Polymer Industry and Innovation in Macromolecule Science and Technology in China

Hong Dingyi

Science & Technology Development Dept., SINOPEC Corp., A6 BLD., Huixin East Str., Chaoyang, Beijing, 100029, China
E-mail: hongdy@sinopec.com.cn

Summary: The paper describes the recent technological progress in synthetic resin, synthetic fiber and synthetic rubber in China, as well as the achievements obtained in process technology development, catalyst R&D, the adjustment of product slate, and product capacity and output. Also, in the paper, an expectation image of next decade has been drawn.

Keywords: block copolymers; polyesters; polyolefins; Ziegler-Natta polymerization

After more than 20 years' efforts, China's polymer industry, keeping the same developing pace of the world, has been made distinctive progress in both production capacity, production output and process technology[1] of three synthetic materials(synthetic resin, synthetic fibre and synthetic rubber). China has become one of the largest manufacturers and consumers of macromolecule materials.

In 2001, China's total capacity of five synthetic resins, PE, PP, PS, PVC and ABS, has reached 11.3Mt/a, production output 11.2Mt, ranking the fifth in the world (the world's total output in 2001 is about 127 Mt); apparent consumption 22.7Mt, sharing 18% of the world's total consumption in 2001; and the capacity of main monomer ethylene is 4.8Mt, ranking the seventh in the world. Also in 2001, the capacity of five synthetic fiber: polyester fibre, polyacrylonitrile fibre, nylon, polypropylene fibre and polyvinyl fibre, has reached 7.1 Mt; production output 7.6Mt, ranking the first in the world; and apparent consumption 8.9Mt. The capacity of synthetic rubbers-SBR, BR and SBS, in 2001, has reached 1.2Mt; production output 1.0Mt, being the fourth in the world, and apparent consumption 1.7Mt, sharing 20% of the world total consumption.

As the main manufacturer of polymer in China, China Petrochemical Corporation (SINOPEC) which ranked the 68th among the world top 500 enterprises according to Forbes, produced ethylene 2.9Mt, sharing 61% of the whole country's capacity; synthetic resin 5.0Mt, sharing

 CCC 1022-1360/00/$ 17,50+.50/0

45%; synthetic fiber 1.4Mt, sharing 19%; and synthetic rubber 0.6 Mt, sharing 60% in 2001. SINOPEC's subsidiary, Shanghai Petrochemical Company (SPC) located in Hangzhou Bay, has become the first million tons scale of manufacture base of synthetic materials.

With the increasing demand and production capacity of macromolecules, great progress has been made in the development of technology and new products through the so-called alliance of enterprises, universities, research institutes, especially, including Chinese Academy of Science (CAS).

1. Technological Progress in Synthetic Resin

1.1 Development of Whole-Set Process and Engineering Technology

Currently, a great breakthrough in the development of PP process technology has been made. Loop reactor liquid phase bulk polymerization PP process and engineering technologies have been developed. By applying self-developed Ziegler-Natta catalyst, PP products from homopolymerization, random copolymerization and block copolymerization are produced through the coordination polymerization of monomers. Eight sets of 70-100kt/a plants have been constructed since 1998 and the second generation of whole-set 200kt/a loop PP process technology has been developed in 2000. SPC plant, applied this technology, has been put into operation smoothly in February 2002[2].

In PE process technology, the whole-set slurry high density PE technology has been successfully developed. PE products from homopolymerization and copolymerization are produced through the coordination polymerization of monomers upon the reaction of Ziegler-Natta catalysts. A 140kt/a HDPE plant using this technology has been constructed in SINOPEC Yanshan Petrochmeical Company. Also, gas phase PE expanding process technology, which can enlarge PE capacity by 50%-100% in the same reactor has been developed and the product quality remains unchanged. Metallocene PE technology has obtained satisfactory pilot plant results.

1.2 Catalyst Technology

In the development of PP catalyst, the new generation of Ziegler-Natta catalysts, N catalyst and DQ spherical catalyst, have been sequentially developed by using $MgCl_2$ as carrier, $TiCl_4$ as active component, and with electron donor. The activity of the catalysts can reach 40000-50000 g.PP/g.cat. N series catalysts technology granted patents from China and the United States, have been exported to the United States.

In the development of gas phase PE catalyst, a series of Ziegler-Natta supported catalysts, such as BCG and SCG, has been successfully developed[1,2], with the activity of 8000-10000g.PE/g.cat. SCG has been utilized to produce LIDPE and HDPE in the same plant of Maoming Petrochemical Company.

In the development of metallocene catalysts[3], zirconium metallocene catalysts for PE and sPP have been developed and achieved satisfactory results in pilot plant tests[4]. Titanium metallocene catalyst for sPS has been also developed and the research on post-transition metal catalyst has been carried on. Metallocene adduct catalyst of SINOPEC has been granted America's patents.

1.3 Development of New Product Slate

Visible progress has been made in the development of new product slate of synthetic resin specialty. Take SINOPEC as an example, the ratio of special grades to general grades has been soaring from the past 12% to 41% in 2001. In the development of new product slate, research on the relationship between structure and properties has played an important role. For example, by using TRAF, XRD, DSC, NMR equipment, etc., starting with the characterization of chain structure, the differences between high speed and common BOPP resins in MWD, isotacticity and its distribution have been acquired, based on which, high speed and high stiffness BOPP specialty has been successfully manufactured. In addition, the R&D has also been focused on developing new product slate by using physical blending modification technology. SMA, compatibilizer for PP and EPDM blending modification, and MBS for PVC modification, as well as nano powder rubber for toughing and reinforcing of PP, PA, PVC and EP, have been developed.

2. Technological Progress in Synthetic Fibre

2.1 Development of Whole-Set Synthetic Fibre Polymer Technology

Whole-set 100 kt/a polyester production technology with five polymerizers have been developed. Through the research on polymerization dynamics and melt monomer removal dynamics, the esterification reactor and end polycondensation reactor have been successfully developed. 100kt/a polyester production unit was successfully constructed and put into production in December 2000 in SINOPEC Yizheng Chemical Fibre Company with the highest production capacity of 420 t/d.

Whole-set 30 kt/a continuous polyester solid state polycondensation technology has been developed by using precrystallization, crystallization and solid state polycondensation process, and adding the third monomer and other additives to feedstock chips. Thus, viscosity increased polyester can be manufactured for bottle-use with good barrier property, high softening point and intrinsic viscosity ranging from 0.72 to 1.00. Currently, a 30kt unit is being constructed in Yanshan Petrochemical Company.

Whole set technology of 30 kt/a NaSCN two-stage polyacrylonitrile fibre engineering has been developed from tertiary aqueous phase suspension polymerization technology which uses NaSCN as solvent to realize rapid primary solution and shifting-wet spinning technology route. The technology solves the problems on engineering enlargement, such as polymerizers, heat exchangers, filters, etc., and second monomer replacement, and makes it possible for the successful enlargement of polymerizer to $7.2m^3$. The research results have been contributed to the technical innovation of 66kt/a polyacrylonitrile units in SPC.

On the basis of in situ intercalation polymerization technique and using in situ intercalating agents , the technology for synthesizing nano composite polyester has been developed, which realized nanometer scale dispersion (height about 1nm length and width about 100nm) of inorganic silicate particle in melt polyester. Compared with common polyester, the product is featured by high rate of crystallization, high glass temperature and good air barrier property. Now a 3 kt/a semi-commercial unit has been constructed and the products are developed to be used in thermal filling and packaging of beer.

2.2 Development of High Performance Synthetic Fibre

In recent years, China has paid more attention to the development of differential fiber. Take SINOPEC as an example, the differential rate jumped to 31% in 2001 from the former less than 10%. High performance differential products have been successfully developed, for example, polyester ultra-staple fibre, antibacterial and mould proof polyester fiber, polyester HMLS industrial filament, cationic dye stainable polypropylene fibre, glass fiber reinforced PBT engineering plastics, high shrinkage polyacrylonitrile fibre, ultra high MW PE gel spinning high strength high modulus fibre, polyacrylonitrile fibre for carbon fibre, etc.

3. Technological Progress in Synthetic Rubber

3.1 Development of Whole-Set Technology

The whole-set Ni-polybutadiene rubber technology has been developed and seven commercial units have been constructed, among which, the biggest single line capacity is 120 kt/a. Totally five product brands can be manufactured by applying Ni-catalyst system, three polymerizers flow scheme and raffinate oil as solvent.

Living anionic polymerization process technology has been developed using butyllithium as initiator, cyclohexane as solvent, and after the living ionic polymerization of monomer styrene and butadiene, two-block and three-block, or random copolymer thermal plastic elastomers can be manufactured. And it is realized to produce lithium copolymers including styrene thermoplastic elastomer, SSBR(solution polymerized SBR) and LCBR (low cis-polybutadiene rubber) in a single unit. And the shift of product variety and brand is more convenient. By process revamping, SIS can be also produced in SBS unit.

The R&D of SEBS preparation using metallocene catalyst have been also made progress. SBS hydrogenation experiment has been carried out with high activity metallocene catalyst. Up to now, there have been develooped four new SEBS products.

3.2 Development of New Products

In recent years, focusing on market orientation, research has been carried out on the development of new products. A series of products have been promoted to market. For example, SINOPEC has developed oil extended rubber (SBR, BR), LCBR, SSBR, SIS, SEBS as well as nano powder rubber to be applied in tire-making, adherent, sealing material and toughing and reinforcing modifier.

4. Prospects

It is estimated that in the next decade, the average increase of China's GDP will keep 7%. There will be a tremendous developing space of China's synthetic material industry to provide materials for agriculture, automobile, textile, construction, and packing industries. As primary estimated, in 2010 China's requirements for equivalent ethylene volume will be 23.6 Mt; for five synthetic resins about 39.80 Mt; for synthetic rubber about 1.4 Mt; and for synthetic fibre about 13 Mt. China's ethylene capacity is expected to exceed 10.0 Mt/a in 2010 which still cannot meet the market demands, thus the three big synthetic materials will need a large amount of import (the present import volume occupies about 50% of the demands).

The output of the world synthetic resin from 1995 has exceeded that of steel, if calculated by volume. Compared with the world advanced level, there is still a gap for China's polymer industry. From the point of occupation per capita, currently, the consumption of 5kg synthetic resin, 3.5kg synthetic fibre and 0.5kg synthetic rubber per capita are far lower than that of the developed countries, such as USA, European countries, Japan, etc. Therefore, to strengthen the development of polymer industry, advanced technologies will be applied, and meanwhile, R&D will be more focused on the projects with fundamental and forecast aspects, for example living polymerization technology (anionic, cationic, radical, etc.), polymer alloy technology for direct synthesizing within reactor, polymer unit enlargement engineering technology, super-critical polymerization, continuous polymerization and gas phase technology for elastomer making, catalyst preparation technology for new Ziegler-Natta catalyst, single-site metallocene catalyst, and post-transition metal catalyst, technology development for engineering plastics (PU, PC, PMMA, PPS, EP), as well as for fine polymer such as oligochitosan, polyaspartic acid, macromolecule for polymer flooding for enhanced oil recovery in oil field and biological degradating polymer.

In the new century, China's polymer industry will further promote the alliance among manufactures, universities and research institutes at home and abroad. The newest research achievements of domestic and international macromolecule fields will be adopted and accelerately converted to commercialization in order to provide more macromolecule synthetic materials for China's economic development and the improvement of people's living standard.

[1] Wang Jiming, Yuan Qingtang,Technological Development of Petroleum and Petrochemicals, SINOPEC Publisher, 2002.
[2] Hong Dingyi, Handbook of Plastics Industry, 1999, Chemical Industry Publisher.
[3] H.Sinn, W.Kaminsky, H.J. Vollmer, R.Woldt. Angew. Chem., Int. Ed. Engl., 1980, 19,396.
[4] Wang Hongtao, Chen Wei, et al, Shiyou Huagong, 1998, 3,27.