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The Research and Development of Thermoplastic Elastomers

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Abstract:

In this article, the types, market overview, industrialization progress, and the latest research and development directions of chemically synthesized and blended thermoplastic elastomers were reviewed. Several new types of thermoplastic elastomers with market application prospects were introduced, such as silicone TPE, polyolefin TPE, bio-based TPE, degradable TPE. Their performance and market development were discussed, and the application field and industrialization direction were reviewed and prospected.

Keywords: *Thermoplastic elastomer; TPE; Industrialization development*

Introduction

Thermoplastic elastomer (TPE) is a polymer material with the characteristics of thermoset vulcanized rubber and thermoplastic, which exhibits high elasticity of thermoset vulcanized rubber at room temperature and good processability of thermoplastic at high temperature. Due to this special property, TPE is also called "third-generation rubber" [1]. Because the vulcanization is not required and the molding process is simple, the industrial production process of TPE is shortened by 25%, the energy consumption is saved by 25% to 40% and the efficiency is increased by 10 to 20 times compared with traditional thermoset vulcanized rubber, which can be called another technological revolution in the rubber industry. What's more, TPE can be processed and recycled for many times, saving the petroleum resources required for synthetic polymer materials and reducing environmental pollution [2,3]. At present, TPE is widely used in many industries such as automotive, construction, household equipment, wire and cable, electronic products, food packaging, medical equipment. Under the background of increasingly scarce petroleum resources and serious environmental pollution, TPE has extremely important commercial value and environmental protection significance, and it has become a research hotspot in the field of polymer materials. In recent years, continuous product innovation by TPE manufacturers has promoted the development of the downstream application market. They have replaced traditional synthetic rubber in different application fields, and their applications have grown significantly. China's industrialized production of TPE began in the 1990s and China has been the world's largest TPE consumer after more than 20 years of rapid development.

1. Supply and demand of TPE in the global market:

The application fields of TPE are very extensive. It is the potential replacement products of most rubber products and it can also be used for polymer modification. TPE can be blended with various polymers such as polypropylene (PP), polyethylene (PE), polystyrene (PS). The blend shows excellent impact resistance, flexibility, and flexural properties, which is widely used in many fields like automotive, construction, electrical appliances. With the fast development of China's auto industry and home appliance industry, the amount of TPE used in polymer modification will grow rapidly. According to American Freedonia Group data, the global TPE market exceeded $ 24 billion and market demand reached 6.7 million tons in 2019, which will grow at a rate of 5.2% each year in the future. China's TPE market consumption accounts for about 36% of the global total consumption and it is one of the fastest growing countries in the world. The average growth rate of the global TPE market is tending to moderate, the report said: This is because the TPE market is gradually maturing. Asia and the Pacific will be the markets with the greatest demand for TPE and demand for TPE in these two regions will grow at an above-average rate. In 2019, demand in these two-regions accounted for about 50% of global demand. Among them, China will be the world's largest consumer of TPE products, and the annual market demand growth rate is close to 8% while the growth rate in the European and North American markets is slowing down and the growth rate in other parts of the world is more moderate.

2. Development status of various thermoplastic elastomers

After years of development, TPE has formed more than 30 varieties in 10 categories. The main varieties of TPE are thermoplastic styrene elastomer (SBC or TPS), thermoplastic polyolefin elastomer (TPO), thermoplastic polyurethane elastomer (TPU), thermoplastic polyester elastomer (TPEE), thermoplastic polyamide elastomer (TPAE), thermoplastic vulcanizate (TPV), organo-fluorine elastomer (TPF), organic silicones, etc., covering almost all fields of synthetic rubber and synthetic resin. In recent years, many new varieties of TPE have been developed by researchers to meet some special needs of users, such as high temperature resistance, heat oil resistance, high barrier properties, high insulation.

2.1 Styrenic block copolymer TPE (SBC)

Styrene-based thermoplastic elastomers are ABA-type triblock copolymers. The remarkable structural features are that some chemically different plastic segments (hard segments) and rubber segments (soft segments) are connected or grafted in series between polymer chains to form a microphase separation structure and the hard segments are dispersed in the soft elastic matrix, which enhances the creep resistance, while the soft rubber matrix provides elasticity so that the temperature range of TPEs can be from the low Tg of the soft segment to the high Tg of the hard segment [4,5]. At present, the SBC is the largest production of thermoplastic elastomer with the closest performance to rubber. SBC series products include styrene-butadiene block copolymer (SBS), styrene-isoprene block copolymer (SIS) and styrene-isoprene-butadiene block copolymer (SIBS), and the corresponding hydrogenated copolymers are SEBS, SEPS, SEEPS. SEBS is the most common type of hydrogenated styrene block copolymer. Compared with SEBS, SEEPS have higher tensile strength, better oil filling performance, smoother surface and better low temperature performance [4,5]. SBS has the largest output, accounting for more than 70% of SBC consumption; SIS roughly accounts for 20% of SBC consumption, and SEBS-based hydrogenation products account for about 7% of SBC consumption.

2.1.1 Development of market application of SBC products

The application of SBC series products and its market capacity: In 2017, the global production capacity of SBC was 2793kt, of which China was 1230kt, accounting for 44% of the world. In 2018, SBC production capacity increased to 1395kt, and the output reached 1081kt in China [6]. Since SBC entered commercialization in the 1960s, SBS has been one of the most successful commercial products in history [7]. The total production capacity of SBS in the world accounts for 80% of the total production capacity of SBC. Shoemaking is still the largest consumer market for SBS, accounting for about 34% of the total consumption; followed by the asphalt modifier and polymer modifier market, accounting for about 19%; The third-ranked waterproof membrane accounts for about 15 %; The adhesive market accounts for about 13% of total consumption. It is expected that SBS consumption will grow at an average annual rate of 3.5% in the future. The SBC consumption of developed countries such as the United States, Western Europe and Japan will grow more slowly in the future due to the relatively mature markets, and the Asia-Pacific region will become a new round of development center for SBS. In recent years, the demand for the SBS market has shrunk, and the proportion of consumption has decreased year by year. The development direction is SEBS, SIS and high-end SBS products. At present, the proportion of SBS in SBC product consumption structure is as high as 95% while SEBS and SIS only account for 5% in China, far lower than developed countries such as the United States and Japan. This is because Chinese SBC mainly focuses on low-end products, while many high-end products such as SEBS and SEPS mainly rely on imports compared with countries besides China.

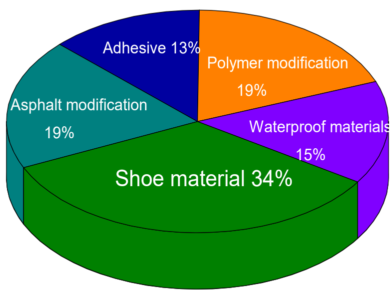

Figure 1. The proportion of global SBC consumer markets

2.1.2 The development trends of SBC

SEBS is a widely studied thermoplastic triblock copolymer [8,9]. SEBS was firstly industrialized by the US Shell company in 1972, and the equipment and technology were inherited by the US Kraton company. Due to the excellent performance and a wide range of applications of SEBS, there are currently many companies engaged in the production and R & D of SEBS, like Kraton Company of the United States, Asahi Kasei Corp. of Japan, Kuraray and JSR, Eni Chem of Italy, Repsol of Spain, TSRC Corporation, Formosa Plastics Corporation, LCY Chemical Corp., and Baling Petrochemical, Sinopec Group, TSRC (Nantong) Company, Zhejiang KEYUAN Petrochemicals Company. At present, the total production capacity of SEBS in the world is close to 500,000 tons / year and in China is about 150,000 tons / year, and there are also manufacturers who are actively planning to build devices. The range of application SEBS is very wide, such as auto parts, children's toys. [10]. SEPS is industrialized by American Kraton and Japan Kuraray Corporation while China Baling Petrochemical realized industrialization in August 2017, and SEEPS is only produced by Japan Kuraray Corporation.

2.1.2.1 Research progress of hydrogenated SBC

The SEEPS has high added value and wide application fields, because it combines the performance of SEBS and SEPS, and has unique structure, excellent performance and product monopoly. In addition to the same use as SEBS and SEPS, it can also be used on the occasions with special requirements for flexibility, strength, shock absorption and comprehensive performances.

2.1.2.2 Polarization modification

The SBS / SIS block copolymer has limited molecular polarity, poor oil resistance and solvent resistance, which limits its compatibility and adhesion with polar materials. At present, the chemical modification of SBS is mainly to introduce polar groups through unsaturated double bonds, such as epoxidation, grafting, sulfonation. Introducing polar groups into the molecular structure of styrene-butadiene-styrene (SBS) as a compatibilizer can improve the compatibility of non-polar and polar materials [11]. A systematic study on the polarized modification of SBC was conducted by Baling Petrochemical, Sinopec Group, using n-butyl lithium as an initiator and introducing polar groups at the end of the synthesized active SBS to prepare polar SBS. Epoxy SBS was prepared by modifying epoxidation of SBS with peroxyformic acid generated in situ from formic acid and hydrogen peroxide at South China University of Technology. Polar functionalized styrene-butadiene-styrene block copolymer was synthesized through the coupling method by LI Jingjing, etc [12].

For SBS graft modification, Yang grafted hydroxyethyl methacrylate (HEMA) and N, N-dimethyl aminoethyl methacrylate (DMAEMA) to SBS by radiation grafting [13]. Li applied a 2% mass fraction of SEBS toluene solution to the silicon wafer with a clean surface at high speed, and successfully grafted the polyethylene glycol monomer onto the SEBS film using a combination of oxygen plasma pre-treatment and ultraviolet radiation. [14]. Nithin Chandran found that SEBS-g-MAH can significantly improve the impact property when studying a new type of natural rubber / polypropylene thermoplastic vulcanization formulation [15]. SBS in-situ polymerization modification: In the synthesis process, a blocking agent can be added to directly prepare SBS containing certain special functional groups when the SBS polymerization is terminated. In this way, not only the polarity of SBS is strengthened, but also the adhesion of SBS to other polar substances is improved. Common blocking agents include $C0_2$, $S0_2$, Schiff base, chlorinated polyols, cyclic anhydrides and cyclic amine compounds [16].

2.1.2.3 Research of flame retardant SBC

The SEBS / PP composites have excellent mechanical properties, processing properties and aging resistance, which are widely used in industries such as automotive, electrical cables and toys. However, its application is greatly limited because of the poor flame retardant performance of SEBS / PP with a large amount of heat generated when the polymer is burned and the droplet phenomenon caused by the fast flame propagation speed [17-19]. Therefore, the necessity of its flame retardant research is very obvious.

Mishra et al. [20] showed that a large amount of inorganic flame retardant needs to be added to improve the flame retardant performance of the SEBS / PP system, which seriously affects its processing performance.

Japan's Aaron Chemical Co., Ltd. has used magnesium hydroxide as a non-halogen flame retardant, and successfully developed AR-NF0 series non-halogen flame retardant TPE with low hardness.

Zhang et al. [21] selected phosphate esters (such as RXDP and triphenyl phosphate) as the flame retardant of SEBS elastomer blending system. When the content of phosphate ester was 19.7%, the flame retardant performance of the elastomer reached UL-94 V-0.

2.2 Olefinic thermoplastic elastomers (TPO)

Polyolefin thermoplastic elastomer can be processed but by blending ethylene-propylene-diene rubber and nitrile rubber (NBR) with polypropylene or polyethylene, or by synthesizing block-structured elastomers. At present, the consumption of TPO in developed countries such as Europe, America and Japan are large while the market share of TPO in China is still relatively small. TPO is mainly used in the fields of automotive, wires and cables, electronic appliances, building materials and sports equipment.

TPO mainly has two kinds of production processes: one is blending compound type, and the other is reactor type. Blending compound type includes dynamic vulcanization (TPV) and mechanical blending (CTPO). TPO products mainly include ethylene-octene copolymer (POE) which is synthesized using metallocene catalysts, TPV and ethylene-octene block copolymer (OBC), POP and other types [22-26].

2.2.1 Market application development of TPO products

In 2019, TPO's global production capacity is approximately 1.08 million tons, and the demand of TPO still maintains rapid growth. The main consumption areas of TPO are North America, Western Europe and Japan. Among them, Japan has the largest consumption, about 33%, followed by North America about 32%, then Western Europe 25%, China 5%, and other regions 5%. China's demand increases rapidly, but the required products are mainly dependent on imports because Chinese petrochemical companies have failed to achieve the commercialization of TPO. Different from the global consumption structure, the largest consumption of TPO in China is for the automotive industry, accounting for 68%; polymer modification accounts for 19%, wire and cable accounts for 9%, and other uses account for 4%. The major global TPO producers are Dow Chemical, Mitsui Chemicals, ExxonMobil and SK Korea. Dow Chemical can produce more than 30 brands with a total production capacity of 455,000 tons, accounting for 42% of global production capacity; In addition, ExxonMobil accounted for 19%, Mitsui Chemicals accounted for 16%. SK put into 200,000 tons production of POE and polyolefin plastomer (POP) in 2014, accounting for 19% of global production capacity.

In recent years LG has also developed POE technology and achieved commercial production.

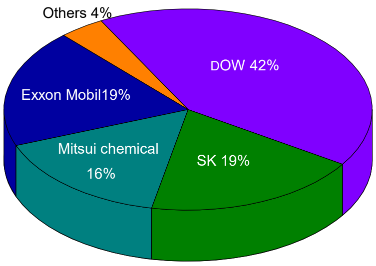

Figure 2 Major global TPO manufacturers

TPV is a milestone in the development of TPO and the fastest growing variety in the TPE field, the average annual compound growth rate of which in the world from 2019 to 2024 is about 6%. TPV is replacing traditional thermosetting vulcanized rubber in more and more applications, becoming one of the most promising polymer material varieties [27-30]. The main manufacturers of TPV include Exxon Mobil, Tenor Eppers, Shandong Dawn Polymer Co., Ltd., and Mitsui of Japan. Its main varieties are EPDM / PP type TPV, accounting for more than 90% of the output of all TPV varieties. ExxonMobil is the leader in the global TPV market with a relatively high global market share. China Shandong Dawn Polymer Co., Ltd. is the leader in the Chinese market of TPV whose products are widely used in automotive, industrial products and end consumer products.

Up to now, there are more than 20 TPV manufacturers in China, but most of them have relatively small production capacity. China's first 10,000-ton TPV production line was completed in Shandong Dawn Polymer Co., Ltd in early 2012. In 2018, Dawn 's TPV capacity expanded to 33,000 tons, ranking third in the world and first in China. TPV consumption is increasing rapidly around the world. In 2017, the global TPV market demand was about 600,000 tons and North America was the main TPV consumer market, accounting for more than 40% of the world. The Asia-Pacific region has the fastest growth rate with a forecast annual compound growth rate of 7.4%. Thanks to the rapid development of China's auto industry and the advancement of automotive lightweight, domestic TPV demand in 2019 increased to about 50,000 tons, of which more than 60% is used in the automotive industry.

2.2.2 Development Trend of TPO R & D

2.2.2.1 Synthetic polyolefin elastomer

The synthetic polyolefin elastomer was successfully developed by US DOW Chemical Company in 1993 with the trade name Engage [31].

The current research in the field of synthetic thermoplastic polyolefin elastomers is mainly focused on the development of post-metallocene palladium (II) and nickel (II) diimine complexes. The application of various complexes enables the synthesis of new polymers to be compounded with precise control of the polymer microstructure [32-35]. Such TPOs include branched and hyperbranched polyolefin and olefin segment polymers. The block copolymer has semi-crystalline and amorphous regions, which give TPO mechanical stability and flexibility, respectively. ExxonMobil uses Exxpol patented technology to produce random copolymers of ethylene, propylene, and α-olefins with bridged metallocene catalysts whose products are mainly plastomers under the trademark ExactTM and special elastomers under the trademark VistamaxxTM [36]. Lyondellbasell has developed a unique C4 copolymer with thermoplastic elastomer properties and commercialized it in 2009, and its product trademark is KoattroTM.

China has no POE production capacity and can only rely on imports to meet market demand. At present, metallocene catalysts and non-metallocene organometallic catalysts with high copolymerization performance were developed and the research on copolymerization technology of ethylene and α-olefin was carried out by many scientific research institutes and universities including Zhejiang University, Institute of Chemistry Chinese Academy of Sciences, Sinopec Beijing Research Institute of Chemical Industry, etc., providing technical support for the industrialization of China's POE production.

DOW has successfully developed a new olefin block copolymer (OBC) with the trade name" Infuse" by Insite catalyst technology [37,38]. Insite catalytic technology is realized by using two kinds of catalysts, and the polymer segments are transferred back and forth between the two catalysts to grow, and finally form polyolefin elastomers with unique block structures. Therefore, compared with POE, OBC's heat resistance and mechanical properties are significantly improved, and it also has excellent processing properties and wear resistance [39].

Many properties of OBC surpass traditional TPO. Compared with styrene TPE, OBC shows excellent compression set, aging resistance, chemical resistance, and processing performance. In addition, OBC's products have slippery appearance and silky feel, especially suitable for soft handles and surfaces. The potential market of OBC includes the application areas previously dominated by TPV and TPE, especially in the application of automotive soft materials, such as refrigerator gaskets, flexible extruded materials. OBC has excellent elastic recovery performance, which is taken advantage by elastic films, diaper materials and other products. The gasket of the beverage bottle made by OBC has the advantages of small compression deformation, light weight, and better sealing.

2.2.2.2 Thermoplastic vulcanized rubber

In recent years, with the needs of the market, some new TPVs have emerged. Such TPVs mainly include silicone rubber TPV (TPSiV), acrylate rubber TPV (ACM), TPV based on NR or ENR, polyolefin elastomer (EOC) / PP TPV, TPV with excellent barrier properties [40,41].

TPSiV is developed by Dow Corning of the United States and produced and sold by its subsidiary Multibase. This type of TPV has features of good sealing properties, good oil and chemical resistance, stain resistance and excellent adhesion to many engineering plastics [such as polycarbonate, nylon (PA), ABS, etc.] , which have received increasing attention in recent years [42,43]. At present, Dow Corning's silicone elastomer products have three series: nylon matrix, TPU matrix and polyolefin matrix. This type of TPV is used in automotive hoses and industrial hoses, automotive engine cabin structural parts and so on.

ACM / PA type TPV with excellent heat resistance and oil resistance is the strong competitor of ACM in the automotive field, especially for the components used under the working condition of engine cabin temperature reaching 150 ℃ [44-46]. The current ACM or ethylene acrylate rubber (AEM) oil seals all use a metal skeleton, and the metal skeleton needs to be coated with an adhesive or the like for surface treatment. Using this type of TPV, it can be directly overmolded and the oil seal production process is simplified. In addition, it is also used in automotive high-temperature intake pipes, turbine exhaust pipes and diesel oil line sensors.

Natural rubber is a renewable green material with excellent elasticity and good dynamic mechanical properties, so it is widely used in industrial field [47,48]. Natural rubber / polypropylene thermoplastic elastomer is a very important thermoplastic elastomer, which is widely used in the automotive industry [49,50]. In addition, among various types of PE, HDPE is most commonly used to produce NR / HDPE TPV [51, 52].

EOC is a non-polar a-olefin copolymer prepared from metallocene. Compared with EPDM rubber, crystalline EOC blended with PP shows higher rigidity and impact resistance [53-55]. EOC has a lower molecular weight than EPDM and has better processing performance. In addition, EOC has a cost advantage and is expected to replace EPDM / PP TPV, which is currently receiving more attention in the automotive field [56-59].

IIR has excellent gas barrier property, which can be used with PP, PA and other material to prepare TPV with excellent gas barrier properties for medical stoppers, tire innerliners and other fields [60-62]. Exxon and Yokohama Rubber have recently developed dynamic vulcanized alloys (DVA) of brominated poly (isobutylene-co-p- methylstyrene) (BIMSM) and PA, which is suitable for the production of flexible, durable, high barrier tire air dense layer and hose. DVA replaces thermosetting vulcanized butyl rubber to prepare the tubeless tire gas barrier layer, which not only reduces the weight of the tire gas barrier layer by 60%, but also improves the air tightness by more than 10 times than that of the original [63]. Therefore, this type of TPV material is of great significance for improving the fuel economy, form safety of automobiles, saving automobile manufacturing costs and reducing energy consumption. Beijing University of Chemical Technology and China Shandong Dawn Polymer Co., Ltd. began basic research on the technology in 2008, and are currently cooperating with Chinese tire plants in the application testing research phase.

The research and development of bio-based TPV is also receiving more and more attention because polylactic acid has high strength, rigidity and transparency, good biocompatibility, biodegradability, reproducibility, and easy processing, and it is often used as TPV Plastic phase. However, its application is limited by its inherent brittleness, low crystallinity, and low heat distortion temperature [64,65].

2.3 Thermoplastic polyurethane elastomer

Thermoplastic polyurethane (TPU) was first started by Otto Bayer and his colleagues in the I.G. Farben (predecessor of Bayer) laboratory in Leverkusen, Germany in 1937 [66]. They used liquid isocyanate and liquid polyether or glycol polyester to synthesize polyurethane elastomer for the first time. In the 1950s, the United States took the lead in synthesizing polyurethane flexible foam composed of propylene oxide and ethylene oxide copolyether and toluene diisocyanate (TDI), which was a major milestone in the development of the polyurethane industry.

2.3.1 Development of market application of TPU products

In 2018, the output of the global TPU industry was 1.167 million tons, and the demand was 1.142 million tons. Driven by increasing market demand, the construction of new global TPU projects will continue to increase, and the production capacity and output of TPU will continue to increase. It is expected that the global output of TPU products will reach 1.314 million tons in 2020, an increase of 6.0% year-on-year. The market concentration is very high: The TPU market is very concentrated, BASF, Covestro, Lubrizol, Huntsman occupy 40% of the global market share; Europe, Asia-Pacific and the United States dominate the polyurethane elastomer market, of which Asia-Pacific is also the world's leading and fastest-growing regional market. New products are emerging one after another: For example, Adanc 3 D Materials has developed a new type of TPU-Ad Sint TPU80sh A with excellent elasticity which is available for selective laser sintering process and can be used in most printers with printing temperature <100 ℃ . It has excellent chemical resistance and wear resistance, elongation at break up to 600%, which can be used in shoe soles, orthopedic models, hoses, pipes, seals and wheels, etc. [67]. DuPont has launched 2 kinds of 3D printing materials with different hardness, which has high flexibility, high heat resistance and chemical resistance, and has both high strength and durability.

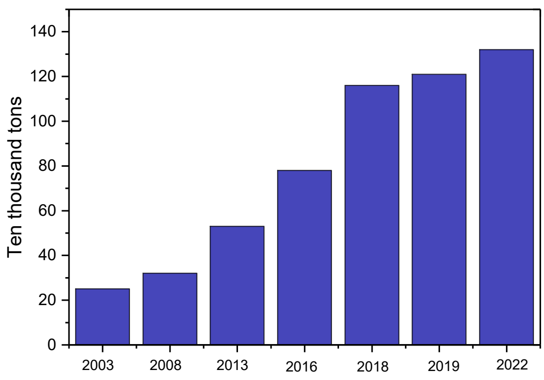

Figure 3. Global output and forecast of TPU products

China's TPU industry started late, but it has developed rapidly with a total production capacity of more than 750,000 tons in 2019. So far, China's TPU production and consumption have been in the forefront of the world. In 2018, China's TPU consumption has reached 436,000 tons, surpassing Europe and the United States to become the world's first TPU consumer market, and the average annual consumption maintains a rapid growth of about 15%, much higher than the 3%-4% annual average growth rate of the European and American markets. However, due to the relatively late start of China's TPU research and market development, there are obvious gaps with BASF, Covestro, Huntsman, Lubrizol and other multinational companies in terms of product formulation technology, production process, product application technology, etc., so TPU products are mainly used in the low-end consumer field. TPU in high-end fields (resource exploration, military, medical, automotive, high-end sports equipment), high-end products (oil resistance, high temperature resistance, environmentally friendly flame retardant, functional products) is still in the early development stage, and there is still a big gap between technology and multinational companies.

The market concentration of the thermoplastic polyurethane industry is relatively high. In recent years, manufacturers of upstream polyurethane raw materials represented by Wanhua and Huafeng have begun to extend the industrial chain to the production of downstream TPU. These enterprises that have the advantages of supporting raw materials can well balance the risks caused by raw material price fluctuations and gradually occupy an active position in the market competition while small enterprises are greatly affected by raw material prices and supply volume, lack of technology, pressure on environmental protection, and relatively lack of competitiveness. Lubrizol, BASF, Covestro, Huntsman and other multinational companies have invested in factories in China, established sales channels, and been in fiercely competition with local companies in terms of talents and markets. Judging from the perspective of the development experience of global giants, the integration of upstream and downstream is also the trend of future TPU industry development. The current status of the global TPU production industry has the characteristics of high vertical integration.

2.3.2 Development Trend of TPU R & D

In recent years, the development of TPU products has developed towards high-end and personalization. The products developed are:

(1)TPU inner tube: Due to TPU's excellent mechanical properties, the wall thickness of the inner tube processed by TPU can be greatly reduced while maintaining excellent performance. (2) TPU smart film (TSPU): By adjusting the type of soft segment phase, bonds length, and ratio of hard and soft segments, TSPU materials with different switching temperatures can be produced. The voids' size of the film made from this material will change with temperature, which is used in the fields of smart fabrics, leather, membrane separation materials and drug sustained release [68]. (3) TPU-coated fabric products: TPU-coated fabric products are a kind of products designed and molded by coating TPU on the fabric skeleton material through hot melt method, which has a wide application value. (4) TPU for 3D printing: In 2020, DSM has established partnerships with chromatic 3D Materials and German RepRap for working together to promote the production of 3D printed polyurethane parts; Raffles of Germany has successfully 3D printed Commercialized with TPU, and cooperated with Adidas and American footwear brand Underarmor. Product sales are concentrated in European and American countries, which does not exclude large-scale sales in China in the future [69]. (5) TPU foam particles: The TPU foam particles first developed by BASF are widely used in sports shoe midsoles, which reduces the weight of the sole and has good rebound & shock absorption to reduce the impact on the ankle and better protect for the safety of the wearer. The popcorn sole shoes produced with TPU foam particles in Adidas detonated the market and perforated artificial leather based on flexible thermoplastic polyurethane (TPU) foam has also been reported to successfully used for external negative pressure wound therapy for lower extremity venous ulcers [70,71]. (6) Flame-retardant modified TPU: TPU itself is a flammable material and it will release heat violently, toxic gas, and produce smoke accompanied by melt dripping once burned. There are more and more researches on TPU halogen-free flame retardants. The flame retardants with better flame retardant effects include phosphine flame retardants, nitrogen flame retardants and nano inorganic flame retardants. Environmentally friendly bio-based intumescent flame retardants are also one of the research hotspots of TPU flame retardants [72-74]. (7) Biodegradable TPU: The traditional preparation method of thermoplastic polyurethane relies on fossil resources, which exacerbates the depletion of fossil resources. What's more, most TPUs are not biodegradable and the utilization rate is low, therefore improving the biodegradability of TPU and reducing nonrenewable resources has become a trend [75-78]. It is very necessary to modify the flame retardant of TPU with its currently wide application, increasing society's demand higher requirements put forward under many occasions such as cable coating materials, automotive industry.

In addition, it has become a general trend for TPU to replace PVC in many fields. With the sharp decline in the price of the TPU raw material market, the price of the TPU mainstream market has also gradually declined. The price difference between the TPU and PVC markets has gradually reduced, providing a basis for TPU to replace PVC and promoting the process of replacement. PVC is a non-environmentally friendly material (has toxic and harmful substances to the environment) with poor overall performance, which opens up more space for TPU to replace PVC. Medical TPU catheters will completely replace PVC hoses.

2.4 Thermoplastic polyester elastomers

Thermoplastic polyester elastomers (TPEEs) are a type of block linear copolymers containing a hard crystalline segment [poly (butylene terephthalate) (PBT)] and a soft amorphous segment [poly (tetramethylene oxide) glycol (PTMO)]. PBT polyester hard segment (crystalline phase, providing strength) and polyether soft segments (continuous segment). The rigidity, polarity and crystallinity of the TPEEs hard segment make them have outstanding strength and excellent high temperature resistance, creep resistance, solvent resistance and impact resistance; the low glass transition temperature and saturation of the soft segment polyether make it have excellent low temperature resistance and aging resistance. It combines the excellent elasticity of rubber and the processability of thermoplastics [79-81].

2.4.1 Market application development of TPEEs products

TPEEs were first developed by DuPont in the United States and Toyobo in Japan. In 2019, the total global TPEEs production capacity has exceeded 150,000 tons / year, and the market demand has reached more than 120,000 tons. There are more than 10 major manufacturers in the world including Du Pont, GE, Hoechst-celanese and Eastman chemical. TPEEs have developed for application in areas such as automotive, hydraulic hoses, cables and wires, electronic, sporting goods, biological materials. Among them, the most widely used is in the automotive industry, accounting for more than 70% [82,83]. Ford Motor Company has used Arnitel's TPEEs resin on many vehicles such as Mondeo, S-Max, Galaxy and Focus, and recently adopted Arnitel's TPEEs as the vacuum brake tube material for Fiesta cars. The Royal Dutch DSM Group has developed a new Arnitel Foaming TPEEs foam material for the preparation of running shoes, which considers the four characteristics of softness, rebound, lightness and durability, greatly enhancing the runner's sports experience. China's research and development of TPEEs was late. Until 2003, China Blue Star Chemical Research Institute took the lead in realizing the industrialization of TPEEs production in China.

2.4.2 Development Trend of TPEE R & D

Poly (glycerol sebacate) (PGS) is a tough polyester elastomer with good flexibility (like vulcanized rubber) and has the attributes of biocompatibility and biodegradability.

Most importantly, the monomer used for the preparation of PGS, namely, glycerol and sebacic acid (SA), is bio-derived and renewable [84- 86]. Runcy W [87] et al. prepared bio-based semi-interpenetrating polymer network blend elastomers of PGS-b-PTMO and TPEE, and the elongation of the interpenetrating network elastomer is up to 2574%. At present, compared with traditional petroleum-based TPEEs, people are more willing to introduce sustainable monomers in TPEEs to develop bio-based TPEEs with excellent properties [88-90]. Dequan Chi et al. Combined neopentyl glycol (NPG) and bio-based 2,5-furandicarboxylic acid (FDCA) to produce Poly (neopentyl glycol 2,5-furandicarboxylate) (PNF) with both high melting temperature and crystallization ability, which was used for developing the hard segment of the new bio-based TPEEs. Compared with the TPEEs that have been commercialized and petroleum-based preparation, they possess excellent properties [91].

Jian xiang C et al. studied the effects of nano-silica on the hard segment crystallization performance in TPEEs. The crystallization temperature of TPEE is more sensitive to the surface treatment of silica, while its crystallization rate shows a higher dependence on the particle size of silica. Different types of silica have evident nucleating effects on the crystallization of TPEE, leading to a remarkable increased crystallization temperature and overall rates without changes in the crystallite size and crystal structure. [92].

At present, many new TPEEs have been developed abroad. Japan Sekisui Chemical Co., Ltd. uses three monomers include dihydroxytetraphenyl, dimethyl adipate and ethylene glycol, to melt polymerize into a multi-block copolymer at a high temperature of 200 to 300 ℃; Gagon used microbial fermentation to produce β-hydroxyoctanoate-containing poly (β-hydroxycaprylate, PHO for short) biodegradable TPEE. In addition, 2-hydroxypropionic acid and caprolactone are used as raw materials to convert 2-hydroxypropionic acid Lactide, then copolymerized with lactide and caprolactone (75/25) to obtain degradable TPEE; Air Productsandchem Company researched on the method of reacting CO2 with ethylene oxide to produce polyethylene carbonate (PEC) copolymer of polypropylene carbonate (PPC) (PEC-PPC).

The DuPont Company of the United States and the Mitsubishi Company of Japan have prepared a flexible TPEE that combines heat resistance and oil resistance by adopting the method of dispersing the cross-linked rubber particles during dynamic cross-linking when TPEE and rubber are mixed. Japan Toyobo Textile Co., Ltd. used random copolymerization of PBT and aliphatic polycarbonate butanediol to prepare high heat resistance TPEE with the trade name Perupuren C. DuPont used polytrimethylene ether butanediol extracted from corn as a soft segment to develop bio-based TPEE.

2.5 Thermoplastic polyamide elastomer

Thermoplastic polyamide elastomers (TPAE) is a newly developed class of alternating block copolymer elastomers. This type of copolymer has many advantages of polyamide, polyether and polyester at the same time, such as good processability, high temperature resistance, good solvent resistance, creep dimensional stability, wear resistance, good low temperature flexibility, impact resistance and elastic recovery. TPAE was first developed successfully by the German company Huls in 1979 and achieved commercial production. Later, Upjohn Company in the United States, Emaster Company in Switzerland, Arkema Company in France, Japan Ink Company and Japan Amide Company successively launched TPAE products of different brands [93-95].

The long carbon chain nylon elastomer derived by polyamide elastomer that uses long carbon chain polyamide (LCPA) as the hard segment has the dual advantages of long carbon chain nylon and elastomer, like good flexibility, high impact resistance at low temperature, high elastic recovery rate and good wear resistance. It is a high value-added and high-performance material, which has a wide range of uses in medical devices, electrical components, mechanical parts, high-end sports shoes, and clothing.

At the present stage, the long carbon chain polyamide elastomer market is mainly occupied by four multinational companies. Arkema of France and Evonik of Germany are leaders in this field, supplying Pebax XX33 series and Vestamid E series products to the market, respectively. In addition, Swiss EMS companies and Japanese UBE companies also have corresponding products. Since the monomer required for PA12 is monopolized by Evonik in Germany and the monomer required for PA11 is monopolized by Arkema in France, domestic manufacturers have not yet been able to mass-produce the monomers and corresponding elastomers required for PA11 and PA12. In recent years, China has adopted the method of microbial fermentation to convert n-alkanes in petroleum by-products into long-carbon chain dibasic acids, and has successfully synthesized even-even long-chain polyamide varieties with independent intellectual property rights and realized industrial production,such as PA1010, PA1012, PA1212.The hydrophilic polyether segment amide (PEBA) developed in recent years is composed of a polyamide rigid segment (PA12) and a soft hydrophilic polyether. In addition to being hydrophilic, the main advantages of this material are its flexibility, portability, ease of processing and good compatibility with traditional medical polymers, which commonly is used in surgical gowns, medical sheets, wound dressings, and bandages [96].

2.6 Other types of thermoplastic elastomer

2.6.1 Bio-based thermoplastic elastomer

In order to reduce dependence on non-renewable resources such as petroleum and achieve sustainable development of the polymer materials industry, bio-based polymer materials are favored by more and more people.

Bio-based thermoplastic elastomers are a type of thermoplastic elastomer materials prepared from biomass monomers, whose resources are very sustainable because their monomers are derived from organisms in nature. For example, the bio-based thermoplastic elastomer Hytrel developed by DuPont is a kind of bio-based thermoplastic elastomer material prepared by copolymerizing the bio-propylene glycol (Bio-PDO) intermediate obtained from corn sugar during fermentation of corn sugar with polyester, which contains 40% to 60% (mass fraction) Bio-PBO and possesses very excellent elasticity and biodegradability [97].

The TPUs sold by Lubrizol under the trade name Pearlthane ECO were developed based on various plant resources and have been widely accepted by the market, which have similar properties to conventional TPUs [98].

The bio-type EPDM produced by using organically derived raw materials, under the trade name Keltan ECO, is used for the synthesis of ethylene produced from sugar cane. Depending on the composition, it contains up to 30-40% of bio-based components with the same performance as standard products when processed to be thermoplastic elastomer, [99].

Because of its biodegradability, PLA is widely used in packaging, biomedicine, and other fields [100,101]. Bio-based elastomer is an important direction of its development. According to different preparation methods, polylactic acid TPE mainly includes block copolymer type TPE and blend type. Polylactic acid TPE is mainly produced by copolymerization, introducing a certain number of flexible segments with low glass transition temperature into rigid polylactic acid (PLA) molecular segments [102,103]. Due to the thermodynamic incompatibility of the soft and hard blocks, micro-phase separation and self-assembly into ordered domains of different morphologies can occur, thus exhibiting the performance of TPE. At present, it mainly includes three types of ABA triblock copolymer, multi-block copolymer and star block copolymer. Compared with physically cross-linked TPE prepared by complex synthesis steps, TPV has the advantages of wide performance range, simple preparation process and economic feasibility. To improve the toughness of PLA, SIS and SEPS were added to PLA and blended to prepare a blended bio-based elastomer [104].

2.6.2 Silicone thermoplastic elastomer

Silicone materials have high and low temperature resistance, low glass transition temperature, surface tension and viscosity temperature coefficient, excellent electrical properties, breathability, and biocompatibility, which are incomparable and alternative to other organic polymer materials, thus aroused widespread concern. Silicone thermoplastic elastomers mainly include chemically synthesized and mechanical blending silicone thermoplastic elastomers. Wang Y et al.

[105,106] used the UPy structure with self-identifying, four-fold hydrogen bond as the hard segment and polydimethylsiloxane as the soft segment for block copolymerization to prepare silicone thermoplastic elastomer with the structure based on multiple hydrogen bonds. Dow Corning uses ionic interactions to produce silicone thermoplastic elastomers. This high modulus ionic silicone thermoplastic elastomer has high tensile strength at room temperature [107]. Amanda S. F et al. introduced coumarin groups on the linear polysiloxane backbone to create a physical cross-linking network and showed the performance of thermoplastic elastomers [108]. At present, the research and development of silicone thermoplastic elastomers mainly focus on the design and synthesis of supramolecular elastomers and the research of elastomer processing technology. In the study of processing technology, the processing method of thermoplastic elastomer is changing from simple mechanical blending to dynamic vulcanization. Dynamic vulcanization not only improves the compatibility between resin and rubber, but also improves the mechanical properties of the elastomer. Based on the advantages of silicone thermoplastic elastomer, silicone thermoplastic elastomer will have great application prospects in future production. At present, most of the technology of silicone thermoplastic elastomer products is mastered by foreign companies. Therefore, the development of new silicone thermoplastic elastomers will be a hot spot for the future development of China's silicone industry.

Conclusion

Due to the recyclability and simple processing characteristics, thermoplastic elastomer materials make the global growth rate of TPE much higher than traditional rubber. In recent years, research on the high-performance and functional type of TPE materials has been very active, and many new types of thermoplastic elastomers have been emerging. It can be predicted that with the development of polymer synthesis technology and dynamic vulcanization technology, the development of thermoplastic elastomer materials and their industrialization will become brighter. In addition, with China's increased awareness of environmental protection, environmentally friendly materials such as TPE are bound to receive widespread attention and long-term development.

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