

Mechanical Properties and Preparation Process of Bio-Based Degradable Polyurethane

Zhang Hongyuan¹, Sun Dawei², Cao Tieping^{1,*}

¹Department of Chemistry, Baicheng Normal University, 137000, Baicheng, Jilin Province, China

²Department of Chemistry, Jilin Normal University, 130000, Jilin Province, China

Keywords: Degradable Polyurethane; Mechanical Properties; Preparation Process

Abstract: This paper briefly introduces bio-based degradable polyurethanes from natural bio-based degradable polyurethanes and synthetic bio-based degradable polyurethanes. After a series of experimental studies, the synthetic synthesis of castor oil-based polyurethane porous sponge, polyhydroxybutyrate valerate-based polyurethane and polyvinyl alcohol-based polyurethane was carried out, focusing on its mechanical properties and preparation process, aiming to provide some reference for the development of related work.

1. Introduction

Polyurethane materials have been applied in many fields, and their biocompatibility and antithrombotic properties are strong. Together with high quality mechanical properties and low cost, they are widely recognized and welcomed. Polyurethane materials are commonly used in the production of plastics, rubber, fibers, water-repellent materials, etc., but the materials themselves are not degradable, and long-term use does not meet the sustainable development strategy. Therefore, degradable polyurethane has become a subject worthy of study.

2. Bio-based Degradable Polyurethane

Bio-based degradable polyurethanes include: natural bio-based degradable polyurethanes, synthetic bio-based degradable polyurethanes. The former includes the following: 1. Cellulose synthesis. Cellulose belongs to polyhydroxy compound and reacts with isocyanate to form polyurethane. After a long time of exploration, the researchers found that the bio-degradable polyurethane is synthesized by this method. Both theory and practice are relatively mature, but there are still certain Insufficient; 2. Vegetable oil synthesis. Vegetable oil is widely used as a mixture of fatty acid triglycerides. It is used at a low cost and is a renewable resource. Currently, the most common ones include castor oil, soybean oil, linseed oil, etc. Among them, castor oil is widely used but not available. In the food industry; 3. lignin synthesis. The lignin molecules include alcoholic hydroxyl groups and phenolic hydroxyl groups, which are similar in nature to polyether and polyester polyols, and thus can be used to prepare polyurethanes; 4. Oligosaccharide synthesis. The hydroxyl group in the oligosaccharide can be used in the preparation of polyurethane after reacting with other substances; 5. Starch synthesis. Since the beginning of the research on degradable plastics, starch has always played an important role in the corresponding raw materials. In order to increase the starch content in starch plastics, thermoplastic starch began to appear[1].

The principle of synthetic biodegradable polyurethane is as follows: using the same method of analytical design, the highly functionalized polyurethane is gradually synthesized. This kind of polyurethane not only has good physical properties, but also has obvious degradation performance. Such degradable polyurethane materials are mostly embodied in the medical field, such as polyether polyurethane, polyester polyurethane, etc., and are often applied to artificial skin, artificial heart valves, and surgical sutures. In general, the above-mentioned polyurethanes have different degradation characteristics. Polyether polyurethanes are mostly oxidative degradation. Polyester polyurethanes and polycarbonates are mostly hydrolyzed. Scientifically selected soft segments can

achieve various environments, degradation methods and Effective control of the rate.

3. Bio-based Degradable Polyurethane use

In terms of biomedical materials, polyurethane has obvious advantages in use, such as good biocompatibility, adjustability, kink resistance, etc. The physical and mechanical properties are widely used and the surface is smooth and intact. It is usually used as tissue engineering materials and surgery. Use materials. Polyurethane molecular structure design is more convenient. Compared with other materials, it is easy to process and shape. In the design process, porous preparation methods can be used. After effective combination with molecular design methods, tissue engineering materials can be obtained. Polyurethane can be used as a base material for medical surgical films with high safety and reliability.

In terms of shape memory materials, thermoplastic degradable shape memory polyurethanes and thermoset degradable shape memory polyurethanes can be synthesized. Linear structure thermoplastic degradable shape memory polyurethane is easy to process and supports re-use, but the shape memory performance is not high and can not be used multiple times. In this context, thermoplastic degradable shape memory polyurethane came into being. Thermoset degradable shape memory polyurethane is more susceptible to degradation than other materials, and the prepolymer has a star structure. This structure also gives the material more mechanical strength, so it is more widely used.

In addition to the above fields, degradable polyurethanes are used in other fields, such as packaging materials, agriculture, forestry, and gardening. According to relevant tests, polyurethane can be used as a pesticide coating material. By generating an in-situ reaction, a hydrophobic film is formed on the surface of the fertilizer, and the time and speed of fertilizer nutrient application are controlled within a reasonable range, and the amount of fertilizer used is reduced while being significantly improved. Fertilizer use rate. Even if the degradation is good, there is still controversy, but on the whole, the application of polyurethane in agriculture is conducive to protecting the soil environment and reducing pollution. According to its preparation method and design method, the existing preparation techniques in China include the following: 1. Natural polymer compound; 2. Modified natural polymer compound; 3. Plant polyol; 4 Main chain design type.

4. Preparation Process and Mechanical Properties of Bio-Based Degradable Polyurethane

4.1. Preparation and properties of castor oil-based polyurethane porous sponge

Experimental materials and equipment include: castor oil, polyethylene glycol, modified mdi, butanediol, triethylene diamine, silicone oil, deionized water, dichloromethane, homemade pbs solution, infrared spectrometer, cold field emission scanning electron microscope , vacuum freeze dryer, vacuum drying oven, precision electronic balance, blast dryer, electronic universal testing machine, etc.[2].

The preparation process is as follows: First, the raw materials are subjected to pretreatment. Castor oil, polyethylene glycol, and diphenylmethane are placed together in a vacuum drying oven to ensure the dehydration treatment of the above materials on the basis of vacuum drying in the tank. In this process, the vacuum drying oven should be kept at all times. Around 80 ° C, the dehydration time is controlled at 12 hours. After this step is completed, an appropriate amount of castor oil and polyethylene glycol are selected and placed in a three-necked flask to carry out a secondary dehydration operation. In this process, special attention must be paid to the fact that no water is present in the reactants to prevent the corresponding substances from reacting with water in the prepolymer stage; secondly, the prepolymer is synthesized. After the temperature of the three-necked flask was lowered to normal room temperature, mdi was placed therein, maintained at a temperature of 70 ° C, stirred for 90 minutes, and thus entered the prepolymerization treatment stage. Oh reacts with mdi to form a prepolymer; finally, a foaming reaction. Various types of foaming agents, catalysts, etc., are appropriately adjusted in proportion, mixed at room temperature,

and left to stand for about one minute. When the mixed liquid is clearly separated, it is placed in a mold and stirred again. The foam thus grows significantly, and finally the foaming reaction is completed, the sponge is aged at room temperature, and the mold release treatment can be carried out in about 24 hours.

The thermogravimetric analyzer was used to accurately detect the thermal stability of the above materials. The amount of the sample used during the experiment was 10 mg, the experimental temperature was controlled between 25 ° C and 600 ° C, the heating rate was 10 ° C per minute, and the nitrogen gas flow rate was 10ml per minute.

The mechanical properties of the mechanical properties were tested in terms of tensile properties and compression properties. The tensile performance test standard is “plastic tensile performance measurement method”, the test equipment is a physical property analyzer, the experimental temperature is maintained at 20 ° C, the air humidity is 65%, the average speed is 5 mm per minute, and the parallel sample index is 5. The compression performance test standard is “plastic compression mechanical properties”, the test temperature and humidity conditions are the same as above, the average speed is 1mm per minute, and the number of parallel samples is 5.

4.2. Functionalized modified castor oil based polyurethane sponge preparation

Experimental materials and equipment include: castor oil, polyethylene glycol, chitosan, glucose, homemade solution, dimethyl sulfoxide, infrared spectrometer biological microscope, microplate reader, precision electronic balance, universal testing machine, carbon dioxide incubator, etc. .

The preparation process is as follows: the preparation process of the composite poly-lysine amino acid is as follows: a certain dose of lysine powder is weighed, mixed into distilled water and continuously heated and stirred, and when poly-lysine is completely dissolved, the corresponding poly-lysine can be obtained. Acid, and the mass fraction of the solution is substantially 1%.Castor oil polyurethane sponge is placed in poly-lysine solution, the time is controlled within 24 hours, and finally washed with distilled water several times; the preparation process of composite chitosan is as follows: weigh a certain dose of chitosan powder, and mix with acetic acid The solution is continuously heated and stirred. When the chitosan is completely dissolved, the corresponding lysine solution can be obtained, and the mass fraction is also 1%.The castor oil polyurethane sponge is placed in the chitosan solution, the time is controlled within 24 hours, and finally rinsed several times with distilled water; the preparation process of the composite nano-Ag is as follows: after the appropriate amount of NaOH is dropped into the AgNO₃, the two react A white silver hydroxide material is formed and then decomposed into silver oxide and water. An appropriate amount of concentrated ammonia water was added dropwise to the solution, and the brown precipitated substance was completely dissolved, and then the solution was made up to a volume of 1 L to finally obtain a silver ammonia solution. During the foaming of the sponge, glucose is used as a foaming agent, the sponge is placed in a silver ammonia solution, and treated in a water bath. The water temperature is controlled at 40 ° C, the time is controlled for 10 minutes, and the water is washed several times with distilled water.

4.3. Preparation of new degradable polyurethane

Experimental materials and equipment include: phbv, polyethylene glycol, ethylene glycol, non-ionized water, chloroform, acetone, stannous octoate, homemade solution, infrared spectrometer, nuclear magnetic analysis instrument, thermogravimetric analyzer, vacuum drying oven, Precision electronic equality.

The preparation process is as follows: First, the PHBV is subjected to a purification treatment. Weigh a certain dose of PHBV powder, set its mass to volume ratio to 1:25, and then fuse with chloroform solution, and it is clear by magnetic stirring. The solution was filtered under reduced pressure and placed in a rotary evaporator. The filtered solution was concentrated and placed in ice methanol. This process requires the attention of the experimenter, the solution needs to gradually form a precipitate during the stirring. After proper treatment, the floc is obtained in the form of white, and the PHBV powder can be obtained by drying under reduced pressure; secondly, the spherical PHBV-diol is prepared. The purified powder obtained in the previous step is fused with

chloroform to synthesize a reagent with a mass fraction of 10%. When the solution is in a clear state, the ethylene glycol containing the catalyst is added to the toluenesulfonic acid, and the two undergo transesterification reaction. The conditions were 70 ° C and the exchange reaction time was 4 hours[3]. The remaining solution was washed three times with water washing. After standing for a while, the solution was obviously stratified, and then the liquid was filtered again, and the precipitate was placed in a vacuum drying oven to finally obtain PHBV-diol.

Each sample was made into a uniform shape, and the tensile mechanical property test standard was “Method for Measuring Plastic Tensile Properties”. The test equipment was a physical property analyzer, the temperature was adjusted to 20 ° C, the air humidity was 65%, and the average speed was 5 mm per minute. The number of parallel samples is 5.

5. Conclusion

In summary, the research on degradable polyurethane materials will be further developed in the context of the comprehensive development of green development concepts. Due to the influence of market price and production cost factors, the scale of degradable polyurethane in the market in the current stage is relatively small, but the development is extremely rapid. The existing technology in China is not yet immature, and the degree of commercialization of products is low, and systematic research must be carried out.

Acknowledgement

In this paper, the research was sponsored by National natural science foundation of China project: construction of TiO₂ based rare earth composite nanofiber heterojunction materials and degradation of pollutants (21573003).

References

- [1] Jiang Xiaotong, Jiang Yan, Zhang Wei. Synthesis and Characterization of Bio-based Degradable Crosslinked Polyurethane. *Journal of Polymer Materials Science and Engineering*, 2017, 33(11):22-28
- [2] Degradable polyurethane to rejuvenate its ingredients. *Global Polyurethane*, 2019 (08): 88
- [3] Wang Wei, Feng Hui. Analysis of Patented Technology of Degradable Polyurethane. *Jiangxi Chemical Industry*, 2019(04):171-173