrate 1,2-ethanodiol dibenzoate tetrahedral intermediate at the enzyme active site (Figure 2). Several cutinase mutants, all of which exhibited an enlarged active site, showed up to five-fold higher activity on PET. The structure and function of cutinases are well studied, and genetic engineering was previously used to improve their properties for several applications: for example, fat stain removal in detergents [62–65].

As well as the architecture of the active site other structural elements of the enzymes, such as the regions necessary for sorption and for guiding the enzyme along the substrate, might be important for polymer hydrolysis. It is well established that cellulose-binding modules (CBM) fulfill these functions in cellulases. More recently, a CBM has been attached to the *C. antarctica* lipase B, which is used for polyester coating of cellulose [44]. Similarly, enzymes hydrolysing microbial polyesters (i.e. polyalkanoate depolymerases) have binding domains with an essential function for PHA (polyhydroxyalkanoate) hydrolysis [66]. In nature, fungi have also developed strategies to direct enzymes to the surface of hydrophobic polymers. *Aspergillus oryzae* uses the hydrophobin RolA protein, and also the even more hydrophilic protein HsbA, to recruit high levels of its cutinase (CutL1) onto the surface of the polyester polybutylene succinate-coadipate (PBSA). RolA was also shown to move laterally on the PBSA film surface [67,68]. The potential influence of structural elements responsible for binding in polyesterases and the possible role of hydrophin-like molecules in the enzymatic PET hydrolysis remain to be investigated.

Conclusion and perspectives

Enhancement of the hydrophilicity of synthetic polymers is a key requirement for many applications ranging from electronics to functional textile manufacture. Enzymes have proved to be environmentally friendly tools for hydrolysis of synthetic polymers, specifically on the polymer surface, without compromises in polymer bulk properties such as strength. Screenings with short-chain model substrates has led to identification of novel polymer-modifying hydrolases suitable for industrial applications such as PET processing [3,5,6]. However, the power of genetic engineering approaches has not yet been fully exploited. A better understanding of the interaction of the enzyme with the substrate with regard to factors such as sorption, movement on the polymer surface, and the role of hydrophobins or binding modules, will be necessary to develop enzymes with further enhanced activity.

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