

Chapter 4

History of Polyester Resin Development for Synthetic Fibers and Its Forefront

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Abstract Polyethylene terephthalate (PET) was invented about 50 years ago, and now it is widely used for synthetic fibers, films, bottles, and so on. In a half century, the polymerization process has been improved, for example, from DMT method to direct polymerization method and from batch process to continuous one. Various new polymerization catalysts also have been developed. For production of fibers, a variety of copolymerization composition has been developed to control and improve the properties, such as flame retardancy, dyeability, solubility, and shrinkage. In addition to PET, polyethylene naphthalate, polybutylene terephthalate, and polytrimethylene terephthalate are now used for various usages. Nowadays, bio-based polyesters polymerized from bio-based ethylene glycol, propylene glycol, terephthalic acid, and so on are also developed and some are already commercialized.

Keywords Polyester • Polycondensation process • Flame retardant • Polyethylene terephthalate • Bio-based polyester

4.1 Introduction [7]

Due to the good balance between performance and cost, polyester fiber has addressed rapid growth in global scale among synthetic fibers and has the largest production quantity today among different types of fibers including natural fibers.

During the dawn of synthetic fibers, the first great topic is the invention of Nylon 66 by Carothers at the US DuPont. However, the types of polyester that had been examined at the same time were mainly aliphatic polyesters. As the polyester is appropriate for synthetic fibers, later invention of the aromatic polyester introducing the terephthalic acid unit, namely, polyethylene terephthalate (PET) by Whinfield, Dickson, and so forth at British Calico Printers, had to be waited. Production of the fiber using this PET began by ICI and DuPont during the

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mid-1950s. In Japan, Teikoku Jinzo Kenshi Co., Ltd. and Toyo Rayon Co., Ltd. introduced the technology jointly in 1957, starting production in 1958.

This chapter takes the general view on the history of development and current situation of polyester resins for synthetic fibers with main focus on PET.

4.2 Methods of Synthesis [6] [8] [9]

4.2.1 DMT Method and Direct Polymerization Method

Typical manufacture methods for PET include the DMT method which uses dimethyl terephthalate (DMT) and ethylene glycol (EG) as the starting materials and the direct polymerization method (TPA method) to start from terephthalic acid (TPA) and EG, and in the beginning DMT method was adopted. DMT was popularly used because of its simple refining processes such as distillation and recrystallization compared to TPA which had no boiling point, poor solubility, and high difficulty in refining.

However, it can also be said that DMT method contains an extra process to replace the methanol added to TPA, which is added to facilitate purification, with EG and collect by transesterification during the PET production processes. Because of this, direct polymerization method became more popular and has become the mainstream today as a technique to manufacture TPA with high purity (called PTA) was developed later.

Manufacture of PET mainly comprises of the transesterification (EI reaction) to form the intermediate bis(hydroxyethyl) terephthalate (BHT or BHET) from DMT and EG or the direct esterification reaction (DE reaction) to form BHT from TPA and EG in the first part and the polycondensation reaction to form PET polymer from BHT in the second part. In addition, processes to facilitate the reactions efficiently are usually adopted in PET manufacture systems by dividing the system into a reaction tank for EI or DE reaction process and a reaction tank for polycondensation reaction.

In EI reaction, DMT and EG are heated and made into a uniform phase in a reaction tank, and the reaction is facilitated under the existence of an appropriate catalyst and atmosphere of normal pressure while removing methanol, which is a reaction by-product. Since DMT has the melting point approximately 140° C, reaction uniformity and production efficiency can be improved by melting it in a separate dissolver and supplying it into the EI reaction tank as necessary, although it can also be injected into the reaction tank as powder or flakes.

The factors that affect the EI reaction rate include the reaction temperature, the ratio of charged quantities of DMT and EG (molar ratio), and EI reaction catalysts, and catalysts are especially important as they also have great influence on the quality of the polymer that is formed in the end.

As EI catalysts, various compounds have been tested after those seen in initial patent by Whinfield and Dickson, and there have been many reports on the reaction mechanism and reaction kinetics. For example, in Japan, there was a series of examinations by Ida et al. [1] which organized the EI reaction rate by its relationship to the electronegativity of the catalyst compound.

While DE reaction is classified as an esterification reaction between carboxylic acid and alcohol which are generally well known, it is rather difficult to handle in studies on reaction kinetics as TPA has poor solubility to EG, and thus creative measures are required in industrial processes. As DE reaction is an autocatalytic reaction in which proton from the acid functions as a catalyst, reaction continues by mixing and heating TPA and EG together and removing water, which is the reaction by-product. This reaction starts in a heterogeneous system (slurry state) from the beginning until the middle of the process since TPA is poorly soluble in EG as discussed above. Therefore, how this TPA/EG slurry properties are controlled is one of the most important points in controlling the DE reaction. Examples of various creative measures in industrial processes to improve the handleability and fluidity of slurry and ES reactivity include optimization of the size and shape of TPA particles as well as mixture ratio with EG and use of BHT instead of EG.

4.2.2 Polycondensation Reaction

BHT which is formed by transesterification or esterification reaction is normally transferred to the polycondensation reaction tank, which is a separate reaction tank, to go through the polycondensation reaction under high temperatures and high vacuum to form PET.

Unlike polycondensation of polyamides, the equilibrium constant for PET polycondensation is close to 1. Therefore, how fast EG forming as a by-product in polycondensation in order to facilitate the reaction in product system is removed from the system becomes the important point in reaction process. That is, the creative measures taken include setting the reaction tank shape with shallow liquid depth and large surface area for reacting substances and promotion of driving the by-product EG out of the system by making contrivances on mixing impeller shape.

It is also necessary to set the reaction temperature to extremely high around 280° C in order to obtain sufficient polycondensation reaction rate as the melting point for the polymer formed is high. However, coloration due to thermal decomposition and so forth are also facilitated under high temperatures, indicating that control and optimization of polycondensation temperature and good design on polycondensation catalyst are important. Polycondensation catalysts will be discussed in more detail later.

4.2.3 Molecular Weight

The molecular weight of the PET manufactured through polycondensation reaction needs to be optimized depending on the purpose. Molecular weight is an important basic property which can influence the mechanical properties as well as forming processability when used as fiber.

The average molecular weight for PET used in fiber for clothes is approximately 20,000 (g/mol) with degree of polymerization approximately 100 and intrinsic viscosity about 0.62–0.65. This value of molecular weight is similar to that of biaxially oriented polyester film used for packaging or general industrial material applications.

Compared to this, PET for tire cords and seatbelts which are required to have high strengths usually has molecular weight of 30,000 (degree of polymerization 150 and intrinsic viscosity 0.80) or higher.

Furthermore, the PETs used in fiber for clothes usually have the melt viscosity of around 2000 poises (200 Pa s) at 290° C, which can be stirred, and thus PET can be manufactured with the specified molecular weight by only melt polymerization. However, PETs of higher molecular weights have extremely high viscosity, which prevents uniform stirring of melt and continuation of melt polymerization. Therefore, solid state polymerization method is used to further increase the molecular weight after melt polymerization.

4.2.4 Polymerization System

PET polymerization processes started from batch method, and continuous polymerization method became more widely used as the production quantity increased.

While the two-tank structure comprising of the reaction tank to conduct EI reaction or DE reaction process and the reaction tank to conduct polycondensation reaction is typical in general in batch polymerization, multiple reaction tanks are often adopted in continuous polymerization method, due to the necessity to vary the temperature and degree of vacuum in stages to increase the degree of polymerization in polycondensation reaction. For example, a system may adopt a five-tank system with two EI (or DE) reaction tanks and three polycondensation reaction tanks.

The continuous polymerization process is suited to mass production of only a few species or favorably one species, and cost reduction is addressed by the merits of efficiency improvement through continuous production and scale increase with large equipment. To produce multiple species of copolyesters and so forth in relatively small quantities, on the other hand, batch method is better suited.

4.2.5 *Polycondensation Catalysts*

Although the polycondensation reaction for PET is a transesterization reaction in a similar fashion to the reaction to form BHT from DMT and EG, it has a high reaction temperature compared to the EI reaction between DMT and EG. Due to the restrictions including consideration of competing reaction called thermal decomposition, metallic compounds different from EI catalysts are selected in many cases.

Antimony compound catalyst which is most generally used at present was already indicated in the initial patent by DuPont [2], indicating that they had thoroughly searched for the catalyst at the time.

As the catalyst added/contained in polymer by several tens to hundreds of ppm can affect the various properties of fiber products such as thermal stability in addition to the polymerization reactivity, catalyst design is positioned as one of the most important elemental technology in PET polymerization and has motivated various research and development activities. Here, this section mentions some of the attempts to further activate and improve the various properties of polymer by catalytic compounds other than antimony from the 1990s to 2000s to exceed the antimony compound catalyst which has been used most generally.

It has been long known that a titanium compound has catalyst activity 10–20 times that of antimony compound. However, use of it in PET polymerization had been limited because coloration of the polymer cannot be avoided as it also has high decomposition activity. To address this problem, new titanium catalysts have been developed by several domestic and international companies since the 1990s. Although many of the details in catalyst design have not been disclosed, various methods have been tried to control the catalyst activity of titanium such as a composite oxide with elements other than Ti such as Si and a titanium compound with modification using organic complexing agents based on the disclosed information.

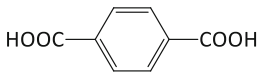
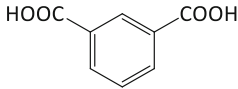
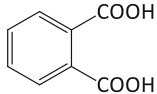
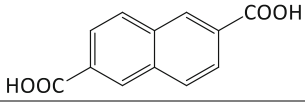
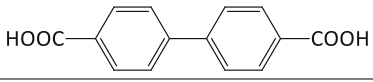
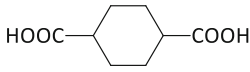
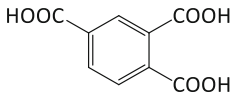
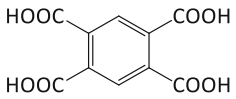
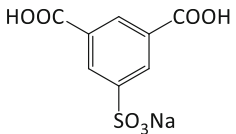
In addition, DuPont [3] and Toyobo Co., Ltd. [4] proposed attempts to use aluminum compounds, which they had thought to have little catalytic activity against polycondensation, as polycondensation catalysts. Especially the latter case is interesting in that it claims that the activity is improved by combining the aluminum compound with no catalyst activity by itself with a specific compound.

4.3 Copolymerization Polyester

4.3.1 *Copolymerization Components and Manufacture Method*

An example of copolymer components used in the production of copolyesters is shown in Tables 4.1 and 4.2. By copolymerizing these components, it is possible to make polymer design to suit the application by adding mechanical properties,

Table 4.1 Monomer adopted for copolymerization of polyester. (1) Polyvalent carboxylic acids

Terephthalic acid	
Isophthalic acid	
Orthophthalic acid	
2,6-Naphthalene dicarboxylic acid	
Paraphenylene dicarboxylic acid	
1,4-Cyclohexane dicarboxylic acid	
Succinic acid	$\text{HOOC}(\text{CH}_2)_2\text{COOH}$
Glutaric acid	$\text{HOOC}(\text{CH}_2)_3\text{COOH}$
Adipic acid	$\text{HOOC}(\text{CH}_2)_4\text{COOH}$
Suberic acid	$\text{HOOC}(\text{CH}_2)_4\text{COOH}$
Azelaic acid	$\text{HOOC}(\text{CH}_2)_7\text{COOH}$
Sebacic acid	$\text{HOOC}(\text{CH}_2)_8\text{COOH}$
Dodecanedioic acid	$\text{HOOC}(\text{CH}_2)_{10}\text{COOH}$
1,2,4-Benzenetricarboxylic acid	
1,2,4,5-Benzenetetracarboxylic acid	
5-Sulfoisophthalic acid monosodium salt	

thermal properties, chemical properties, and so forth to polyester that cannot be delivered by homogeneous PET.

The basic manufacture method is similar to that of homogeneous PET, and it is manufactured by mixing the copolymer components with TPA and EG in

Table 4.2 Monomer adopted for copolymerization of polyester. (2) Polyhydric alcohol

Ethylene glycol	$\text{HO}(\text{CH}_2)_2\text{OH}$
Propylene glycol	$\begin{array}{c} \text{HOCH}_2\text{CH}_2\text{OH} \\ \\ \text{CH}_3 \end{array}$
1,4-Butanediol	$\text{HO}(\text{CH}_2)_4\text{OH}$
1,5-Pentanediol	$\text{HO}(\text{CH}_2)_5\text{OH}$
1,6-Hexanediol	$\text{HO}(\text{CH}_2)_6\text{OH}$
Neopentyl glycol	$\begin{array}{c} \text{CH}_3 \\ \\ \text{HOH}_2\text{C}-\text{C}-\text{CH}_2\text{OH} \\ \\ \text{CH}_3 \end{array}$
Diethylene glycol	$\text{H}(\text{OCH}_2\text{CH}_2)_2\text{OH}$
Triethylene glycol	$\text{H}(\text{OCH}_2\text{CH}_2)_3\text{OH}$
Polyethylene glycol	$\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$
Polytetramethylene ether glycol	$\text{H}[\text{O}(\text{CH}_2)_4]_n\text{OH}$
1,4-Cyclohexane dimethanol	$\text{HOH}_2\text{C}-\text{C}_6\text{H}_{10}-\text{CH}_2\text{OH}$
Bisphenol A ethylene oxide	$\text{H}(\text{OH}_2\text{CH}_2\text{C})_n\text{O}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$
Trimethylol propane	$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{H}_3\text{CH}_2\text{C}-\text{C}-\text{CH}_2\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$
Pentaerythritol	$\begin{array}{c} \text{CH}_2\text{OH} \\ \\ \text{HOH}_2\text{C}-\text{C}-\text{CH}_2\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$

polymerization process to go through the EI or DE reaction followed by polycondensation reaction under high vacuum.

While the melting point for polyester deteriorates due to the molar fraction on copolymer components, thermal properties also vary depending on the structure of copolymer components. The glass transition temperature (T_g) for a random copolymer varies depending on the weight fraction of the copolymer component. T_g is lowered as the quantity of softening components such as adipic acid and sebacic acid is larger and increased as the quantity of rigid molecular structures such as paraphenylene dicarboxylic acid and naphthalene dicarboxylic acid is larger. Crystallinity also deteriorates due to copolymerization in general.

Copolymerization is also used as a measure to add various properties such as flame retardant introducing phosphorus element into molecular chains, improving affinity to dyestuff introducing ionic group, in addition to addressing control on melt viscosity and control of affinity to solvents or alkaline solutions.

4.3.2 *Dyeability*

One of the most important copolymerization technologies regarding fiber polyester would be the technology to improve the dye affinity. There is a problem with homogeneous PET that it is difficult to dye with its glass transition temperature around 70° C, which is close to the boiling point of water under normal pressure.

In the design concept to promote dye diffusion by copolymerizing a soft 3rd component and lowering T_g and crystallinity, polyethylene glycol (PEG) is an effective compound as a copolymerization component which can reduce T_g while suppressing the drop in melting point. However, there is an issue of PEG polymerization of certain amount being necessary to address sufficient coloring in dyeing under atmospheric pressure, and obtaining balance with other physical properties of fiber being difficult, and thus industrial application seems to be limited.

In contrast to this, a method to address brighter dyeing by using a cationic (basic) dye has also been examined. To address this method, a copolymerization component with an acidic functional group that can react with the dye would be required for PET. However, this copolymerization technique has already been applied for patent [5] by DuPont in 1957, and the sulfoisophthalic acid sodium salt indicated here is still used as the most typical cationic dyeable component. The issue about this copolymerization component is that it leads to increased melt viscosity of the polymer as the intermolecular interactions are strong, leading to lower fiber strength as the final polymerization degree for the polymer needs to be lowered due to the restrictions of the polymerization system. As methods to compensate for this flaw, the use of sulfoisophthalate quaternary phosphonium salt with lower intermolecular interactions, a method to further copolymerize a soft component with viscosity reduction effects such as PEG and so forth, has been proposed.

4.3.3 *Hydrolyzability*

While increasing hydrolysis resistance is demanded from the viewpoint of addressing durability of the fiber products, polyester with high rate of hydrolysis is required when shaping it into fiber with special cross section shapes by alkaline hydrolysis and removal of one polymer component during the fiber product manufacture process.

The sulfoisophthalic acid sodium salt copolymerization polyester described in the previous section has also been used as an easily soluble component in manufacture of modified cross section yarns and extremely thin yarns as its hydrolysis rate is extremely high under the existence of alkali.

4.3.4 Flame Retardant Property

In fiber products, flame retardant property is also considered an important function other than the stainability. Synthetic fibers such as polyester, nylon, and acryl have low LOI (limiting oxygen index) values in general and are flammable, and flame resistance is improved by polymer modification and post-processing.

Although various methods have been adopted for polyester including kneading or copolymerizing flame retardants into the polymer, copolymerization of flame retardants into polymer before spinning has an advantage that it causes relatively low deterioration in mechanical properties and that its flame retardant property persists as excelling in durability.

In copolymerization, the method to increase phosphorus content as polyester by copolymerizing a compound containing phosphorus atom which introduces flame retardant property to polymer is most typical. The major copolymerization components are shown in Fig. 4.1. Figure 4.1a has phosphorus atom on the main chain of polyester, while Fig. 4.1b is believed to be resistant to decomposition of the main chain as phosphorus atom exists on the side chain.

4.3.5 Mixed Filaments of Different Shrinkage

Introduction of the 3rd component into PET by copolymerization disturbs the regularity of polymer chain, and rigid segments especially deteriorate the crystallinity. The fiber made of this amorphous polyester has large rate of shrinkage, and the filament yarn combined with homogenous PET gives difference of yarn lengths due to the difference in shrinkage properties by adding thermal history during the post-processing and thus gives bulky touch to the fabric.

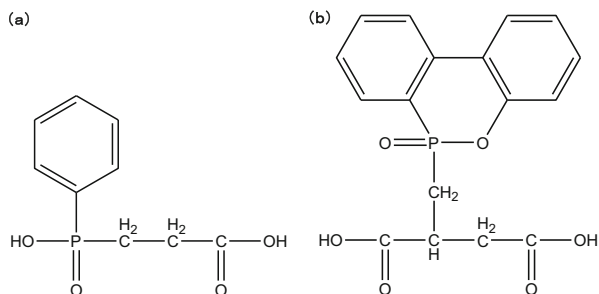
Copolymerization technique is an effective method for the polyester properties, and it is expected to be examined further in various ways to be utilized as a method to clear the paths to new applications of fibers in the future.

4.4 Bio-based PET

4.4.1 Background

Petroleum, which is a fossil resource, is a major raw material in chemical industry. However, it is a limited resource which is feared to be depleted in the future, and it causes a global environmental problem as it emits a large amount of carbon dioxide during the manufacture process as well as disposal by incineration. Under such circumstances, attempts to replace the petroleum chemical products which are currently mass consumed with recyclable products made from biomass resources

Fig. 4.1 Major copolymerization components for flame retardant property with phosphorus atom on the main chain (a) and on the side chain (b)



or products with lower environmental loads have attracted great attention. Consumption of Polyethylene terephthalate (PET) is especially large as various mold goods including fiber, films, and bottles. Movements to develop bio-based versions of such polymers with large consumption levels have become active these few years. It was Coca Cola which announced the adoption of bio-based PET bottles and released their sales ahead of the world in 2009 [10] that triggered these movements. These bio-based PET bottles (PlantBottle™) were manufactured by developing bio-based ethylene glycol as PET raw material, and their biomass content (^{14}C concentration measurement method: described later) is approximately 20%.

It is possible to produce bio-based PET by using bio-based ethylene glycol and terephthalic acid as raw materials in existing polymerization facilities. Therefore, raw materials made from biomass resources would be the key point.

4.4.2 Bio-based Ethylene Glycol

India Glycols has manufactured bio-based ethylene glycol since 1989 by using exhausted molasses from sugarcane, and its manufacture method comprises of forming bioethanol from the sugar by fermenting, dehydrating it into ethylene, oxidizing into ethylene oxides, and hydrolyzing into ethylene glycol. At present, Toyota Tsusho and China Man-Made Fiber in Taiwan founded Greencol Taiwan Corp. (GTC) by joint venture with matching investments [11] and established a technique to manufacture bio-based ethylene glycol industrially through a similar route. The bio-based ethylene glycol manufactured by this method is high in purity and can be used to produce PET with equivalent performance as that of PET manufactured from petroleum-based ethylene glycol. However, they still have the problem of high costs compared to petroleum-based PET.

This tendency to develop businesses for PET manufacture with bio-based ethylene glycol is seen in active market expansion promotion for bottles and automotive interior materials by Toyota Tsusho, films by Iwatani Corporation and Dai Nippon Printing [12], bottles by Kirin Beverage Company [13], thermal shrinking films and long fiber nonwoven fabric by Toyobo [14], and fibers for

clothes by Teijin [15] and Toray in addition to the bottles by Coca Cola mentioned above [16].

4.4.3 Bio-based Terephthalic Acid

Various examinations have also been made regarding development of bio-based terephthalic acid (TPA), which is the other raw material for PET. If both ethylene glycol and terephthalic acid can be bio-based, biomass content of PET made with those raw materials will be 100 %. PepsiCo made a press release in March 2011 that it had addressed the completely bio-based bottles [17], and Toray succeeded in trial manufacture of completely bio-based PET film and fiber for the first time in the world in a joint effort with Gevo in June and November 2011 [18, 19]. Gevo formed bio-based paraxylene by forming isobutylene through dehydration after forming isobutanol with fermentation method using sugar obtained from sweet corn and so forth as the raw material, followed by dimerization by radical reaction and cyclization. Completely bio-based PET fiber and film were delivered eventually as Toray converted this bio-paraxylene into terephthalic acid with its proprietary technique. Virent, Anellotech, and so forth have also been working on examination of industrialization of bio-based paraxylene production besides Gevo above.

In the future, both bio-ethylene glycol and bio-terephthalic acid will secure their markets once their relatively high costs compared to petroleum-based products are mitigated and supply stability is ensured. It is also an important matter to use nonedible resources with no competition for food as the starting materials in order to form larger markets in the future. Since PET is popularized in wide applications due to its excellent properties, bio-based PET is superior to other bio-based polymers in versatility, demand scale, and replaceability. It is surely expected to become popularized widely.

4.4.4 Biomass Content of PET

This section mentions how to measure the biomass content (^{14}C concentration measurement method) for reference.

Biopolymers can be analyzed for how much carbon originating from biomass resources is contained in the total carbon atoms comprising the polymer. Specifically, it is calculated by measuring the ^{14}C concentration (ratio between ^{14}C and ^{12}C detection values in substance) using Accelerator Mass Spectrometry (AMS). ^{14}C is an isotope of ^{12}C , and it is a radioactive element (half-life: approx. 5730 years). While ^{14}C is supplied into the atmosphere at a stable quantity every year as it is formed by cosmic rays falling onto the earth constantly, it also vanishes by radioactive decay in a certain quantity every year. The quantity of ^{14}C in atmosphere is therefore nearly constant in equilibrium. As ^{14}C supplied into the

atmosphere is distributed widely into plants by photosynthesis and then into animals through the consequent food chain, the concentration of ^{14}C (ratio between ^{14}C and ^{12}C detection values) is nearly constant for all organisms on earth.

Meanwhile, the most convincing theory for the origin of petroleum is that it was made from organisms from 100 to 200 million years ago, and the ^{14}C concentration in petroleum is nearly zero as its half-life is long past. Since biomass products contain certain level of ^{14}C and petroleum-based products do not as explained above, it is possible to calculate the ratio of carbon derived from biomass or the rate of bio-based production for the sample by measuring the ^{14}C concentration in the sample [20].

4.5 Polyesters Other Than PET (3GT, PBT, and PEN)

4.5.1 Major Aromatic Polyesters Other Than PET

While polyester represented by PET is synthesized by condensation polymerization between diol and dicarboxylic acid, polyester fibers other than PET include 3GT (PTT) fiber using propanediol instead of ethylene glycol as diol, PBT fiber using butanediol, and PEN fiber using naphthalenedicarboxylic acid instead of terephthalic acid as the dicarboxylic acid. An outline is provided for each of them below.

4.5.2 3GT Fiber [21]

3GT fiber (polytrimethylene terephthalate fiber) delivers both morphological stability of polyester and softness of nylon. It also excels in stain resistance and has no yellowing as nylon does. It also has large molecular deflection and excels in elasticity.

A major development target is the bulk textured yarn mainly for carpets. Side-by-side bimetal composite yarns in which the stretch recovery property is maximized have also been manufactured. In this purpose, high crimping is addressed by utilizing the thermal shrinkage property of the polymer comprising the fiber to form crimps during the heating stage in high-order processing so that excellent soft stretch property and stretch recovery property unlike any other fibers are addressed. It is also applied in other daily commodities such as clothes to be worn in the middle layer with characteristics of small thickness, lightweight, heat retention, moisture permeability, and flexibility; padding with excellent shape recovery, no dust, and moisture permeability; and toothbrush with little opening of tips and high plaque removal capability.

Meanwhile, it also attracts attention for biomass conversion of raw materials. Although the ethylene oxide method by Shell and acrolein hydrating method by Degussa (both using petroleum-based resources) were available as the industrial production methods for propanediol, DuPont developed a technique to convert sugar derived from plant materials into glycerin and further convert it into propanediol using microorganisms. By producing 3GT with this propanediol, 3GT made from biomass resources has been addressed with approximately 27 % biomass content (^{14}C concentration measurement method as described earlier).

4.5.3 PBT Fiber

Polybutylene terephthalate is a typical engineering plastic, and it is widely used in electric and electronic parts, automotive parts, and so forth as it excels in thermal stability, dimensional precision, and electric properties while being easy to process with high crystallization rate although it is inferior to PET in melting point. However, use of it as fiber is small in quantity. The production quantity remains small due to the restriction in price, although it is easily dyed and excels in elasticity during the false twist process (suited to stretching materials).

4.5.4 PEN Fiber [22]

Characteristics of polyethylene naphthalate fiber include high melting point (265° C), high T_g value, high strength, high modulus, low heat shrinkability, high chemical resistance, and high hydrolysis resistance.

It is often favorably used in industrial fiber applications utilizing these characteristics, such as fiber to reinforce the automobile tires (tire cords), reinforcing materials for hoses and transmission belts for automobiles, and heat-resistant canvas. In Japan, Teijin succeeded in industrialization in 1989 and sales was begun in 2001.

4.6 Concluding Remark

Now, we reviewed some current topics of polymer for synthetic fiber. Development of novel polymer materials has brought new high-performance fibers or enlarged the field of the fibers to be applied until now and also in the future.

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