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The development of polyurethane

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ABSTRACT

Polyurethane is one of the six promising synthetic materials in the world. Due to its excellent product performance and wide application field, it is a crucial industry of development in the world. This paper introduces the progress of polyurethane industry in recent years which includes polyurethane raw materials, classification and application prospects. The research methods and principles of waterborne polyurethane were mainly studied. At the same time, the development of new polyurethane materials was held forward.

KEYWORDS: Polyurethane; Application; Waterborne polyurethane synthesis; Development

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1. Overview

1.1. History of World Polyurethane

Polyurethane (PU) is made from polyisocyanate (OCN-R-NCO) and polyhydroxy compound (HO-R-OH) and there are a plurality of -NHCOO-repeating macromolecular compounds in the main chain. Polyurethane is known as the 'fifth largest plastic'. In modern industry it is more routinely used as a polymer organic materials. Due to its relatively superior performance, it is widely applicable in daily life. For instances, its application in building construction metallurgy, automobile construction, light industry, textile industry, building construction, medical equipment, energy, defense equipment and ships are evident.

Professor Otto Bayer is the founder of polyurethane. Professor Otto Bayer had successfully synthesized polyurethanes in Germany in 1937. Without his discovery, the current industrial development would not be such rapid. PU has almost 80 years of history. After the end of World War II, Britain and the United States obtained the method of production of polyurethane from Germany and had applied the technology to the industrial production. However the use of PU was of limited function initially. As time passed, the technology had flourished. The United States begun active research about polyurethane after its introduction. In the early 1950s, they were the pioneer in combining polyurethane, ethylene oxide, copolymer ether and toluene diisocyanate into polyurethane soft foam plastic. It was a major invention and was a crucial milestone for PU development in the world. The original German companies utilized high cost synthetic raw materials which was not suitable for a wide range of applications. However after this invention, the cost for PU production had greatly reduced which created an important foundation in PU's industrialization and its development. Within 1950 to 1960, the United States, Germany and British team had made a great contribution to the development of PU. They developed castor oil and polyether polyol synthetic PU adhesive, with polyester polyol and NDI composition of the liquid PU cast rubber (CPU), polyester rigid PU foam technology and PU flexible fiber (Lycra) Lycra. After the mid-1960s, PU industry developed more rapidly and was widely used in various industries. By the mid-1980s, the world's polyurethane consumption had reached four million t/a. By the 1990s, the consumption of PU had doubled. With the passage of time, the world's consumption of polyurethane is multiplying and PU industry is developing more rapidly.

1.2. History of the development of polyurethane in China

From the late fifties of the last century to the late seventies, China's PU industry has entered the germinating period [1]. China's first PU industry was launched in the 20th century which was 50years from now. In 1958, the synthesis of isocyanates (TDI) in Dalian and in 1968 the creation of production machine which had a production capacity of 500T per year production. These two achievements has laid a vital foundation in China's polyurethane industry in order to create a favorable development conditions. In the early 60s, China had independently developed a polyether PU soft foam. At the same time, China had also introduced three polyurethane foam production lines and they were installed in the three relatively large plastic factory. In the early 1970s, China had successfully synthesized the mixture of PU elastomer (MPU) and PU coating and had developed the PU adhesive for industrial production. In 1974, China developed a PU waterproof material and grouting material. In 1976, the technique of PU runway glue was discussed and researched. In 1978, it was applied to all kinds of sports places in the country. Before the 1970s, although PU industry was nearly starting to develop, the amount of production was still insufficient to provide industrial development due to the lack of equipment and smaller modality. The initial era of China's PU industry was from 50s to late 70s.

20th century 80s is the period whereby domestic PU industry started to reach a stable state of development. Advanced PU synthetic machine was introduced in Jiangsu and Guangzhou from abroad as the domestic economic policy was remodel. Meanwhile, PU synthetic leather technology was introduced in Shandong from and later a 10,000 t/a MDI production device is also introduced and was officially utilized. At the same time, Gansu Silver Chemical Industry Company introduced TDI manufacturing technology and equipment and the use of this technology in 1990 built 20,000 t/a production scale. From the late 80s to the late 90s, a number of advanced PU production machines was introduced in the domestic industrial from some of the most developed countries. This initiative for China's PU industrial development had laid a huge foundation. In the mid-eighties of last century, the line of professional organizations set up a PU industry collaboration group. The efforts of all parties finally won the national approval and the 'China PU Industry Association' was established in a decade later. Since then, China's PU industry has undergone a qualitative improvement as evident by annual increment of PU resin production. Until 2000, a variety of PU products had reached an unprecedented peak.

After 2000, China's PU industry has entered a period of rapid development and had gradually became one of the fastest growing domestic chemical production among the industry. From 2000 to 2005, the domestic PU production and consumption of the annual growth rate are maintained at a relatively high position as evident by increment of almost 2.5 times of production and consumption than before. According to this development, in the future China will become the world's largest PU production and consumption among the developed countries. Shanghai Gaoqiao Petrochemical, Tianjin Petrochemical three plants, Jiangsu Chemical Industry and other units have made a lot of contributions for the PU industry had laid an important foundation.

1.3. Chemical properties of polyurethane

Since the molecular chain has a carbamate group, the polyurethane has a strong polarity and is insoluble in a non-polar solvent. Its molecular material has excellent toughness, anti-aging properties. In the synthesis of PU products, the use of different raw materials and composition, the resulting products will have different properties, including elastomers, thermoplastic resin and thermosetting resin.

There are many monomers for polymerizing PU products. For example, toluene diisocyanate (TDI), diphenylmethane and the like simple polyols. Preparation of polyester-based polyurethane required terminal hydroxyl-containing polyester oligomers. Preparation of polyether polyurethane requires terminal hydroxyl-containing polyether oligomers. Since the nature of the polymer material is different, the polymerization method also varies. The resulting products are also different which include thermoplastic elastomers, cast elastomers, elastic fibers, rigid foams, flexible foams, paint and adhesives.

The advantages is extensive. PU elastomers are commonly used in conveyor belts, hoses, auto parts, soles and medical artificial organs. On the other hand, soft foam are used in home cars, insulation, noise and packaging. PU paint can be effective for the protection of wood and metal integrity.

1.4. Polyurethane varieties

Polyurethane Adhesive is also known as Ulida gum. Polyurethane adhesives contain NCO-groups and NHCOO-groups in the molecular structure, and the polyurethane adhesives can be divided into polyisocyanates and polyurethanes because of their ranking in the molecular chain and the structure of the molecular chains. Since the polyisocyanate contains a carbamate group (-NH-COO-) and isocyano (-NCO), the polyurethane adhesive has a high activity and polarity. Foam, glass, rubber, plastic, wood and other substances containing active hydrogen have a good sticky nature. Polyurethane adhesives are used in a wide range of applications, and can be used in other aspects of automotive, wood, footwear, packaging, construction, book binding and railway construction.

Polyurethane coating, can be divided into two-component and one-component polyurethane coating. It is a more common coating. The two-component polyurethane coating is typically composed of a low molecular weight urethane polymer (commonly referred to as a curing agent component) and a hydroxyl-containing resin (commonly referred to as a main component). This kind of coating performance is excellent and has a great developing potential. PU coatings are usually used for repair, leak-proof aspects. However the shortcomings are obvious. Its construction process is complex which demands a high construction environment. One-component performance on the other hand is not as good as two-component, this is why the range of applications is not wide enough for both components.

PU foam is the product of isocyanates and hydroxyl compounds from the polymerization reaction. Polymerization of PU foam has distinct textures. Sometimes they are hard and sometimes they are relatively soft. Hence, it can be easily distinguished based on their hardness. It has good elasticity, softness, chemical stability, adiabatic function and is a good cushioning material. It usually acts as a cushioning material for some of the more expensive upscale items to avoid damage to the items.

Polyurethane leather is soft, natural color, strong. It has an excellent wear resistance, aging resistance, cold breathable and low cost advantage. Thus it is the best alternative to natural leather. It is mostly used among the ordinary citizens.

Polyurethanes are the main components of polyurethane rubber and polyurethane prepolymer. PU Polyurethane Sealant has many good properties such as good elasticity. PU polyurethane sealant can be used for a long time. However, the polyurethane sealant also has some shortcomings. It could not withstand heat for a long time, slower curing rate and has poor water resistance. PU polyurethane sealant is commonly used in the construction and transportation.

Polyurethane fiber is known as polyurethane elastic fiber but is named as spandex in China. Spandex is very flexible and elastic and is widely used in the textile industry. Due to its outstanding elasticity, the general clothing is not 100% of the use of spandex to maintain appropriate flexibility. This is done by involving the usage of different proportions of spandex.

Polyurethane paint has strong adhesion, water and abrasion resistance and is widely used in the surface of advanced wood furniture and metal. Its main drawbacks are formation of bubble on the surface when come in contact with water and turns yellow when time goes. 'Polyester paint' sold in the market nowadays is in fact the polyurethane paint. They are the master paint, while the other is a curing agent. They should be used in accordance with a certain ratio of deployment and it is achievable after mixing. It is suitable for the use of family.

2. Polyurethane raw materials

Toluene diisocyanate (TDI), diphenyl methane diisocyanate (MDI), acrylic (AA) and other organic matter should not be referred as polyurethane products. They can only be said that they contain raw materials of polyurethane. Polyurethane raw materials also include: isocyanate, polyester polyol, polyether polyol (PPG, POP, PTMEG), solvent (DMF, TOL, MEK), chain extender (BDO) and various additives.

2.1. Isocyanates

The ester compounds of isocyanic acid are collectively referred to as isocyanates. (R-N = C = O ~ N-). Isocyanates can be classified according to the amount of the NCO group. For instance, Isocyanates (O = C = N-R-N = 1) and polyisocyanates. Toluene diisocyanate (TDI) is the largest yield and the most commonly used material in the daily life among them.

TDI applications are mainly paint, glue and soft foam. Among them, soft foam is the largest area of consumption TDI, its consumption accounted for 70% of total consumption, while the coatings industry accounted for 15 percent. Soft polyurethane foam (referred to as polyurethane soft foam) are applied in the furniture mats, vehicle seat mats and a variety of soft cushion layer. In addition, TDI can also be used to produce other polyurethane products such as rigid polyurethane foam, polyurethane coatings and polyurethane elastomer intermediates.

MDI can be further divided into pure MDI, polymer MDI, liquefied MDI and modified MDI [2]. TDI and MDI are the raw materials for the production of polyurethane as they are substitutes for each other. Pure MDI is mainly used for the production of slurry and polyurea spray. Polymer MDI mainly produces polyurethane foam which is mainly used for refrigerators, water heaters and other facilities of the insulation [3].

Polyphenylene polyisocyanate (PAPI), English full name polyaryl polymethylene isocyanate is a well-known crude MDI. It is a mixture of MDI and polyisocyanates with more than two functional groups. Self-polymerization occurs automatically at elevated temperatures. It can be used to create polyurethane adhesives or directly into the rubber adhesive to improve the adhesion properties.

In addition to the above mentioned PU synthetic raw materials, other raw materials are HDI, XDI and NDI. Xylylene diisocyanate (XDI) and naphthalene 1,5 - diisocyanate (NDI) have relatively limited role and hence smaller production in domestic industries. On the contrary, l, 6-diisocyanate (HDI) has a good resistance for yellowing so HDI will replace TDI's in the coatings industry. It has now become increasingly common for HDI to be used as high-grade car paint.

2.2. Polyols

A product derived from condensation of an organic dibasic acid with a polyol - a polyester polyol.

1,4-butanediol is referred to as BDO. It is a very useful polymer raw materials in the daily life of industrial development and is used in different fields. Because BDO can be used to synthesize PU resin. In the PU industry, it plays a very important role to produce pulp and spandex. Currently there are four ways to produce BDO technology in the world. The four methods are Reppe method, butadiene method, butane anhydride method and propylene alcohol method.

In addition to BDO, there are several products that are similar. It is the main production of polyester polyol raw materials (ethylene glycol and propylene glycol.). Although they are the production of polyester polyol raw materials, but as compared to BDO, the role and application of these raw materials in the PU industry is still relatively small.

Polyacrylic polyols (collectively referred to as PPG), derived from the condensation of propylene oxide, are one of the most crucial raw materials for polyurethane synthesis. However, due to the use of different types of starting agent, the type of polyether polyols produced are also different. The production of polyurethane plastic is the best application of polyether. In addition, it can also be used as a surfactant, the manufacture of industrial defoamers, high efficiency,low foam detergent, lubricant, heat exchange fluid and quenching Agent, drafting agent components and special solvents.

Polytetramethylene ether glycol, referred to as PTMEG, the main purpose is the production of spandex, polyurethane elastomer, synthetic leather, and other substances.

2.3. Chain extender

Chain extenders are essential reagents for PU production. Other polyurethane raw materials fully react with each other, the polyurethane ready to condense into the product, this time should be added to the amount of chain extender resin molding. A relatively small molecule of alcohol or ether containing two or more hydroxyl groups.

The principle of the use of chain extenders in the production is to allow the isocyanate-terminated prepolymer to react with some active hydrogen-containing compounds, which extends the chain diffusion of the molecules and cure the resin into the desired shape.

2.4. Catalysts

(1) Polyurethane catalyst A-1 catalyst is mainly used in the production of soft polyether polyurethane foam and packaging with a rigid foam. It can be brought to reduce the foam density, because he has a strong catalytic effect with water. The A-1 catalyst controls the gas production to account for 80% of the reaction, controlling the effectiveness of the gel reaction of 20%. This type of catalyst has a high activity and is used in a small amount. With appropriate timing and the correct adjustment on the amount of catalyst, the gel time can be controlled precisely. The use of a tin-tin catalyst with this catalyst can improve the fault tolerance in the production of foam and prevent the quality problems in the production due to some artificial or non-human, careless or computational errors. The quality of the soft foam is guaranteed. The A-1 catalyst is quite popular in the industrial manufacture of various polyurethane foams, especially for high resilience, semi-rigid and low density foams.

(2) Polyurethane Catalyst A-33 This highly active catalyst promotes the reaction of the polyurethane feedstock, crosslinking the foam, and imparts good mechanical properties to the flexible polyurethane foam. The best outcome could be expected while using A-33 together with NIAX catalyst A-1.

3. Polyurethane synthesis process

3.1. Polyurethane synthesis method

PU synthesis method has a one-step synthesis process and two-step synthesis process. Although the two methods are different, the chemical principle behind both methods is similar.

3.1.1 One step synthesis process

The one-step synthesis process is a step in which the reaction of the isocyanate and the polyol and the reaction of the produced prepolymer with the chain extender are completed at the same time by mixing the various polyurethane synthetic materials in a one-time reaction.

3.1.2 Two-step synthesis process

The two-step process involves reacting the polyol with the polyisocyanate first, and then producing a prepolymer of sufficient molecular weight. A sufficient amount of chain extender is then added to the resulting prepolymer to form the prepolymer into a high molecular weight compound.

Polyols and polyisocyanates produced by the reaction of the prepolymer is a very soft material, its own strength is very low, it must be added chain extender to form a polymer polymer has just the value of the use. The prepolymer can also be sold, but some need to add some other chemicals, so that the shelf life of the prepolymer can be extended.

Although the synthesis of polyurethane can be divided into two methods, but the principle is similar. The only difference is the order of sequence. However most of the experts suggested that two-step method is generally better than the one-step system as the product quality is better.

3.2. Waterborne Polyurethane

Waterborne polyurethane is a new polymer material with water as the dispersion medium and PU resin as the base material. It retains the advantages of traditional polyurethane, but also has some traditions do not have new advantages such as non-toxic, energy conservation and so on. Because of its advantages, water-based polyurethane became the center of attention.

3.2.1 Preparation of aqueous polyurethane

Due to polyurethane strong hydrophobicity and isocyanate can react quickly with water, the traditional synthetic technician cannot produce the desired waterborne polyurethane. In this regard, both local and abroad expertise carried out various researches to create such properties. Finally, they divide the waterborne polyurethane into two categories which include external emulsification and self-emulsification.

3.2.1.1 External emulsification method

The outer emulsification method [4] refers to the preparation of the corresponding prepolymer in various organic solvents in an organic solvent, which has a strong hydrophobicity and is difficult to dissolve in water. This necessitate the addition of appropriate high-performance emulsifier and through the external force to form a polyurethane emulsion. The lower the viscosity of the prepolymer, the easier it is to emulsify it. The addition of emulsifiers is sodium alkyl sulfate polyoxyethylene ether and other substances.

3.2.1.2 Self-emulsification method

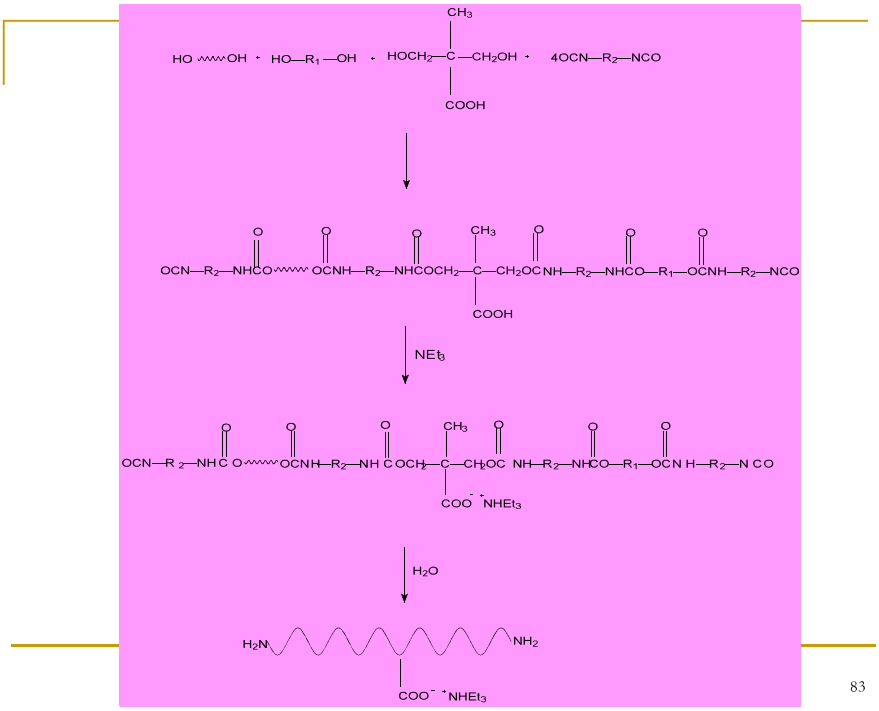
Self-emulsifying method [5] is the introduction of hydrophilic groups in the molecular skeleton of polyurethane. PU molecules have a certain hydrophilicity. PU molecules dispersed into the water to get waterborne polyurethane and then through the hydrophilic group emulsified PU molecules made of waterborne polyurethane emulsion. Until now, self-emulsification can continue to be broken down into several ways. The way is as stated below.

3.2.1.3 Prepolymer dispersion method

The prepolymer with -NCO end group was synthesized and a small amount of N-methylpyrrolidone was added to the prepolymer to adjust the viscosity of the prepolymer. Next, it is placed in a water with diamine. With high-speed mixing, the prepolymer dispersed into the water while expanding the water-based polyurethane.

3.2.2 Water-based polyurethane synthesis principle

Anionic water-based polyurethane is the most important water-based polyurethane products, the following is the synthesis of aromatic water-based polyurethane chemical reaction, said the synthesis of aromatic water-based polyurethane principle:



After neutralization, the addition of water and water played the role of emulsification and chain extender, and the terminal-NCO group of the macromolecule changed to -NH2, and the -NH2 was further reacted with –NCO. The molecular weight of the aqueous polyurethane is further improved by -NH-CO-NH-.

4. Practical applications of polyurethane

Polyurethane is known as the fifth largest plastic, it is a modern industrial emerging polymer organic materials. It has a relatively superior performance, so in all areas of national life are more commonly used. It covers a wide range of applications, including building construction metallurgy, automobile construction, light industry, textile industry, building construction, medical equipment, energy, defense equipment, and ships.

4.1. Application of PU Material in Daily Life

Polyurethanes play an important role in life. We can see its application virtually anywhere including at home and on the streets. Even what we are wearing are made from it but we do not realize what is made of polyurethane. Our home furniture, sofa, mattress, refrigerator, water heater insulation layer, seat armrest are made of polyurethane. We see the wire insulation paint, cable sheath, floor paint, shoes, outsole, shoes, adhesives, sports track, plastic stadium (soccer, basketball and badminton) and plastic flooring are made of polyurethane. Also, its application also includes things we do not usually see in daily life which embraces aircraft car interior parts seats, door panels, dashboard, bumper and fender.

4.2. The specific application of various PU materials

4.2.1 PU soft foam Flexible PU

PU soft foam in mat materials has sound-absorbing properties whereas fabric composite materials has a considerable application areas. Polyurethane soft foam texture is relatively soft, feel comfortable, so often with the same to manufacture mats, sofas. The aperture of the PU has a good sound-absorbing effect, it can be used to install in the indoor noise and is a good sound insulation material. As for fabric composite material, due to it has good flexibility, it is usually used to make cotton.

4.2.2 PU Rigid PU

PU foam has excellent insulation properties, so most of the refrigeration equipment (refrigerators, cold storage and refrigerated trucks) and industrial equipment insulation are applied to the PU foam. In addition to thermal insulation in

this area of application, it can also be applied to transportation such as car roof, imitation wood, grouting material and flower industry.

4.2.3 Semi-rigid PU

Absorbent foams are often used in the production of automobile bumper, because the energy-absorbing foam has a good shock absorption capacity and cushioning ability, which has these two excellent performance can improve the life of the bumper.

The Integral Skin Foam is used to make car steering wheel, handrails and car interior trims. Since the crust foam products are usually RIM processing technology.

Polyurethane microporous elastomers are the most widely used for the footwear industry.

4.2.4 Polyurethane elastomer

PU elastomers are classified into three categories: cast PU elastomer (CPU), thermoplastic PU elastomer (TPU) and kneaded PU elastomer (MPU) [6]. CPU production is much higher than the other two and the scope of application is far greater than the other two drugs. These three elastomers have a vital role in the mining, metallurgy, machinery industry, automobile industry, light industry and construction industry. It plays an excellent performance in these aspects.

4.2.5 Polyurethane slurry

PU slurry is divided into wet PU slurry and dry PU slurry. Artificial leather can be synthesized with the PU slurry, the use of PU slurry synthetic leather looks naturally comfortable and soft as compared to the natural leather. And most importantly, it has anti-aging properties and the cost of producing artificial leather is low, so in the future it will be the best alternative to natural leather material. Where there is leather applied to the field, it can replace some of the high price of natural leather.

4.2.6 Spandex

Spandex has a very high resilience (sponge high resilience is now the best of all elastic fibers), good tensile strength, tear strength, resistance to ultraviolet radiation, chemical resistance, does not damage the material after repeated washing and the affinity of the dye is good.

Because spandex has so many advantages, so it is now widely put into the production of textile materials. In the traditional textiles, addition of a small amount of spandex can greatly improve its traditional fabric quality. It is also more comfortable, beautiful and stylish.

5. Development and Development of Polyurethane and Its Raw Materials

5.1. The future of polyurethane

At present, the world's annual demand for polyurethane is 7 million T, and now the annual growth rate of 7 percent faster growth. Advancement in industrial development have contributed to the advancement of the polyurethane industry and the increased demand for polyurethanes has led to a gradual increase in the demand for synthetic polyurethane feedstock. PU is one of the world's most promising synthetic materials. PU industry and national economic life are closely related, in all areas have played an important role. So PU industry and its raw materials will usher in a chance to play.

5.1.1 Market analysis

PU products and more types, each with a different nature and superior performance, so the scope of application and the area involved is quite wide [7]. So far, the world's annual consumption of polyurethane is considerably huge, of which the United States accounted for one-third of the weight, Europe is slightly less than the United States, the Asia-Pacific region is similar to Europe. Currently the global demand for polyurethane on average has reached the annual growth rate of seven percent while the growth rate of some developing regions are even higher [8]. In the near future, the Asian region's PU industry will be developed with Europe, the United States is not comparable. In the Asia-Pacific region, China and Japan's PU products production and demand is the largest [9].

5.1.2 Raw material market demand

TDI and MDI are the main raw materials for synthetic PU. With a variety of TDI, MDI raw materials for the preparation of a variety of PU materials widely used in the production of auto parts, coatings, adhesives and so on. The world's MDI and TDI are almost in the hands of several well-known companies. MDI appears later than TDI and is slightly higher in price than TDI. However, toxicity of MDI is minor and mold better than TDI, so the future TDI is likely to be replaced by MDI. As the demand for PU continues to increase, the market with MDI and TDI increases. Some domestic and foreign businessmen want to expand their share in this market, so they make investment in China's productivity to expand their industry accounted with a larger market share [10].

5.1.3 China PU industry status and progress

In the near future, China will become the global PU consumer products center [11]. China is now accounted for 30 percent of the total consumption of PU products, and is currently one of the fastest area in MDI and TDI production in the world. As China's PU industry is developing more rapidly, it catches up with the pace of Europe and the United States. Multinational companies had spotted this point and they focus investment on PU production in China, hence shifting the global PU development center from Europe and the United States and other countries to China.

In recent years, well-known foreign companies continue to increase investment in China's PU production industry. Relevant research and development centers were established in China together with introduction of some of the international advanced technology. This fully demonstrates the shift of development of the world's PU from Europe and the United States to China. China will become the world's top PU industry to and acts as a fundamental driving force [12].

6. Conclusions

Polyurethane products is inseparable from our daily life. It is virtually everywhere and is readily available. Polyurethane synthesis and synthesis of raw materials are diverse. Different types of synthetic materials will produce polyurethane products with different natures. According to their different characteristics, they play different roles in field. Polyurethane is the most promising polymer organic materials and in the future its development will promote the rapid development of world industry.

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