Proc. KSAM International Symposium
June 20-22, 2001, Chonan, Korea

Biodegradation of Xenobiotic Polymers by Microorganisms

Fusako Kawai
Research Institute for Bioresources, Okayama University, Kurashiki 710-0046, Japan

Various kinds of polymers have been commercialized and produced in large quantities. They are divided into commodity plastics and specialty polymers: The former is water-insoluble solids like polyethylene (PE), polystyrene and polyethylene terephthalate. The latter is, generally speaking, water-soluble like polyethylene glycol (PEG), polyvinyl alcohol (PVA), and polyacrylate, which are used for various applications as liquids or in solution. Most of plastics can be recycled from industrial sites or from commercial sites, but some of them are littered to yield environmental issues. Thus biodegradability is required even for plastics, although distinct biodegradability is limited to polyesters, natural or synthetic. All the biodegradable plastics are polyester types including various commercialized aliphatic (partially aromatic) polyesters, polylactide, polycaprolactone so on. Extracellular hydrolases like lipases, esterases and peptidases are produced by microorganisms, which hydrolyze polymers into small molecules to be incorporated into cells for metabolization. Specialty polymers are used as components of liquids or in solution, which are eventually liberated into sewage treatment systems or streams. Biodegradability is requisite for materials entering streams because they can neither be recycled nor incinerated. However, biodegradability up to high molecular sizes is limited to PEG, PVA and polyamide, e.g., polyaspartate (PAA). Oxidation is playing an important role in the metabolism of PEG and PVA. Oxidative steps are, in most cases, linked with respiratory chains and localized in membranes; macromolecular substrates have to be incorporated into cells for being oxidized. Thermally synthesized PAA was hydrolyzed by a membrane-associated enzyme, suggesting the transport of PAA up to 5,000 daltons. Thus the degradation of polymers by intracellular enzymes is more complicated than extracellular degradation. Bioabsorbable polymers used for medical application are non-enzymatically hydrolyzable and metabolized as monomer units; polylactide, polyglycolate, polymalate etc. Other polymers based on homocarbon-chains are non-biodegradable, although molecules up to a few thousands of daltons are found to be biodegradable anyway, as the cases of PEwax or polyacrylate. Homocarbon-chains seem to be biodegraded mainly by terminal oxidation and-oxidation processes, the enzymes of which are localized in membranes and substrates have to be incorporated into cells for their reaction. Long carbon-chain polymers are crystalline and insoluble in water, resulting in no affinity to living cells and no incorporation of them into cells. I will summarize the microbial aspect of degradation of xenobiotic polymers and introduce more detailed works on microbial degradation of polyethers.

Polyethers have a long history as specialty polymers used as raw materials for synthesizing detergents or polyurethanes. They are either water-soluble or oily liquids, which eventually find their way into environmental or waste water systems. The polyethers include PEG, polypropylene glycol (PPG), polytetramethylene glycol (PTMG) etc. PEGs are manufactured in large quantities and used as commodity chemicals in various industrial products such as pharmaceuticals, cosmetics, and lubricants. The most common hydrophilic moieties contained in the nonionic surfactants are the ethylene oxide polymers. The majority of PEGs produced are used as nonionic surfactants. PPGs are used in their original form in lubricants, inks and cosmetics, but most are transformed to polyurethanes or surface active agents. PTMG is used exclusively as a constituent of polyurethane. Oligomers up to octamer are water-

soluble and can be washed out from polymers with water.

Since the first report on microbial degradation of PEG 400 in 1962, extensive studies have been done and PEG up to 20,000 is thought to be sufficiently biodegradable. PEGs have been well studied and several metabolic pathways have been proposed, although most characterized one is that by Sphingomonads: The well documented metabolic pathway for PEG is based on the oxidation of the terminal hydroxyl groups to carboxylic acids and following breakdown of a terminal ether bond. PEG dehydrogenase (PEG-DH), PEG-aldehyde dehydrogenase and ether bond cleaving enzyme (diglycolic acid dehydrogenase) are independently involved in the metabolism as membrane-associated enzymes; the first and the last enzymes have been purified and characterized. Genes for inducible and constitutive PEG-DHs were cloned; PEG-DH belongs to the group of GMC flavoprotein as a distinct flavoprotein alcohol dehydrogenase that can accommodate rather large-sized substrate in its active site. Furthermore, all the observations strongly suggest that PEG-utilizing Sphingomonads must have a special uptake system for those xenobiotic polymers as well as sensing system in those species where enzyme induction is required for PEG degradation. A few groups studied anaerobic metabolism of PEG; PEG-acetaldehyde lyase was proposed for the metabolism by Schink et al, which is analogous to diol dehydratase. As the enzyme was found in the cytoplasm fraction, the permeability of a large molecule through the outer and cytoplasm membranes is necessary for the metabolism. Dehydrogenation with PPG and PTMG were detected with crude extracts of PPG- and PTMG-utilizing bacteria; PPG-DHs were localized in the periplasm, membrane and cytoplasm of *Stenotrophomonas maltophilia.* The results so far suggested indicate that polyethers seem to be metabolized by common metabolic pathways; the primary oxidation of terminal alcohol groups into ketone or carboxyl groups and subsequent cleavage of a terminal ether bond, resulting in the depolymerized molecules by one monomer unit. As neither reliable evidence for hydrolysis nor extracellular metabolization was suggested for polyethers, substrate up to 20,000 daltons have to be incorporated into cells, although the exclusion limit of bacterial outer membranes is, in general, 1,000 daltons or so. Was the transport system of the outer (and cytoplasmic) membranes for macromolecules acquired by mutation or dependent on the specific membranes? How can these polymers be transported? What regulate metabolic genes, instead of polyethers in the cytoplasm? To answer these questions, further studies remain to be done.