R&D Status of Biodegradable Polymers in Korea

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SUMMARY: Several companies have developed inherently biodegradable plastics based on starch and foam for loose-fill packaging material was the representing case. It is water soluble, but the change of the resilience and volume is less than several % when it is laid open at 32 °C, RH 70%. Starch-based polyvinylalcohol, aliphatic polyester, polycaprolactone biodegradable polymers were developed also. The PET fiber manufacturing companies have developed aliphatic polyester biodegradable plastics based on diol (butanediol, ethylene glycol) and diacid (succinic acid, adipic acid). The polymers have shown good mechanical properties and processibilities. They have succeeded to apply for injection, films, sheets, extrusion coatings, filaments, non-woven products, foams, and blow molding and lead this area in Korea. Polyhydroxybutyrate(PHB) and its copolymer were the first biodegradable polymer introduced in Korea. The gene cloning and recombinant technology was succeeded to produce PHB and PHB/V by E-coli and to yield the higher productivity than before. Lactic acid production and direct condensation polymerization of lactic acid is also being developed.

1. Research activities on inherently biodegradable plastics

It is true that public concerns for the environment are greatly increased, especially, for waste treatment in a small dense country. The government has introduced several policies to reduce and recycle the wastes. The volume based collection fee (VCF) system is the most representative case[1]. The system was accepted by the people without a strong opposition. Other policies to decrease the municipal solid waste (MSW) including plastics are active and are expected to be expanded in the future. In Korea there is a deposit system for drink containers and bottles etc, and a product charge system for plastics etc. Biodegradable plastics are needed also in Korea to help to decrease the waste problem.

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In the last few years several completely biodegradable plastics have been introduced into the market[2], however they have difficulties in penetrating the real market due to the high prices. The government is hesitating to recommend them eg. for trash bags for the VCF system. Furthermore, the waste treatment in Korea is still mainly by landfill which is planned to be replaced by incineration in a long period. People are just starting to recognize composting and the government is beginning to invest in composting facilities. Setting up a composting infrastructure would not justify expensive biodegradable plastics such as trash bags. Very recently there has been a severe restriction by the landfill operators of the Seoul metropolitan area on accepting wet food waste[1]. The separate collection of food wastes followed by composting would be the ideal way to solve the problem. In the case, the use of biodegradable trash bags can be driven under better circumstances.

Starch-based and aliphatic polyester biodegradable plastics were developed also in Korea few years ago. The technology for and the characteristics of such plastics are very similar to those commercialized in U.S.A, Japan, and Europe[2]. Their prices are very high ; 5～8 times of commodity plastics as in other countries. Furthermore, peoples seem not to understand the difference between the biodegradable and bio-disintegrable plastics to overcome the extra premium for the biodegradable plastics. There is a strong consensus among the scientists and organizations, but we don't have yet any regulations to prevent overclaiming bio-disintegrable plastics (especially starch-filled plastics) as truly biodegradable. The R&D of biodegradable plastics in Korea is being carried by few starch companies, petrochemical and especially fiber manufacturing industries. They know that this area is very active in Japan to have a big potential market in the future. In Korea Japan seems to be the model for the Korean industries in many cases.

Since 1992 Biodegradable Plastics is the one of the national project on which research organizations and industries have worked together. It is belonging to the Advanced Materials Programme sponsored by Ministry of Science and Technology. For the 1st period of 1992-1994 there were running 5 projects:

1. Sarch foam by Sunhill Glucose Co. (now Samyang Genex)/Hanyang Univ.,
2. Polylactic acid by Sunkyong Ind., Yukong Ltd., Samyang Co., Kolon Ind., Cheil Synthetics Inc./Korea Institute of Science and Technology (KIST).
3. Polyhydroxybutyrate by Sunhill Glucose Co./Genetic Engineering Research Institute (now Korea Research Institute of Bioscience and Biotechnology),
4. Lactic acid by Hankuk Yakult/Korea Advanced Institute of Science and Technology,
5. Biodegradability test by the above companies/KIST.

The programme leader was Dr. Young Ha KIM, KIST and the total budget was about 1.5 million US$ for 3 years. Under this projects several successful products resulted, among which biodegradable starch foam was the representing case. However, in the 2nd period from 1995 this programme is dispersed so that the projects are being carried individually in the companies or in the programme. At present the project on polylactic acid by Samyang Co. and Kolon Industries/KIST is running in the programme. The reason is that the actual business of biodegradable polymers is not developing as fast as expected by the industries.

2. Starch-based biodegradable plastics

For years after the introduction of starch-filled plastics several companies have developed inherently biodegradable plastics based on starch and a few products have been marketed. In Korea starch is manufactured mainly from corn imported from the United States and China. Samyang Genex Co. and Sewon Co. are the main producers. They have tried to develop new high value products from corn starch for many years.

Samyang Genex Co. developed a starch-based biodegradable foam product for loose-fill packagings on Feb., 1995[3]. It is now on the market but the sale volume is not growing as fast as expected. In Korea the total market for expandable polystyrene is very large to be over 120 million US$. But the loose-fill packaging is quite new and the market is very small. Very recently the Korea Research Institute of Chemical Technology announced also the development of starch-based packaging materials[4]. These starch foams are known to be quickly biodegradable but not resistant to moisture.

The technology for starch/polyvinylalcohol or starch/aliphatic polyester of eg. Novon, U.S.A. or Novamont, Italy is well introduced in Korea. Kolon Industries had a connection with Novamont to sell the product MATER-BI in Korea on 1994 but they have not been active in marketing. Cheil Synthetics Inc. commercialized starch-based plastics for injection to bring into the market together with aliphatic polyester on 1993[5]. Yukong Ltd joined into this area by starch/polycaprolactone composites on 1996[6]. However, the whole R&D activities on starch-based plastics can be estimated less than those on aliphatic polyester in Korea.

Samyang Genex Co. (former Sunhill Glucose Co.):

As a main producer of starch and glucose, they have been investing the most R&D activity in biodegradable plastics in Korea. Following the development of starch-filled plastics on 1992, they introduced starch-based biodegradable foam for loose-fill packaging material on Feb., 1995[3]. That was succeeded by a cooperation with Hanyang Univ. The material is based on corn starch containing some water soluble polymer and plasticizer. It is prepared by extrusion foaming. The trade name is BIOFIL®. It's property and absorbance claimed in the catalog was shown on the table 1. The resilience and compression creep is rather better than those of the expanded polystyrene loose-fill. It is water soluble, but the change of the resilience and volume is less than several % when it is laid open at 32 °C, RH 70%. They are actively marketing to replace the expanded polystyrene foam loose-fills. However, the annual sale for 1996 is less than 120,000 US$, so less than expected. As mentioned above, the loose-fill material market is just new and in the initial stage in Korea. The price of the product is about 50 US ¢ /kg similar to the expanded polystyrene. Several companies producing measuring equipments and electronic appliances are using the product.

lljin Industries/Korea Research Institute of Chemical Technology (KRICT):

It was announced on Nov., 1996 that KRICT/Iljin Industries successfully developed starch-based packaging foam material[4]. They explained that it contains over 90% of corn starch and some polyvinylalcohol and plasticizer and is processed by extrusion foaming. Although the detailed data is not published, it looks similar to the product of Samyang Genex Co..

Table 1. Physical properties of starch-based foam loose-fill, BIOFIL®

bulk density	:	0.009 g/cm^3		
resilience[1]	:	83.3% (cf. PS foam 82.8%)		
compression creep		under	3 days	7 days
on time[2]:		load		
		1.3%	8.5%	8.7%
(cf. PS foam		6.0%	11.0%	12.5%)
water absorbance	:	at 13°C, 66%RH	at 25°C, 80%RH	at 40°C, 95%RH
for 24 hrs		1.0%	6.6%	8.4%

1. estimated from the ratio of forces/area when a rod (D 0.5cm) is pressed into the sample to the half length and re-pressed after 1 min.
2. measured under 20kg load onto sheets of about 10cm thickness.

Cheil Synthetics Inc. (former Cheil Synthetic Textiles Co.):

This is the one of the main polyethyleneterephthalate(PET) synthetic fibre companies. They were belonging to Samsung Group but separated from it 3 years ago. They commercialized starch-based biodegradable plastics together with aliphatic polyester in Nov., 1993[5]. Since that, they filed over 20 patents. This material is announced to contain 40~60% starch to have 4 grades for injection and extrusion. The products are named as ESLON GREEN®. Their properties claimed on the catalog are shown in the next table 2. They are trying to get some actual market but it is not yet successful due to the high prices. Their capacity is difficult to be estimated as they would use their existing pilot reactors in the company.

Yukong Ltd.:

As the one of main petrochemical industry in Korea, they have continous activity in this area. On April, 1996 they announced the development of a new type of starch-based biodegradable thermoplastic. The plastic is known to be composed of starch and polycaprolactone[6]. It is claimed to have both proper strength and processiblility and

biodegradability. The trade name is GREENPOL®. They are planning to produce 1,000t/y at the price of about 4 US$/kg. They are aiming especially films and trash bags. The detailed physical properties are yet unknown except some data of films (Table 3).

Table 2. Physical properties of starch-based thermoplastic ESLON GREEN®

grades / properties	method	SI2010	SI2020	SF1010	SS3010
*melt index, (g/min)	ASTM D1238	-	-	3-5	-
tensile strength (kg/cm^2)	ASTM D638	570	602	220	244
elongation at break (%)	"	3	3	420	43
flexual strength (kg/cm^2)	ASTM D790	560	877	210	252
Izod impact strength(kg· cm/cm)	ASTM D256	3	8	10	3

* melt index was measured at 150 °C under 2.16kg.

Table 3. Properties of starch-based polymer film, GREENPOL®

property	density	melt index	starch content	max. tensile stress		Elongation At break		tear strength	
				MD	TD	MD	TD	MD	TD
ASTM	D1505	D1238	-	D882		D882		D1004	
unit	g/cm^3	g/10min	wt%	kg/cm^2		%		kg/cm	
value	1.2	2.0	40	280	200	500	350	140	135

3. Aliphatic polyesters based on diol and diacid

In Korea we have large facilities for PET fiber manufacturing by several companies. The aliphatic polyesters are not new for them as some companies have already related products such as hot melt adhesives etc. There are also several companies which produce aliphatic polyester polyols, mainly low molecular weight polyethyleneadipate, for polyurethane industry. After the product of Showa Highpolymer, Japan (BIONOLLE®) was publicized, a couple of companies in Korea have worked on the aliphatic polyester. Sunkyong Industries[7] and Cheil Synthetics Inc.[5] have developed their own aliphatic polyester biodegradable plastics. They are also based on diol (butanediol, ethylene glycol) and diacid (succinic acid, adipic acid), which is very similar to BIONOLLE®. They have surely tried to find their own unique polymerization technology to avoid the possible patents conflictions with Showa Highpolymer or each other. The both company are trying to penetrate into the market, but it is not yet successful due to the high prices of about 6 US$/kg. They have pilot plants using their exsisting reactors. They have shown samples of injected, extruded, and blow molded products.

In Korea butanediol is produced by Shinwha Petrochemical Co., enough for the domestic demand. Ethylene glycol is produced in mass actually for PET, but not enough to import from abroad. Adipic acid is also manufactured domestically by Hanbul Chemical Industries. We don't have a big producer of succinic acid, but maleic anhydride is manufactured by Dainong Petrochemical Ind. and Shinwha Petrochemical Co.. So the supply of raw materials seems not to be the problem for diol/diacid polyester in Korea except succinic acid which is to be derived from maleic anhydride.

Sunkyong Industries:

This is the one of the major PET fiber manufacturer belonging to Sunkyong group. They are also largely investing R&D in new drugs and other fine chemicals. In June, 1993 they developed aliphatic polyesters to bring the product to the market[7]. It is based on butanediol, ethylene glycol and succinic acid, adipic acid. So, the raw materials are almost same as the product of Showa Highpolymer, Japan (BIONOLLE®), but the

polymerization technology seems to be different to register their own patents in Korea and in the United States[12]. They have 4 grades for injection, film, and extrusion. The polymers have shown good mechanical properties and processibilities. They have succeeded to apply for injection, films, sheets, extrusion coatings, filaments, non-woven products, foams, and blow molding and lead this area in Korea. They have also shown that the polymer is practically degraded on time under the soil or in the lake water. The trade name is SKYGREEN®. Their properties claimed in the catalog is shown on the table 4. They have a capacity of about 2,000t/y. They are trying to penetrate into the market, however the actual sale is less than 5 tons per year due to the high price of about 6 US$/kg. Only some buyers are using it for the advertisement items and for blendings with other plastics.

Table 4. Properties of aliphatic polyester, SKYGREEN®

Property	Method	Unit	SG1111	SG1109	SG2109	SG2108
Specific Gravity	ASTM D792	-	1.22	1.17	1.22	1.21
Melting Temperature	DSC	°C	118	93	90	80
Softening Point	ASTM D1525	°C	106	82	79	70
Melt Index 120°C 190°C	ASTM D1238 (2160g)	g/10min	 2 40	 3 40	 1 45	 2 55
Tensile strength Elongation	ASTM M638	Kg/cm^2 %	360 -	370 400	410 380	350 350
Flexural Modulus	ASTM D790	Kg/cm^2	5,400	3,400	3,300	2,200
Izod Impac Strength	ASTM D256	Kgcm/cm	6	20	25	45

Table 5. Claimed applications of SKYGREEN®

Extrusion	Film	Shopping bag, Trash bag, Retail plastic bag, Packaging film, Mulching film, Paper lamination
	Coating	Prepaid card, Paper coating
	Sheet	Tray, Packaging (Thermoforming)
Injection Molding		Stationery, Brush, Disposable spoon, Knife, Razor
Blow Molding		Shampoo bottle, Detergent bottle, Cosmetic bottle
Foam		Food tray, Packaging
Filament		Nonwoven disposables, Fishing gear (net, line)

Cheil Synthetics Inc.:

This is also the major PET fiber company. They introduced their own aliphatic polyester in Nov., 1993, following Sunkyong Industries[5]. When the company belonged to Samsung group 3 years ago, it was responsible for the development of biodegradable packaging material from the master plan of the group. They offer 3 grades for injection, films and sheets. The properties claimed in the catalog is on the Table 6. Their properties and prices are similar to Sunkyong's products. They have the same difficulties in the marketing due to price.

4. Microbial polyester

Polyhydroxybutyrate(PHB) and its copolymer were the first biodegradable polymer introduced in Korea. Early on 1990 Kohap Ltd. announced the development of PHB[8]. They explained later that they worked in a pilot plant to produce PHB and polyhydroxyalkanoate(PHA) on 1991[9]. Since that there is no more activity known. The company and PHB/PHA made a big contribution in Korea to publicize biodegradable plastics to the people, although PHB/PHA are known to be most expensive among them and therefore not so easy to be commercialized.

Table 6. Properties of aliphatic polyester, ESLON GREEN®

Property	Method	Unit	AF1010	AI2010	AS3010
Specific Gravity	ASTM D1505	-	1.24	1.26	1.25
Melting Temperature	DSC	°C	93-95	114-116	102-105
Melt Index 190°C	ASTM D1238 (2160g)	g/10min	3-5	25-30	1-3
Tensile strength Elongation	ASTM D638	Kg/cm^2 %	320 380	350 250	330 240
Flexural Strength	ASTM D790	Kg/cm^2	190	230	210
Izod Impact Strength	ASTM D256	Kgcm/cm	57	5	20
Hardness	ASTM D2240	D scale	57	64	61
Heat of Combustion	DSC	Cal/g	5,850	5,610	5,890

In addition to Kohap Ltd. the R&D on PHB or its copolymer PHB/V (containing valerate) and PHA is carried out by other research organizations and companies. It was a topic in the Biodegradable Plastics Programme for 1992-1994 carried by Korea Research Institute of Bioscience and Biotechnology (KRIBB)/Samyang Genex Co. and still in the Bioengineering Programme since 1995 working by Korea Advanced Institute of Science and Technology (KAIST) /LG Chem Co.. The gene cloning and recombinant technology was succeeded to produce PHB and PHB/V by E-coli and to yield the higher productivity than before. Polymer scientists may be not so optimistic due to the high price of PHB/V to compete with other biodegradable plastics, but bioengineers seem to be fascinated with the fact that they can make plastics by bioengineering. A

breakthrough by new bioengineering technology can change the entire situation in the future[20]. In one research institute of Korea, PHB production from trees is being investigated[13].

Kohap Ltd:

Kohap Ltd. is belonging to Kohap group who has a series of downstream for para xylene, terephthalic acid, and PET fiber factories. They announced the development of polyhydroxybutyrate(PHB) on 1990[8]. They explained later that they worked with a new bacteria (?) to develop PHB copolymers on a pilot plant scale[9]. On 1991 they claimed that they filed patents to produce polyhydroxyalkanoates(PHA) to improve the property of PHB and sametime to avoid possible patent conflictions with ICI, U.K.. They explained further that cheap raw material such as sugar corn residues and fish oils were used for the process to reduce the cost[10]. Since that there is no more activity open. Their polyester might be PHA composed of higher alkyl derivatives prepared by a fermentation using *Alkaligenes eutrophus*. They might be hesitating to invest further R&D because of the high cost after operating a pilot plant. But the company made a big contribution to publicize biodegradable plastics to the people.

Samyang Genex/Korea Research Institute of Bioscience and Biotechnology (KRIBB):

PHB and its copolymer polyhydroxybutyratevalerate (PHB/V) was the one major project in the Biodegradable Plastics National Project during 1992-1994. The project was carried out by KRIBB together with Samyang Genex Co.. They succeeded in developing a lab scale process to produce PHB and PHB/V by *Alcaligenes eutrophus* and to purify them. The coworker isolated genes for PHB biosynthesis and applied for recombinant DNA to produce PHB. The official project has stopped since 1995, but the R&D may still be continued in the company.

LG Chem Co./Korea Advanced Institute of Science and Technology (KAIST):

The other team led by Prof. Ho Nam Chang in Korea Advanced Institute of Science and Technology (KAIST) has been also very active in this area. The team belongs to the Chemical Eng. Dept. and Bioprocess Engineering Research Center, one of the engineering research center supported by the government. Several recombinant

Escherichia coli strains harboring the *Alcaligenes eutrophus* PHA biosynthesis genes were constructed by Prof. Sang Yup Lee of KAIST, and were used to produce PHB in high concentration[21]. Fed-batch culture techniques were developed for the production of PHB with high productivity and high polymer content[21,23]. A new method of producing the copolymer PHB/V by recombinant *E. coli* was also developed[23]. Prof. Lee carried out detailed economic analysis of the processes for the production of PHB, and suggested that the price of PHB can be lowered to US$ 4-5 using current technology[22]. Several other microorganisms are also under investigation for more economical production of PHAs and for the production of novel PHAs including medium-chain-length PHAs (for biodegradable rubber). They claimed that the manufacturing cost can be cut down to 4 US$/kg by using such a bioengineering technology and cheaper raw materials[21]. The project was once supported by Cheil Synthetics Inc. but now by LG Chem Co. in an another category of the national Bioengineering Programme.

5. Poly(lactic acid)

It is well known that polylactide was originally applied for biomedical use together with polyglycolide but it turned out to be a good candidate for environmentally degradable plastics. Polylactide is usually prepared by ring- opening polymerization of lactide which is a cyclic dimeric lactone of lactic acid[15]. Polylactic acid (or polylactide) has been the main subject in the Biodegradable Plastics National Project since 1992. The R&D is being proceeded mainly by Korea Institute of Science and Technology (KIST). Recently a direct condensation polymerization of lactic acid is being developed by Mitsui Toatsu Co., Japan[16]. While polylactide or poly(lactic acid) is very actively commercialized by American or Japanese companies, in Korea they are still in the research stage.

Korea Institute of Science and Technology (KIST)/Samyang Co., Kolon Industries:

KIST has worked on polyglycolide and polylactide for bioabsorbable medical application since years. They have developed polyglycolide suture together with Samyang Co. and almost finished the commercialization. Samyang Co. is sending the

suture samples to the market[17]. KIST has investigated the ring- opening polymerization of lactide in the presence of pentaerythritol to design a star-shaped structure[18]. They are also working now on the direct condensation polymerization of lactic acid[19]. The programme is being sponsored by Samyang Co. and Kolon Industries.

Lactic acid production was also a subject in the Biodegradable Plastics Programme, which is carried by KAIST/Hankuk Yakult Co.. They have worked on the fermentation and purification of lactic acid to yield successful results. They are continuing the research in the newly formulated Bioengineering Programme since 1995. Several other companies are also interested in lactic acid to have R&D inside the companies.

6. Others

For several years the research on biodegradable plastics is greatly increasing in universities and institutes. The number of papers in this area at the academic society meeting is also increasing.

A biodegradable biopolymer used for the water treatment was successfully developed by KIST and Samyang Special Chemical Industries[14]. The biopolymer, zooglan, was isolated from a bacteria, zoogloearamigera, living in activated sludge tanks. It has a function as a flocculent to replace various water treatment chemicals. It has shown a very satisfactory result at a pilot test for the leather industry waste water.

Chitosan and chitin are also being investigated at several universities. There is one small factory producing chitosan in Korea. The application of chitosan for plastics is primitive, but LG Chem Co. commercialized a healthy beverage drink containing chitosan.

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