Transactions of the Materials Research Society of Japan 29[5] 2133-2135 (2004)

Heavy Metal Free Polyester

Yasuhiko Saito, Ryoji Tsukamoto* and Kimihiko Sato**
Teijin Fibers Limited,
77 Kitayoshida-cho, Matsuyama, Ehime, 791-8530 Japan
Fax: 81-89-972-1815, e-mail: ya.saitou@teijin.co.jp
*Teijin Fibers Limited,
77 Kitayoshida-cho, Matsuyama, Ehime, 791-8530 Japan
Fax: 81-89-972-1815, e-mail: r.tsukamoto@teijin.co.jp
**Teijin Fibers Limited,
2345 Nishihabu-cho, Matsuyama, Ehime, 791-8536 Japan
Fax: 81-89-972-5038, e-mail: ki.satou@teijin.co.jp

Teijin group, one of the leading polyester manufacturing companies, aims at realization of a recycling-based society through developing and marketing new technologies and products that can more positively contribute to the environment. One of the essential technologies to achieve the target is heavy metal free polyester. Antimony, the most common catalyst for polyester production, has been restricted in some regulations. For example, antimony migration from polyester fabrics is specified in Oeko-tex standard. In this paper, we introduce a new polyester containing only titanium metal as catalyst without any other regulated metal. Conventional titanium compounds are very active as polymerization catalyst and give the products yellowish color because their decomposition activity are too high. Today, Teijin has succeeded in developing new types of titanium catalyst with a quite different chemical structure. Polyester, produced by using the new catalysts, has no disadvantages and some preferable characteristics compared with the conventional polyester containing antimony.
Teijin intends to supply more environmentally friendly polyester through the new catalyst technology.
Key words: heavy metal, polyester, catalyst, titanium, polymerization

1. INTRODUCTION

With the arrival of the new century, ever-greater attention is concentrated on the global environment. It is said the cumulative impact of the social and economic activities on the environment during the past millennia has exceeded our planet's capacity to maintain its ecological cycle. However, the present social structure still depends on mass production, mass consumption and mass disposal. The reform of this structure is desired.

Teijin Fibers Limited started the development of environmentally-benign technologies based on its own polyester polymerization technology over years ago. One of them is development of the recycling technology of the polyester products.

In 2002, Teijin Fibers Limited started the highly advanced chemical recycling plant, which can recover every kind of waste polyester products to dimethyl terephthalate(DMT) and ethylene glycol(EG). Recently, Teijin Fibers has developed the industrial hydrolysis technology to convert the recovered DMT to highly pure terephthalic acid(TPA).

The other is the development of easy-to-recycle products. We have been developing the polyester that contains the titanium catalyst since 1970s [2]. Some grades have already been commercialized as antimony free polyester (Table I). This time, Though a further research of antimony free polyester we have succeeded in development of the polyester which does not contain heavy metals and has no disadvantages as compared with the antimony-containing polyester. This new polyester can be manufactured according to a newly developed titanium catalyst.

Table I Teijin's heavy metal free polyester

	Year	Progress	Use
Sb Free			
Mn-Ti-P-(Co)	1974	Commercialized	Fiber, Sheet
Heavy Metal Free			
Ti-P for DE and EI	1998	Marketing	Fiber
(No Bluing Metal)	-2003		Bottle, Sheet

2. INFORMATION FOR POLYESTER

2.1 Easy-to-recycle products

The concept Teijin Fibers Limited aimed at in the process of development of easy-to-recycle products was the products of all-polyester materials. Polyester is widely used in fiber, bottle and film use because it is excellent in heat resistance, chemical resistance and dimensional stability as compared with other plastic products. From the environmental viewpoints, polyester has a great advantage because it generates only water and carbon dioxide as combustion gas while other plastics such as polyamide(nylon), polyurethane, polyvinyl chloride, etc. generate harmful gas including nitrogen oxide, hydrogen chloride, etc. as well as water and carbon dioxide. In addition, heat of combustion of polyester is relatively low compared with other plastics.

Table II Characteristic comparison of various plastics

	Thermal Stability	Heat of Combustion	Combustion Gas	Catalyst & Additives	Chemical Recycling
Polyester	**High**	**21.7kJ/g**	**H_2O, CO_2**	**Catalytic Metals (ex. Antimony)**	**Easy**
Polyamide(Nylon 6,6)	High	31.0kJ/g	H_2O, CO_2, NO_x	Organic Polymerization Controller	Difficult
Polyacrylonitrile	High	-	H_2O, CO_2, NO_x	Organic Polymerization Initiator	Impossible
Polyurethane	Low	18.6kJ/g	H_2O, CO_2, NO_x	Organic tin, Amine	Difficult
Polyvinylchloride	Middle	18.1kJ/g	H_2O, CO_2, Dioxine, HCl	Organic Polymerization Initiator Plasticizer(Phthalate)	Impossible
Polyethylene	Low	46.1kJ/g	H_2O, CO_2, Trace Dioxine	$TiCl_4$, Organic Al & Cr	Impossible
Polypropylene	Low	44.1kJ/g	H_2O, CO_2, Trace Dioxine	$TiCl_4$, Organic Al & Cr	Impossible
Polystyrene	High	40.3kJ/g	H_2O, CO_2	Organic Polymerization Initiator	Developed

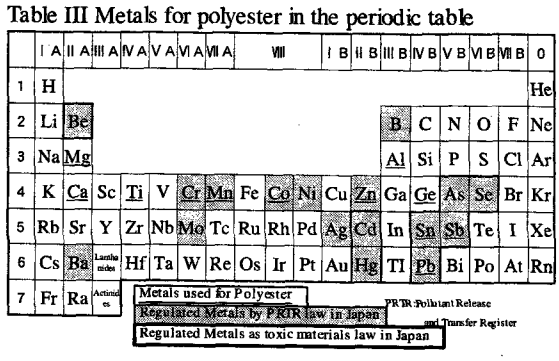
Regarding recycle process, polyester can be comparatively easily decomposed into dimethyl terephthalate(DMT) and ethylene glycol(EG) by methyl esterification after glycolysis. Teijin Fibers Limited has also succeeded in the development of the technology for converting recycled DMT into the highly pure terephthalic acid(TPA). Thus, qualified polyester can be manufactured using either DMT or TPA obtained from chemical recycling process. This recycled polyester manufacturing requires only the general polyester polymerization equipment without any special modification. Therefore, polyester is considered the best "green" plastic and the complete recycling of polyester product is quite promising (Table II).

2.2 Metals for polyester

Two methods are generally known as the manufacturing polyester process. One is the transesterification method, in which DMT is used as the raw material, and the other is the direct esterification method in which TPA is used. In both process, antimony or germanium is usually used as the polymerization catalyst. Manganese, calcium, magnesium, etc. are used as ester interchange catalyst in transesterification reaction.

Recently, potential harmful metals such as beryllium, arsenic, selenium, antimony, cadmium, mercury, etc. are strictly regulated by some of laws and standards in Japan (Table III).

Table III Metals for polyester in the periodic table



Regarding antimony, it is regulated in some countries in the world. In EU, Eco-Label sets a limit to antimony content in polyester less than 260 ppm, and Oeko Tex Standard determines the migration from fibers and textures less than30 ppm. In Japan, Water Pollution Control Law sets antimony the controlled element. Such standards are likely to be reinforced in the future (Table IV).

Table IV Regulations for Antimony

Items	Regulation/Standard	Value
Content in Polyester	BgVV Regulation	350ppm
	EU Eco-Label	260ppm
Migration from Polyester	EU Directive 90/128/ECC 6th Amendment	20ppb(from Food Packaging)
	Oeko Tex Standard	30ppm(Fibers & Textures)
Water Pollution (City Water)	WHO Recommendation	5ppb
	EPA Recommendation	6ppb
	Water Pollution Control Law (Japan)	Under Observation
	IAOIA's Opinion	Regulation should be reviewed
Occupational Standard	ACGIH	0.5mg/m³
	Japan Society for Occupational Health	0.1mg/m³

BgVV : Federal Institute for Health Protection of Consumers and Veterinary Medicine (Germany)
IAOIA : International Antimony Oxide Industry Association
ACGIH : American Conference of Governmental Industrial Hygienists

2.3 Change antimony to new metals

As described above, antimony and germanium are generally used for polyester polymerization. Although calcium, aluminum, manganese, zinc, etc. are used as polymerization catalyst of polyester, they do not have enough catalytic activity. Whereas in the case of germanium, the activity is enough and almost no problems are found in respect of environment, it has a problem that the cost is very high.

On the contrary, titanium catalyst has enough activity, and is less influence to environment, and is obtained with very low cost (Fig. 1). Therefore, titanium is very suitable as a polymerization catalyst.

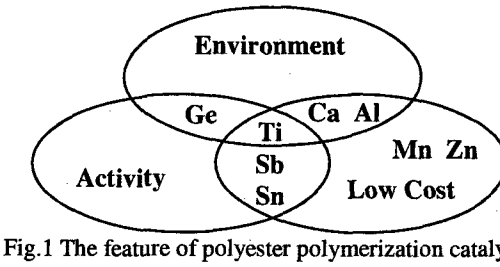


Fig.1 The feature of polyester polymerization catalysts

3. HEAVY METAL FREE POLYESTER TECHNOLOGY

3.1 Teijin's catalysts for polyester

Since the regulations for the heavy metals are likely to be reinforced, some polyester manufacturers have started the development of polyester that does not contain antimony lately [3][4][5]. Teijin has already been developing titanium catalysts since 1970s. Recently, Teijin has succeeded in development of a new type titanium catalyst.

Teijin has traditionally used manganese, magnesium, calcium, and antimony as catalysts when it takes the transesterification method. In the direct polymerization method, antimony and germanium have been used as catalyst. In both methods, cobalt has been used as bluing metal if required.

Though the conventional titanium catalysts have high catalytic activity, polyester which is produced by using such titanium catalysts show yellowish color. On the contrary, because the new titanium catalyst Teijin has developed has been modified to control the activity properly by balancing the catalyst and new phosphorus stabilizers, it can be applied to fibers, films, and bottles (Fig. 2). The new antimony free polyester will show clear and vivid color when processed to textiles.

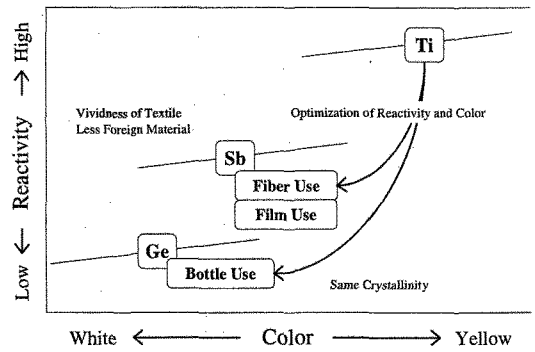


Fig.2 Activity of new catalyst

3.2 Activity of new catalyst

The strong point of a titanium catalyst has been explained so far. However, while the conventional titanium catalyst had high polymerization reactivity, the color of the polymer obtained was yellowish. The titanium catalyst developed this time modified the conventional titanium catalyst. And polymerization activity is controlled. Consequently, the polyester obtained can be used as fibers, films, and bottles. For example, the textile manufactured from this polyester indicates vivid color.

3.2 Specialty of heavy metal free polyester

The heavy metal free polyester has the various features compared to conventional ones. For example, in fibers manufacturing process, the spinneret wiping cycle for the polyester using the antimony catalyst is 6 days (1.1dtex) and 5 days (0.6dtex). While the spinneret wiping cycle for the polyester manufactured using this new titanium catalyst is 11 days (1.1dtex) and 8 days (0.6dtex), respectively, which means that the wiping cycle is improved by about 1.5 to 2 times (at 295 degrees C). Figure 3 shows that the amount of foreign materials deposited on the cap surface can also be reduced greatly (Fig.3).

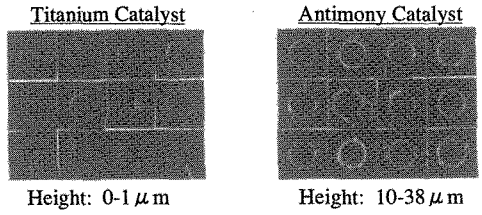


Fig.3 Spinneret Surface

A pre-form of a PET bottle using this titanium catalyst has no disadvantages as compared with that manufactured using the germanium catalyst (Table V).

Table V Resin / preform quality for PET bottle

Catalyst	Germanium	Conventional Titanium	Antimony with Cobalt, IA[1]	Teijin's Titanium
Polymer Color L/b	88/0.0	86/7.7	80/-2.3	**86/0.5**
Crystallization Speed	Std	Same	Same	**Same**
Oligomer[2]	Std	Same	High	**Same**
Other Molding ability	Good	Good	Good	**Good**
Acetaldehyde (ppm)[2]	6.0	11.5	9.0	**6.0**
Cost	Very high	Low	Low	**Low**

1) IA: Isophthalic acid 2) Bottle preform

The surface smoothness of heavy metal free polyester is quite excellent in biaxial oriented film compared to that using antimony catalyst (Fig. 4).

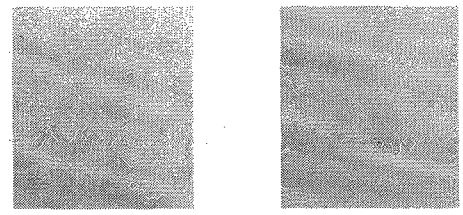


Fig.4 Biaxial oriented film surface

4. CONCLUSION

As is explained so far, polyester is the best "green" plastic and heavy metal free polyester is better for environment. New titanium catalysts will be applied for fiber without any other metal. Heavy metal free polyester fiber has no disadvantages compared with conventional polyester. In fiber manufacturing process, process stability is improved and it is expected that the productivity of fibers make a great improvement. Heavy metal free polyester bottle has no disadvantages compared with conventional polyester. And the cost is also low. The film manufactured from heavy metal free polyester is excellent in surface flatness. The film will be preferably used for the recording media etc.

Teijin intends to supply the ultimate environmentally-friendly polyester by using new catalysts and chemically recycled raw materials.

References

[1] THE TEIJIN GROUP REPORT ON THE ENVIRONMENT, SAFETY AND HEALTH, 2002

[2] Patent JP1985-21172 A2 etc.

[3] F. Kubota, *Japan Textile News*, No.568, 66-68 (2002)

[4] B. Otto and U. Berger, *Chem. Fibers Int.*, **51**, 188-189 (2001)

[5] U. Seidel and T Eckert, *Chem. Fibers Int.*, **49**, 27-29 (1999)

(Received October 10, 2003; Accepted October 31, 2003)