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# A Review of Biodegradation of Synthetic Plastic and Foams

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## Abstract

Synthetic polymeric foams have pervaded every aspect of modern life. Although foams provide numerous benefits, they also cause a significant environmental litter problem because of their recalcitrant and xenobiotic nature. Biodegradation may provide solution to the problem, but not enough is known about the biodegradation process of synthetic plastic and plastic-based foams. This review has been written to provide an overview of the current state of plastic foam biodegradation. Several biodegradation pathways of a few select synthetic polymers are also presented along with a discussion on some of the physico-chemical factors that can influence the biodegradation of plastic foams.

**Index Entries:** Plastic foam; synthetic polymer; biodegradation.

## Introduction

Plastic foams are synthetic polymers that are used widely throughout the world for various applications. The first successful synthesis of plastic foams took place nearly a century ago *(1)*, and since then their use has been increasing incessantly. At present, thousands of tons of plastic foams are used throughout the world for diverse applications. They are used in industry, automobiles, agriculture, space exploration, and irrigation, as well as in environmental, health, and numerous other sectors. Prior to the discovery of the method to synthesize plastic foams, natural sponges harvested from deep-sea beds were in use worldwide for centuries *(2)*. It is not

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Table 1
Global Plastic Market *(7)*

| Plastic type | Market share by volume produced |
|---|---|
| Polyethylene (PE) | 29% |
| Polyvinyl chloride (PVC) | 17% |
| Polypropylene (PP) | 12% |
| Polystyrene (PS) | 9% |
| Polyurethane (PUR) | 5% |
| Others | 28% |
| Total | 100% |

Table 2
US Markets for Polymeric Foam *(8)*

| Foam type | 2001 (million kg) | 2006 (million kg) |
|---|---|---|
| Polyolefin | 136 | 164 |
| Polystyrene | 870 | 923 |
| Polyurethane | 1800 | 2145 |
| Polyvinyl chloride | 525 | 598 |
| Other foam | 41 | 46 |
| Total | 3373 | 3877 |

known when sponges were put to use by humans, but some ancient writings of Plato, Homerus, and Aristotle mention that sponge was an object commonly used for bathing *(3,4)*.

It is estimated that global synthetic plastic production is approx 140 million tons per annum *(5)*. Data between 1939 and 1998 *(6)* indicate that global production of plastic is increasing at a rate of 2.2% per year. Table 1 shows the 1990 data for global market share of different types of synthetic plastics *(7)*.

The synthetic foam market accounts for about 10% of the total plastic resins produced in the United States, which is growing at an average rate of 2.8% annually. The 2003 demand for specialty plastic foams (such as those used in gaskets, heat shields, and seals) in the United States alone was estimated to be approximately at US$1 billion *(8)*. Table 2 provides an example on the current US market trend on cellular foam demand *(8)*.

Similarly, the European polymer foam market was valued at EUR 4.7 billion in 2004, and it has been forecast that it will grow at an annual rate of 5.2% in the coming years *(9)*. This shows that plastic foam production occupies a potentially huge market worldwide.

Although synthetic plastic foams have provided numerous benefits, they have also caused some serious environmental concerns in the form of a solid waste management problem almost in every part of the world. One estimate reports that almost 11.3% of the total municipal solid wastes comprise plastic wastes in the United States, and only a tiny fraction of this is actually recycled *(10)*. The majority of the used plastic foams end up as solid wastes in vast amounts either in landfills or incinerators. Incinerators are used to derive energy; however, they are also associated with hazardous emissions. Similarly, landfills are rapidly filling up and there are always environmental concerns with landfills. Moreover, such waste management techniques are end-of-pipe solutions that cause significant resource loss.

Although plastics do not generally biodegrade, several types of plastics have been found to be susceptible to biodegradation *(5)*. It has also been found that the biodegradation is accompanied with the generation of many valuable byproducts *(11)*. Such byproducts can be marketed and used as raw materials to manufacture other commercial products.

This paper provides a general overview of different types of plastic foams and their potential for biodegradation. More specifically, this paper discusses various ways of synthesizing plastic foams, biodegradation mechanisms of several synthetic plastics, recent works on plastic foam biodegradation, and future potential of biodegrading plastic foams.

## Synthesis and Types of Plastic Foams

Plastic foams consist of a gas phase dispersed in a solid plastic phase. The foamed material derives its properties from both of these phases. The solid plastic component forms the matrix of the foam while the gas phase fills the voids dispersed in the plastic material *(12)*. There are mainly two broad categories of plastic foams: thermoplastic foams and thermoset foams *(13)*. Foams can also be distinguished by their cellular structure, such as closed or open cell foams *(14)*. Similarly, from the point of view of their rigidity, they can be distinguished as rigid, semi-rigid, semi-flexible, or flexible. The density of plastic foams can vary *(12)* from as low as 1.6 $kg/m^3$ to over 960 $kg/m^3$. Figure 1 shows different types of foams.

Thermoplastic foams are formed as solids containing a blowing agent that are first melted and then cooled to solidify and stabilize them *(12)*. Thermoplastic foams are based on linear or slightly branched (non-cross-linked) polymers and thus have properties normally associated with thermoplastics. Examples of thermoplastic foams include polystyrene (PS), polyvinyl chloride (PVC), cellulose acetate (CA), polyethylene (PE), polypropylene (PP), etc. *(15)*.

Thermosetting foams are formed while the reactants are only partially reacted and they are still in the liquid form. This is followed by curing to solidify and stabilize the foam *(12)*. The matrix of these foams is based on cross-linked polymers so that, like the bulk plastics from which they are derived, they have generally good resistance to solvents and most chemicals *(13)*. Examples of thermosetting foams include polyurethane (PUR), phenol-formaldehyde (PF), urea-formaldehyde (UF), etc.

As mentioned previously, the voids in the foams can either be open or closed. Closed-cell foams have a cellular structure in which air bubbles are entrapped within the voids. PS coffee cups consist of closed foam cells.

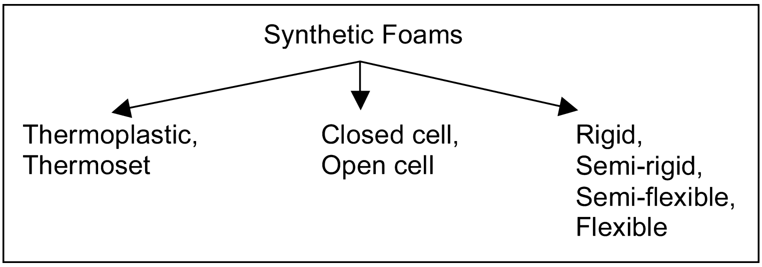

Fig. 1. Types of plastic foams.

Table 3
Foam Types and Applications

| Foam types | Select applications |
|---|---|
| Thermoplastic foams | |
| Polystyrene | Packaging, insulation, cups |
| Polyvinyl chloride | Construction (flooring, roofing), automobile (seat covers) |
| Cellulose acetate | Structural framing, ribs, panels, lifeboats, buoys |
| Polyethylene | Packaging, insulation, construction, toys, office products, aircrafts |
| Polypropylene | Wall insulation, construction, agriculture |
| Thermoset foams | |
| Polyurethane | Cushion, insulation, automobile (body panels, trims and bumpers) |
| Phenol formaldehyde | Construction, insulation |
| Urea formaldehyde | Floating devices |

Open-cell foams have a cellular network and air can flow through them easily. PUR car seats and cushions are two examples of such open-cell foams *(16)*. Table 3 provides examples of different types of plastic foams and some of their applications.

## Biodegradation Definition

In the context of biodegradation of plastic-based materials, including plastic foams, various terms are often used interchangeably without noting subtle differences in their meaning. A few of these terms are mentioned here: environmental degradation, photo degradation, thermal degradation, and biodegradation *(17)*. The term "environmental degradation" refers to the total effect of several environmental factors such as sunlight, heat, oxygen, air, wind, rain, dust, water, chemical pollution, microorganisms, insects, animals, etc. that can bring about degradation in a foam material when left exposed to the ambient environment.

Whereas the above definition encompasses degradative effects of several factors on the plastic foam, other terms are more specific and refer to only one factor. For example, "photo degradation" refers to the phenomenon by which polymeric foams are degraded by the action of sunlight only. Similarly, thermal degradation refers to the phenomenon in which polymeric foams are degraded by the action of heat only.

Biodegradation refers to the degradation and assimilation of polymeric foams by living microorganisms (such as bacteria, fungi, and algae) to produce degradation products such as $CO_2$, $H_2O$, $CH_4$, and biomass *(18)*. Enzymatic degradation of plastic materials is also considered biodegradation, and the term "enzymatic biodegradation" is widely used *(19)*.

It is evident from the above discussion that microbial and enzymatic biodegradation of polymeric foams are achieved under relatively milder environmental conditions of pH, temperature, and pressure. In this paper, "biodegradation" refers to both microbial and enzymatic degradation of polymeric foams.

## A Brief Overview of Plastic Biodegradation and Biodegradation Mechanisms

As mentioned previously, synthetic foams possess both solid and gaseous phases. The solid phase consists of synthetic polymers that form the supporting matrix of the foam. Because the biodegradation of foams occurs in the solid phase that contains plastic, a brief discussion on studies related to plastic biodegradation is provided in this section followed by a discussion on several biodegradation mechanisms.

### Plastic Biodegradation

Numerous published reports *(5,10,20–26)* and the references cited therein provide information on the biodegradation of a variety of plastics. Bushnell and Haas *(20)* reported on the bacterial biodegradation of hydrocarbons *(27,28)*. These works *(27,28)* are probably the first reported accounts on the microbial biodegradation of synthetic polymeric hydrocarbons. Similarly, Berk et al. *(21)* also provided research results on the fungal biodegradation of synthetic hydrocarbons.

Shimao *(5)* has presented a review on the biodegradation of a wide range of synthetic polymers that primarily belong to the following groups: polyesters, polyhydroxybutyrate (PHB), polycaprolactone (PCL), polylactic acid (PLA), PUR, polyvinyl alcohol (PVA), nylon, and PE. Nakajima-Kambe et al. *(26)* and Howard *(25)* have provided reviews on PUR biodegradation studies. Zheng et al. *(20)* provided a review on the biodegradation of a variety of thermoset and thermo plastics. Iiyoshi et al. *(22)* demonstrated experimental results on PE biodegradation while Deguchi et al. *(23)* showed experimental results on nylon biodegradation.

## Plastic Biodegradation Mechanisms

Although not all biodegradation processes of synthetic polymers have been understood fully, details of some of them have been known. Therefore, biodegradation mechanisms of a few select synthetic polymers such as PE, nylon, PS, and PUR are presented here. These synthetic polymers are chosen for discussion because of their versatility in applications, their recalcitrant and xenobiotic nature and growing interest to find efficient biodegradation pathways as a means to control the litter problem.

### Polyethylene

PE is a synthetic polymer with -$CH_2$-$CH_2$- repeating units in the polymer backbone. Among different types of synthetic polymers, PE is considered to be highly resistant to biodegradation. Several features of PE have been identified to make it resistant to biodegradation: (1) highly stable C-C and C-H covalent bonds, (2) higher molecular weight (MW) of PE polymer, which makes them too big to penetrate cell walls of microbes, (3) lack of readily oxidizable and/or hydrolyzable carbonyl, amide, and C=C double bond groups etc. in the polymer backbone, (4) lack of chromophores that can act as catalysts for synergistic photo and biodegradation, and (5) highly hydrophobic nature.

Because of these features, PE has been considered almost inert to biodegradation and a literature review revealed differing views among authors regarding whether to consider PE as a biodegradable polymer or not. The differing views have been attributed to several factors such as (1) lack of standardization in test methods *(29)*, (2) different time scales adopted by different researchers in their test protocols *(30)*, (3) PE's extremely slow process of biodegradation *(31)*, (4) lack of a general consensus among researchers on a universal definition of PE biodegradation, (5) use of several modified forms of PE blended with additives such as starch *(32)*, wood powders *(33)*, and chromophores *(34)*, etc. that are treated using several techniques such as heat *(35)* and ultraviolet irradiation *(31,36)* prior to subjecting PE to biodegradation, (6) lack of overall agreement among researchers on what biodegradation end products would make PE a biodegradable *(37)* polymer, (7) scarce information relating to enzymatic biodegradation *(22,38)*, and no knowledge on genes encoding any specific enzyme that would biodegrade PE *(39)*, and (8) lack of any definitive PE biodegradation mechanism *(39)*. It is out of the scope of this paper to elaborate much on these factors. Interested readers should refer to references cited herein to get more detailed information.

Despite the extremely low biodegradability of PE, biodegradation mechanisms of PE have been proposed in the literature mentioned above. One such mechanism is presented in Fig. 2 *(40)*. As shown in this figure, PE is first altered by adding carbonyl group (C=O) in its polymer backbone. The alteration is achieved through abiotic photoxidation pathway as shown in Fig. 3 *(40)*. Once this is achieved, the altered PE molecule is believed to

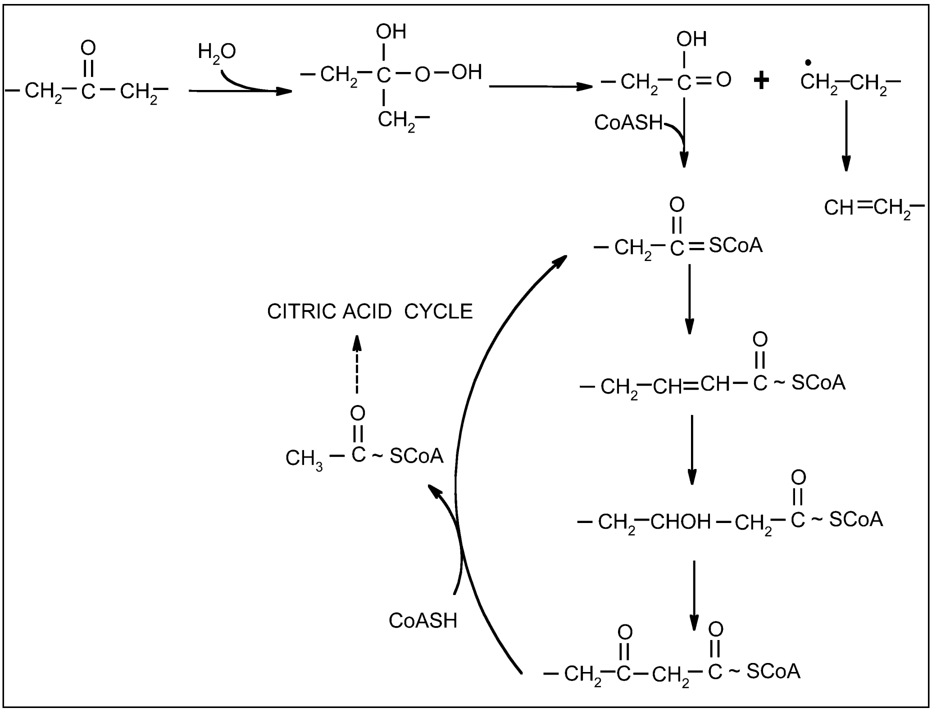

Fig. 2. Proposed biodegradation mechanism of polyethylene (PE) *(40)*. One proposed mechanism of biodegradation of PE polymer that has been altered by the addition of carbonyl (C=O) group in its polymer chain.

undergo biotic oxidation following a similar mechanism as in the case of paraffin biodegradation as shown in Fig. 4 *(41)*. Linear PE polymers are similar to linear paraffin molecules with 10–20 carbons, and it is believed that biodegradation of the linear PE molecules should follow similar pathway as linear paraffin molecules *(37)*. In the process of biodegradation, the PE or paraffin molecules containing carbonyl group first get converted to an alcohol (containing -OH group) by a monooxygenase enzyme. The alcohol is then oxidized to an aldehyde (containing -CHO group) by alcohol dehydrogenase enzyme. An aldehyde dehydrogenase converts aldehyde to a fatty acid (containing -COOH group). This fatty acid then undergoes β-oxidation pathway inside cells. In summary, published accounts *(37,39,40,42)* refer to several synergistic biotic and abiotic factors as listed in Table 4 that help in the biodegradation of PE polymer.

## Nylon

Nylon is categorized as a synthetic polyamide with repeating amide group (-CONH-) in its polymer backbone. Although nylon in general was regarded as nonbiodegradable in the past, some forms of nylons have recently been shown to biodegrade under suitable environmental conditions by both fungi *(43)* and bacteria *(44)*. Nylon-degrading enzymes have also

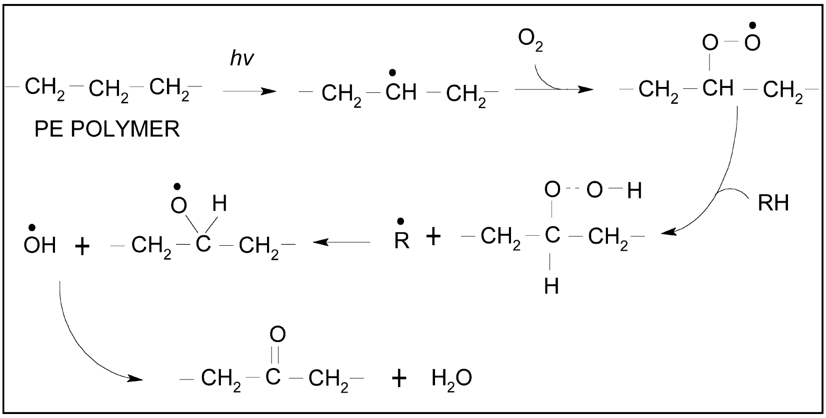

Fig. 3. Addition of C=O group through abiotic photooxidation of polyethylene (PE) *(40)*. PE polymer molecules are treated with ultraviolet radiation (*hv*), which causes radical formation. Oxygen is then absorbed from the surrounding and hyperoxides are formed, which ultimately causes the formation of a carbonyl (C=O) group in the polymer.

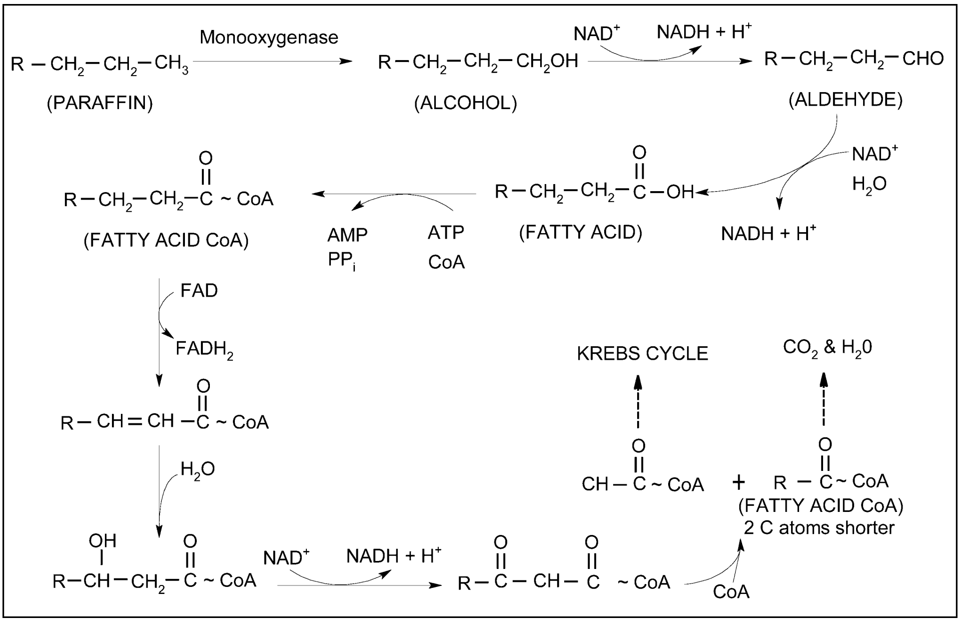

Fig. 4. Paraffin biodegradation pathway *(41)*. Polyethylene polymer molecules containing carbonyl group first get converted to an alcohol (containing -OH group) by a monooxygenase enzyme. The alcohol is then oxidized to an aldehyde (containing -CHO group) by alcohol dehydrogenase enzyme. An aldehyde dehydrogenase converts aldehyde to a fatty acid (containing -COOH group). This fatty acid then undergoes β-oxidation pathway inside cells.

Table 4
Biotic and Abiotic Factors That May Bring about Polyethylene (PE) Biodegradation

| Biotic factors | Abiotic factors |
|---|---|
| • Bacteria, fungi | • Sunlight and photooxidation |
| • Biosurfactants produced by microbes to attach on PE surface | • Addition of carbonyl radicals into -$CH_2$-$CH_2$- backbone due to photo-oxidation and propagation of Norrish type I and II degradation |
| • Biofilm growth on PE surface | • PE fragmentation by mechanical stress, surface erosion, heat, water etc. |
| • Effects of extracellular and membrane bound enzymes on bringing changes on PE at molecular level | • Diffusion of $O_2$ into PE crystals |
| • Uptake of shorter chain PE polymers inside the cells via cell walls and membranes | • Increase in hydrophilicity of PE causing diffusion of water molecules into PE |
| • Assimilation of such short chains via β-oxidation pathway inside cells using intracellular enzymes | • PE chain scission |

been extracted from fungi *(45)* and bacteria *(46)*. Several studies related to the isolation, expression and transformation of genes encoding nylon degrading enzymes are reported in the literature *(47,48)*. Reviews on nylon biodegradation have been provided by Negoro *(49,50)*. These reviews and the literature cited therein give additional details on nylon biodegradation. A summary of proposed nylon biodegradation pathways by bacteria, fungi and enzymes is presented here.

Tomita et al. *(44)* isolated the bacterium *Geobacillus thermocatenulatus* and used it successfully to biodegrade nylon 12 and nylon 66. They proposed that bacterial degradation of nylon 12 was associated with the enzymatic hydrolysis of amide bonds, which was accompanied by the formation of 12-amino dodecanoic acid. They also proposed that further oxidation would result in the degradation of 12-amino dodecanoic acid into carboxyl and other simpler degradation products. Figure 5 shows a simplified diagram of the proposed mechanism of nylon 12 biodegradation *(44)*.

Experimental studies on nylon biodegradation using fungi and enzyme have been carried out and biodegradation mechanism has been proposed. Lignin degrading white rot fungus strain IZU-154 was able to degrade nylon 66 *(43)*. Similarly, an extracellular enzyme (fungus peroxidase) extracted from the same fungus strain was also able to degrade nylon 66 *(45)*. The nylon degradation products showed end groups containing CHO, NHCOH, $CH_3$, and $CONH_2$, which suggested that nylon 66 degradation was oxidative process. It has been noted that bacterial biodegradation of nylon 66 is a hydrolytic process. Nomura et al. *(51)* suggested that me-

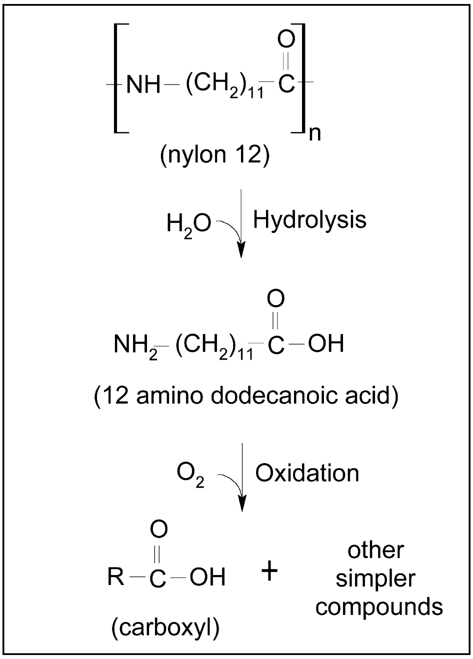

Fig. 5, Proposed mechanism of nylon 12 degradation by bacteria *(44)*. Bacterial degradation of nylon 12 is believed to be associated with the enzymatic hydrolysis of amide bonds. This is accompanied by the formation of 12-amino dodecanoic acid, which undergoes further oxidation and results in the formation of carboxyl and other simpler degradation products.

thylene ($CH_2$) group adjacent to the nitrogen atom in the nylon polymer backbone is first oxidized by the enzyme fungus peroxidase. The $-\dot{C}H-$ radical then undergoes stepwise oxidation process, thereby releasing various degradation products as mentioned above. The proposed nylon degradation mechanism using fungus peroxidase is presented in Fig. 6 *(51)*.

Biochemistry studies on several nylon oligomer-degrading enzymes have been performed in order to know about the genes that encode these enzymes. Three types of nylon degrading enzymes were extracted from *Flavobacterium* sp. KI72 *(47,52–54)*. These enzymes have been named as 6-aminohexanoate cyclic dimer hydrolase (F-EI), 6-aminohexanoate-dimer hydrolase (F-EII), and 6-aminohexanoate oligomer hydrolase (F-EIII). Similarly, two other types of enzymes have been extracted from *Psedudomonas* sp. strain NK87. These enzymes have been named as P-EI and P-EII because they are capable of degrading similar nylon oligomers as are degraded by F-EI and F-EII *(48,55)*. It has been proposed that F-EI degrades cyclic nylon dimer and F-EIII degrades cyclic nylon oligomers. Similarly, F-EII and F-EIII are shown to degrade linear oligomers. The genes associated with F-EI, F-EII, and F-EIII are identified as F-*nyl*A, F-*nyl*B, and *nyl*C, respectively. The plasmid that encodes these genes is known as pOAD2. This plasmid

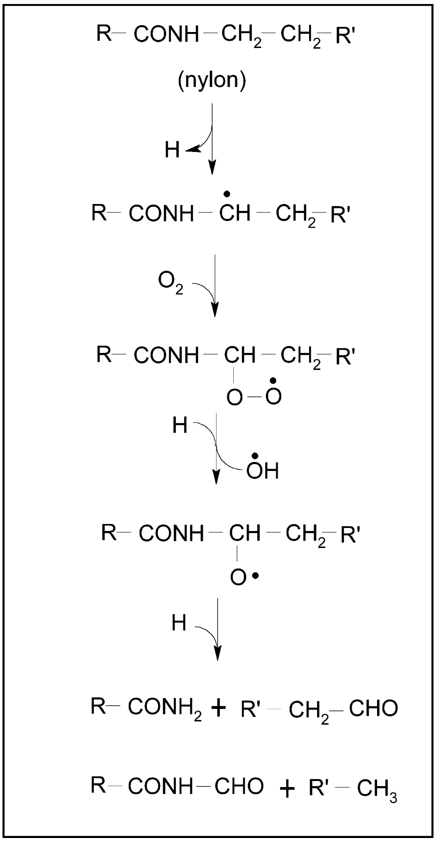

Fig. 6. Proposed mechanism of nylon biodegradation by fungus peroxidase *(51)*. Methylene ($CH_2$) group adjacent to the nitrogen atom in the nylon polymer backbone is first oxidized by the enzyme fungus peroxidase. The -ĊH- radical then undergoes stepwise oxidation process, thereby releasing various degradation products.

comprises a 45,519-base pair (bp) sequence with 66% of G+C content *(56)*. The active site in the F-EII enzyme involves a serine residue (Ser112) *(57)*. Similarly, the genes associated with P-EI and P-EII have been identified as P-*nyl*A and P-*nyl*B, respectively. These genes are encoded on plasmids pNAD2 (23 kb) and pNAD6 (80 kb), respectively. Details of plasmid map can be found elsewhere *(50)*.

### Polystyrene

PS is a synthetic polymer that contains a repeating group, as shown in Fig. 7 in its polymer backbone. PS is also considered to be highly stable and less susceptible for biodegradation.

Biodegradation experiments of PS, styrene oligomers, and PS copolymers have been tried using bacteria *(58)*, fungi *(59)*, mixed culture *(60)*, and enzyme *(61)* under different conditions. Although styrene oligomers and PS copolymers have been shown to biodegrade, biodegradation of PS poly-

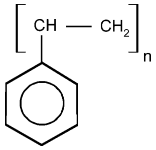

Fig. 7. Structure of polystyrene.

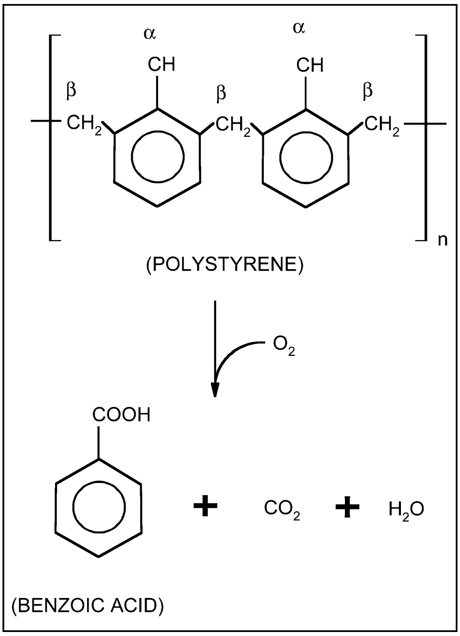

Fig. 8. Proposed polystyrene biodegradation mechanism *(60)*. Oxidation of α and β carbon atoms in the polystyrene polymer results in the formation of benzoic acid and $CO_2$, respectively. Benzoic acid may further be biodegraded to yield various other simpler compounds.

mer has not been successful yet *(62,63)*. Therefore, no definitive pathway of PS biodegradation has been identified. However, one probable pathway of PS biodegradation has been proposed and it is presented in Fig. 8 *(60)*. As shown in this figure, it has been proposed that oxidation of α carbon would result in the formation of benzoic acid and oxidation of β carbon would result in the formation of $CO_2$. Benzoic acid may further be biodegraded to yield various other simpler compounds. Although benzoic acid is considered a biocide, it is also an intermediate metabolite in lignin biodegradation.

Enzymatic biodegradation of PS polymer was tried with hydroquinone peroxidase enzyme with success *(61)*. The enzyme was extracted from lignin decolorizing bacterium *Azotobacter beijerinckii* HM121 and used in a two phase (aqueous and solvent) system. The aqueous phase contained hydroquinone peroxidase enzyme in water whereas the solvent phase con-

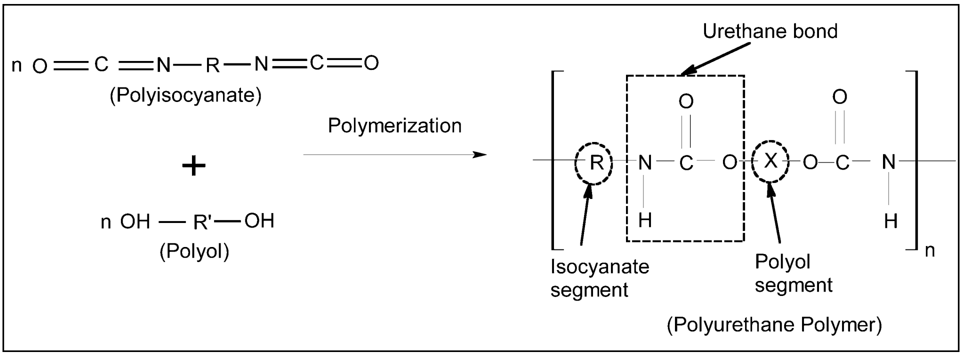

Fig. 9. Polyurethane synthesis by polymerization reaction.

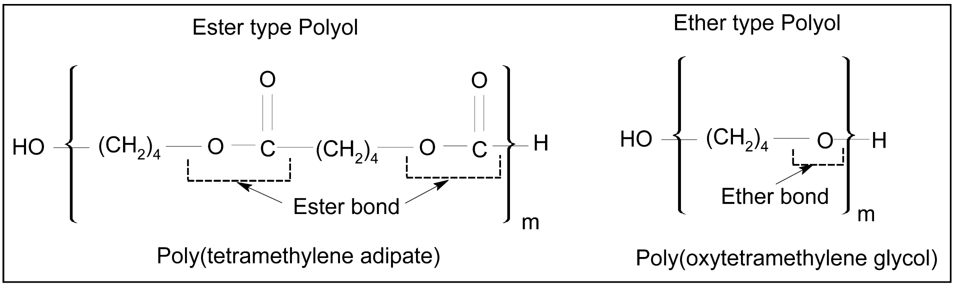

Fig. 10. Typical examples of polyols used in the synthesis of polyurethane.

tained PS in dichloromethane. Biodegradation results revealed that PS was degraded to small water-soluble molecules that could be detected by thin layer chromatography. It was proposed that enzyme could have assisted in forming radical species that further underwent biodegradation to simpler compounds.

### Polyurethane

PUR is a synthetic polymer that is formed by condensation polymerization reaction between polyisocyanate and polyol as shown by the reaction in Fig. 9 *(64)*. Polyol, which is represented by X in this figure, can either be of ester or ether type. Figure 10 shows one example each of ester (polytetramethylene adipate) and ether type (polyoxytetramethylene glycol) polyol. The PUR polymer that contains an ester type polyol is known as polyester PUR, whereas the PUR polymer that contains an ether type polyol is known as polyether PUR. Similarly, polyisocyanate can also be either aliphatic or aromatic type as shown in Fig. 11. In all types of PUR polymers, the polymer backbone mainly contains urethane bonds.

Numerous published accounts report that polyester PUR is susceptible to biodegradation by bacteria, fungi, and enzymes whereas polyether PUR has been found to be relatively more resistant to biodegradation. It has

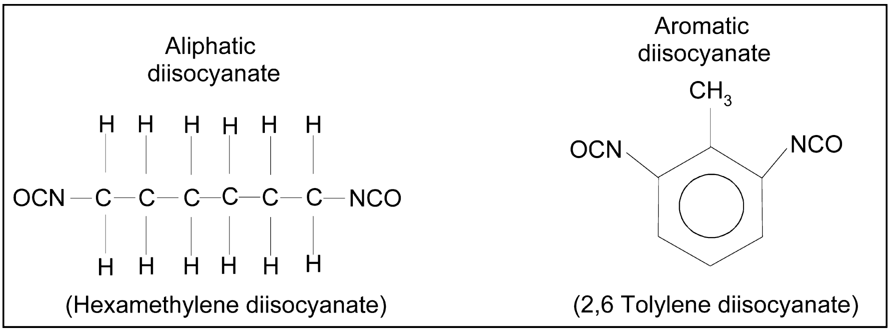

Fig. 11. Typical examples of isocyanates used in the synthesis of polyurethane.

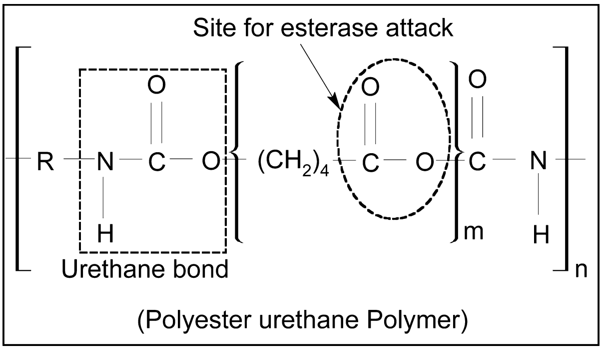

Fig. 12. Typical polyester polyurethane-showing site for esterase attack. Note: in order to distinguish between the polymer chains associated with polyol and polyurethane, two separate notations "m" and "n" are used.

been reported that the biodegradation of polyester PUR is carried out by the esterase enzyme associated with both bacteria and fungi. Furthermore, this biodegradation is achieved mainly by the enzymatic attack on the ester bond in the polyol segment of the polymer backbone as shown in Fig. 12. In the other similar studies involving polyether PUR, ether bonds are shown to be not susceptible to esterase attack (Fig. 13). Reviews on the biodegradation of PUR in general have been provided elsewhere *(25,26)*.

It has been proposed that the esterase enzyme causes hydrolysis of ester bond and biodegrades polyester PUR to generate several known and unknown degradation byproducts. One such biodegradation pathway is shown in Fig. 14 *(26)*. One of the unknown byproducts is believed to further undergo alkaline hydrolysis to produce other degradation products as shown in Fig. 15.

Along with the ester bond, the urethane bond has also been shown to undergo biodegradation by esterase enzyme in low-MW polyester PUR polymers. However, in most high-MW PUR polymers, it is still not clear whether the urethane bond is hydrolyzed directly or after the polymer is reduced to low-MW compounds.

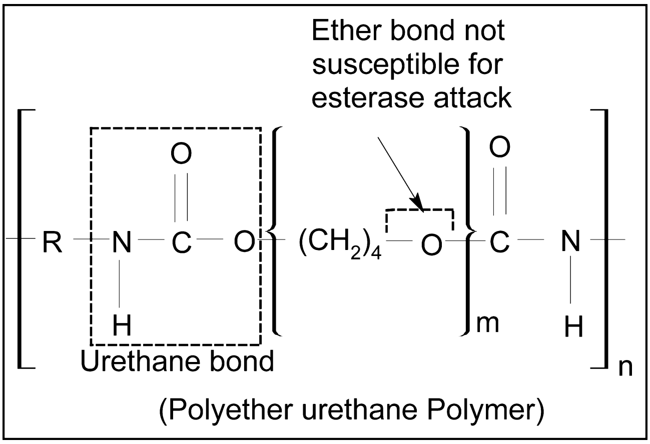

Fig. 13. Typical polyether polyurethane.

Biochemistry studies on the polyurethane esterase enzyme have been performed and genes have been identified. Two such genes that encode PUR esterase enzymes are mentioned here. A cell membrane-bound enzyme (PUR esterase, 548 amino acids, 62 kDa) was extracted from bacterium *Comamonas acidovorans* TB-35 *(65)*. The gene encoding this enzyme has been identified as *pudA*, which consists of 1644-bp nucleotides with a putative ATG initiation codon *(66)*. Similarly, an extracellular enzyme (PUR esterase, 617 amino acids, 65 kDa) was extracted from bacterium *Pseudomonas chlororaphis (67)*. The gene encoding this enzyme has been identified as *pueA*, which consists of a 1854-bp nuculeotide.

It is known that as a result of the hydrophobic nature of solid substrates like PUR, there is inefficient contact between the enzyme and the substrates. In order for the reactions to occur, it is essential for the enzyme to first make good contact with the substrate. This is the only way that the active site in the enzyme can carry out biodegradation. Several studies have shown that PUR esterase enzyme has two different domains, called the "active site domain" and the "substrate-binding domain." The substrate-binding domain is believed to first approach the PUR surface, and after binding to the substrate, the active site domain is believed to catalyze the hydrolysis of ester bond. The PUR esterase possesses the Ser-His-Glu catalytic triad as its active site *(68)*.

## Studies on the Biodegradation of Synthetic Plastic Foams

Although numerous studies have been reported on the biodegradation of different types of plastics, the published literature on the biodegradation of plastic foams appears to be scarce. In this section, a literature review pertaining to plastic foams made from PUR, PS, polymethyl methacrylate (PMMA), PF, and poly(butylenes succinate) (PBS) are presented.

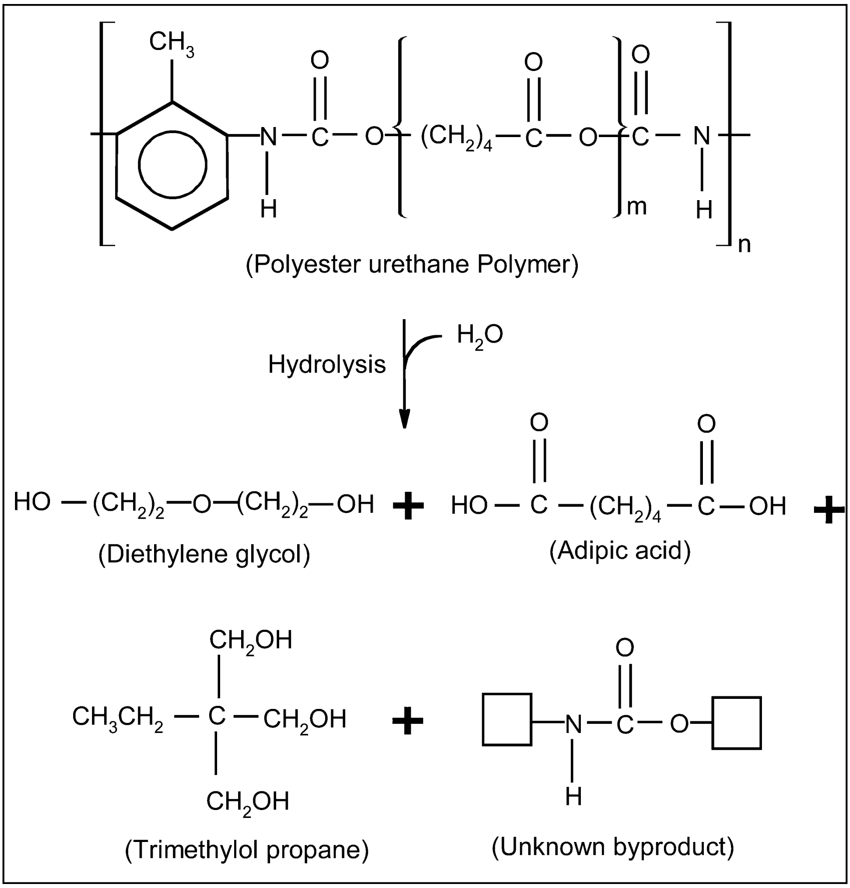

Fig. 14.. Proposed biodegradation pathway of polyester polyurethane *(26).*

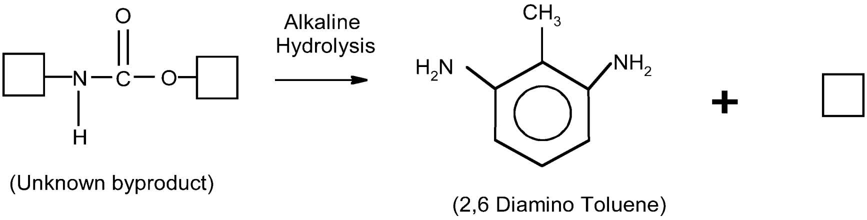

Fig. 15. Further degradation of unknown products.

## *PUR Foam Biodegradation*

The work by Edmonds and Cooney *(69)* is probably one of the oldest published reports on the microbial degradation of PUR foam. In this work, polyester PUR foam samples were obtained from aircraft fuel tanks. The foam pieces were then subjected to biodegradation for a period of 18 d in two different liquid culture media. One of the media contained bacterium sp. *Pseudomonas aeruginosa*, whereas the other media contained a fungal sp. *Cladosporium resinae*. The results indicated that the presence of foam samples in the culture media did not affect the rate or total amount of growth of the bacteria. However, the presence of foam pieces in the culture medium enhanced the growth of the fungal isolate by providing a supporting matrix for mycelial attachment.

Subsequent to the work by Edmonds and Cooney *(69)*, Hedrick and Crum *(70)* carried out experiments that also involved biodegradation of polyester PUR foams obtained from aircraft fuel tanks. In these experiments, PUR foam samples were subjected to longer duration (up to 90 d) of microbial exposure followed by the examination of their physical properties to identify the extent of biodegradation. Bacterium *Pseudomonas aeruginosa* and fungus *Cladosporium resinae* were used in two separate culture media with identical foam samples. The results showed that the presence of PUR foam in the growth media caused increased bacterial cell growth, which was associated with an increase in oxygen uptake rate. Similarly, the presence of foam in the growth media containing fungi caused an extensive matting with fragmentation and decrease in tensile strength of the foam. This study, for the first time, provided a direct evidence that PUR foams can undergo microbial degradation under controlled laboratory conditions.

Filip *(71)* reported microbial degradation experiments using landfill leakage water on polyester and polyether based PUR foams. The results indicated that both types of foams could be biodegraded but polyester PUR foam was more susceptible to biodegradation than the polyether PUR foam. This result was similar to the results obtained by Pathirana and Seal *(72)*, Darby and Kaplan *(73)*, and Nakajima-Kambe et al. *(26)*.

Martens and Domsch *(74)* carried out experiments with polyester and polyether type of PUR foam pieces using a mixture of municipal refuse, sewage sludge and caustic lime that were placed inside closed plastic bags containing foam samples for 13 mo. The test revealed similar results as those obtained by Fillip *(71)*.

It is noted here that the PUR polymer is unique with respect to its polymer backbone as compared with other types of polymers because the polymer can be synthesized using different types of polyisocyanates and polyols as mentioned above. The polymer, therefore, derives its properties from the type of polyisocyanate/polyol used in the polymerization process. This is also one reason why it may sometimes be difficult to compare two different studies involving PUR biodegradation, mainly because each study may use PUR polymers that have different polyol or polyisocyanate compounds *(26)*.

## PS Foam Biodegradation

The Expandable Polystyrene Molders Association (EPSMA) *(75)* carried out an experimental investigation on different types of PS foams ranging in density between 2.4 and 2.7 pcf (pounds per cubic foot). Five fungal species (*Aspergillus niger, Aspergillus versicolor, Penicillium funiculosum, Chaetomium globosum, Aspergillus flavus*) were tested for growth following ASTM C1338 *(76)* test protocols. The results showed that under ideal laboratory growth conditions, the fungi did not grow on any of the test pieces. This result is supported by Hocking *(77)*, who reported that PS foam products are inert to biodegradation. This experimental result was also similar to the result obtained by Kaplan et al. *(78)*, who carried out biodegradation experiments on PS polymers using different fungal species.

### *Biodegradation of Poly(butylene succinate) Foam*

Bahari et al. *(79)* carried out enzymatic and soil burial biodegradation tests on PBS foams. In the enzymatic biodegradation experiments, 6 mg of PBS foam pieces with the dimensions of 10 × 10 × 1.6 mm were used. Lipase enzyme was used in a liquid medium containing phosphate buffer at a pH of 7.4 and temperature of 55°C. The reaction mixture was shaken until the specified time, after which the foam samples were tested for decrease in weight. Similarly, the soil burial test was performed in plastic troughs, 57 cm long by 17 cm wide by 14 cm high. The soil consisted of composted top soil, black garden soil, and pond sludge in equivalent ratios maintained at a pH of 7.0 and about 40% moisture content. The foam samples were buried to about 3 cm from the soil surface for various burial times ranging from 2 wk to 4 mo. After the specified time intervals, samples were retrieved and tested for weight loss. It was observed that the foam pieces experienced surface erosion and weight loss in both the tests. This provided an experimental evidence that PBS foams are susceptible to biodegradation under favorable environmental conditions.

### *Biodegradation of Other Foams*

A research paper by Kaplan et al. *(78)* included biodegradation results on two other synthetic polymers, PMMA, and PF that were tested with 17 different fungal species. Although the test materials used by Kaplan et al. *(78)* were not foam pieces, the experimental results would provide useful information on the biodegradation of foams because the solid matrices of PMMA and PF foams consist of PMMA and PF molecules. Therefore, these experimental results can provide valuable information on the biodegradation of foams that are based on PMM and PF polymers. The results showed extremely low decomposition rates of PF and PMM materials. This indicates that synthetic foams made from these materials would be less susceptible to fungal biodegradation.

## Implications of Different Physico-Chemical Factors on Plastic Foam Biodegradation

Various factors have been attributed to influence the biodegradation of synthetic plastics and plastic foams. Some of these factors are discussed in this section.

1. Evolutionary theory. Plastic-based materials such as plastic foams came into existence not more than 100 yr ago on this planet. Although such materials contain energy sources for microorganisms, it is probably too early for the microorganisms to identify them as an energy source *(80–83)*.
2. Enzyme–substrate complex formation. The formation of enzyme–substrate complex can be explained by either "lock-and-key-fit" or "induced-fit" mechanisms *(80,84,85)*. In both types of mechanisms, some form of geometric similarity between the enzyme and substrate is required for the formation of an enzyme-substrate complex in order to undergo a reaction. In the case of plastic-based substrates, the lack of matching geometric similarity with the available enzymes makes it difficult to form an enzyme-substrate complex and carry out the biodegradation reaction.
3. Branched vs linear structures. Most plastic based materials have highly branched cross-linked structures. Such branched structures are not flexible enough to allow the enzymes to fit and create an enzyme–substrate complex for biodegradation reactions to take place *(86)*. This is supported by the fact that flexible aliphatic polyesters are relatively easier to biodegrade whereas the more rigid aromatics such as polyethylene terephthalate (PET) are not biodegradable *(86)*.
4. Molecular weight. High-MW synthetic polymers have been known to be more resistant to biodegradation than relatively low-MW synthetic polymers *(87)*. For example, Suzuki et al. *(88)* showed that synthetic polymers with MWs greater than 1000 were less susceptible to biodegradation than the ones with MWs less than 1000.
5. Hydrophobicity. The extremely hydrophobic property of plastic-based materials has also been attributed to make them nonbiodegradable. Enzymes and microorganisms often require complex pathways to carry out several stages of metabolism in order to mineralize such hydrophobic materials *(26)*.
6. Cellular structure. As mentioned previously, foams consist of both open- and closed-cell structures. Open-cell foams have high specific surface area; therefore, there is a relatively better contact between microorganisms and foams. This may favor biodegradation. However, closed cell foams have their inner surfaces unexposed to the microbes or enzymes. Such foams may not be favorable for biodegradation.
7. Mass transfer. Open-cell structures are less resistant to mass transfer limitations. However, depending on the size of the foam subjected to biodegradation, the deeper parts of the foams may still be unexposed to air, enzymes, and microbial population. Therefore, size of foam pieces subjected to biodegradation is also a very important factor.

Table 5
North American Biodegradable Polymer Market *(90)*

| Type of biodegradable polymer | 2000 (million kg) | 2005 (million kg) |
|---|---|---|
| Loose-filled packaging | 9.1 | 11.4 |
| Compost bags | 2.3 | 3.6 |
| Other (including agricultural films, hygiene-related products, paper coatings etc.) | <0.5 | 1+ |
| Total | 11.4+ | 16+ |

8. Biofilm/biomat formation. Biofilm and fungal mats have been shown to form in foams during biodegradation experiments. In such a case, there will be severe mass transfer limitations caused by the biofilm/biomat layer around the foam. Therefore, formation of biofilm/biomat is also an influential factor in foam biodegradation.
9. Size of waste foam pieces. Waste foams come in variety of size and shapes. They must be reduced in size before subjecting them to biodegradation in order to avoid mass transfer limitations. However, such size reduction operations can be energy-intensive; therefore, it should be considered in biodegradation experiments.
10. Weight measurement. One of the popular ways of tracking the rate of biodegradation is by using a weight measurement method before and after the samples are subjected to biodegradation. In the case of foams, it has been reported that foam pieces subjected to biodegradation may not show significant weight loss *(89)*. This was attributed to the aggregation of microbial cells in the inner and outer parts of the foam material. Therefore, in order to track the biodegradation occurring in foam structure, only weight measurement method may not be sufficient.

## Plastic Foam Biodegradation Potential

The demand for biodegradable synthetic polymers in North America shows an increasing trend as depicted in Table 5 *(90)*. The biodegradable polymer field has grown in recent years, with steady increase in the number of industries involved in the manufacturing of such products *(18)*. This shows that biodegradable synthetic materials are gaining popularity and the market potential of such materials is increasing.

Because several types of synthetic foams are biodegradable, the technology of biodegradation can be used to tackle solid waste management problem. Moreover, biodegradation of synthetic polymers can produce valuable byproducts *(11)* that can have high market values. Such valuable products can be marketed for income generation. Similarly, biodegradation can be carried out under relatively milder conditions of temperature, pH and pressure, which are less energy intensive to operate. Therefore, biodegradation of plastic foams can be used in resource recovery, income generation, mitigation of adverse environmental impacts from conventional plastic foam waste management techniques.

## Conclusions

Different types of plastic foams are used in huge amounts in every part of the world, and their use is increasing incessantly. Plastic foams often end up as solid wastes in landfills and incinerators, which cause significant environmental concern. Biodegradation of such plastic based materials may provide some proactive and energy efficient solution. Resource recovery through the utilization of degradation byproducts can also be achieved. However, there are many factors that make it difficult to biodegrade plastic and plastic foams. Much research is underway to find out efficient biodegradation mechanisms. Several biodegradation mechanisms have been understood and applied to biodegrade polymeric foams with some degree of success. Therefore, there is a huge potential for conducting research and large-scale biodegradation studies in this field to make valuable contribution in solving environmental and resource depletion problems of the world.

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