Research Progress of Bio-based Nylon 56 in China

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Abstract: Nylon composites are widely used in production and life on the strength of their excellent properties. Traditional nylons were principally made from petroleum. As an emerging material, bio-based nylon has recently aroused wide concern on account of its environmental protection. This paper summarizes the research progress and main problems in the performance and application of bio-based nylon 56 in China.

1. Introduction

Nylon is one of the five most significant materials on a global scale, which can be classified into aliphatic, aromatic, polyimide, copolyamide and other categories, with a range of varieties. Currently, aliphatic nylon is widely used, of which polycaprolactam and polyhexamethylene adipamide are principally used, accounting for more than 90% of the total nylon [1]. In the traditional production process, nylons were principally made from petroleum. Since petroleum resources are non-renewable and excessive use of petroleum resources will lead to environmental deterioration, which violates the concept of sustainable development. As a result, bio-based nylon has begun to come to public attention.

Bio-based nylon 56 is a synthetic process formed by pentamethylene diamine and petroleum-butyladipic acid, which are synthesized by biological method using starch as raw materials. On the one hand, it can decrease the emission of greenhouse gases in the production process; on the other hand, it can decrease the dependence on petroleum resources by using bio-based raw materials, which is both green and environmentally friendly and can alleviate the energy crisis.

2. Physical Properties and Performance

Nylon 56 has a density of 1.14g/cm^3, while polyester has a density of 1.4g/cm^3, so if nylon 56 has the same volume, its mass will be 18% lighter than that of polyester. Hence, using bio-based nylon 56 to prepare military uniforms can tremendously alleviate the burden of soldiers.

In regards to water absorption rate, in line with the test results of Yu Weicai [2], the saturated water absorption rate of bio-based nylon 56 can reach up to 14%, which is obviously higher than that of polyester and even higher than that of nylon 66 (8%) and nylon 6 (10%). The excellent water absorption of bio-based nylon 56 not merely improves its antistatic performance, but makes it have excellent moisture absorption and drainage rate, thus tremendously enhancing the wearing comfort.

Glass-transition temperature. The glass-transition temperature of bio-based nylon 56 is significantly lower than that of nylon 66(65℃), much lower than that of polyester (75℃), which is on account of the good flexibility of bio-based nylon 56 macromolecules and the large number of polar groups in the molecular chain. This makes the bio-based nylon 56 material have low temperature resistance, and it does not make the wearer feel brittle or hard. It can be used in alpine and high altitude areas.

Strength. Yassir A. et al.[3] have studied the mechanical properties and moisture absorption properties of bio-based nylon 56. It is discovered that the strength of bio-based nylon 56 is close to that of nylon 66, which is much higher than that of polyester. When used to prepare training clothes, it boasts better wear resistance and fastness, prolongs the service life and reduces the use cost.

Softness. Cong Honglian et al.[4] studied the application of bio-based nylon 56 in the development of knitted fabrics. They found that the softness of bio-based nylon 56 is close to that of wool, which can replace polyester and wool blending and enhance the fabric quality; besides, it can also decrease the wool content, thus reducing the cost.

Crystallization. Wu Tiantian et al. have systematically studied the crystallization behavior of bio-based nylon 56. [5] They found that bio-based nylon 56 boasts obvious exothermic peaks at different cooling rates, and the rates below 30℃/min are single peaks, while the rates at 40℃, 50℃ and 60℃/min show double peaks. Fueled by the increase of the cooling rates, the crystallization peak moves to the low temperature direction, and the crystallization temperature range becomes wider. The crystallization peak appearing later becomes increasingly obvious along with the increase of the cooling rate, but on the contrary, the original crystallization peak gradually weakens. In their view, there are two reasons: first, nylon generally takes on a polycrystalline state, and the cooling rate increases in the same temperature interval, which results in shorter crystallization time under high temperature conditions while polymer macromolecules are still being folded, rearranged and piled up, and continue to produce crystals, so the crystallization interval becomes larger, the crystallization peak becomes wider, and the location where the crystallization peak is generated corresponds to a lower temperature. Second, it takes time for polymer segments to rearrange and pile up into crystal regions. The crystallization lags behind the cooling, especially the faster the cooling rate is, the more obvious the lag is, so the crystallization summit appears at a lower temperature. Hence, the non-isothermal crystallization performance of bio-based nylon 56 is tremendously affected by the cooling rate. They found in isothermal crystallization experiments that the lower the temperature, the narrower the exothermic peak of nylon 56 crystallization, the shorter the crystallization time, and the sharper the peak shape. They consider that the above phenomenon is on account of the lower free energy of nucleation and easier crystallization at lower crystallization temperature, which is conducive to the formation of crystals and accelerates the crystallization process. Conversely, the increase of crystallization temperature will slow down the crystallization, especially when the crystallization temperature is near the melting point, the micro-Brownian motion of macromolecular segments will intensify, which will hold up the aggregation and nucleation of segments, thus rendering crystallization more difficult [6]. There is an obvious exothermic peak during the heating process, i.e. crystallization behavior exists, and the crystallization degree increases with the increase of isothermal temperature, which may result from insufficient crystallization of nylon 56 during isothermal crystallization at higher temperature. Generally speaking, the increase of isothermal crystallization temperature increases the crystallization time and decreases the crystallization rate. This is because the free energy of crystal nuclei is large and the crystal nuclei generated are unstable at higher temperatures, which can not generate a large number of crystal nuclei in a short time, i.e. the nucleation rate is slow, so the overall crystallization rate is slowed down.

Deng Qinlan et al. studied bio-based nylon 56 fibers. Based on Deng Qinlan et al's observation results [7], the cross section of bio-based nylon 56 fibers is triangular, and there are no grooves in the longitudinal direction. Due to the special structure of triangular fiber cross-section, the excellent pliability of bio-based nylon 56 and its silk-like hand feel, bio-based nylon 56 can be used to weave simulated silk. The bio-based nylon 56 fiber boasts high elastic recovery rate and good durability. The reason for this is principally on account of the molecular structure of nylon 56 itself. Nylon 56 macromolecules are characterized by good symmetry and flexibility, and their molecules have high crystallinity and orientation, thus rendering nylon 56 macromolecules to have good elastic recovery rate. Apart from that, bio-based nylon 56 also possesses fairly good boiling water shrinkage, moisture absorption and desorption properties, strong elongation, and strong antistatic ability. The clothes made from it are of good wearing comfort and functionality. However, bio-based nylon 56 fibers are not resistant to strong acids and cannot be used as acid-resistant materials, because hydrogen ions in the acid will react with weakly basic amides on nylon macromolecules, breaking their amide bonds.

Dyeing properties. The dyes used in traditional nylon fibers are acid dyes, neutral dyes, disperse dyes and reactive dyes. Due to the relationship between the structure and crystal properties of bio-based nylon 56, its dyeing properties are similar to those of traditional nylon fibers to some extent, but are also different to some extent. Li Mengmeng et al.[1] have studied the dyeing properties of bio-based nylon 56 with acid dyes. The results turn out that bio-based nylon 56 is easy to dye under the action of acid dyes, boasts fairly good adsorbability, and can quickly reach dyeing equilibrium. It is derived from the odd and even carbon segments and crystalline structure of bio-based nylon 56 fibers. The current study has laid a foundation for low temperature dyeing of bio-based nylon 56. When acid dyes are used to dye nylon fabrics, the dyes are principally fixed on the fabrics by ionic bonds, hydrogen bonds and van der Waals' forces, while hydrogen bonds and van der Waals forces belong to physical adsorption, so the combination of dyes and fibers is not very firm, and the fabrics absorb the dyes quickly, resulting in more floating colors on the fabric surface, so the fading phenomenon of dyed fabrics is more serious. Yassir A. et al.[3] found through experiments that the soaping color fastness of bio-based nylon 56 fabric dyed with acid dyes is not ideal, and the staining of wool lining, nylon lining and cotton lining is relatively serious. Thus, it is necessary to develop other dyes to dye bio-based nylon 56 to solve the problems of insufficient color fastness and fading. Yu Fangli et al.[8] dyed conventional nylon with reactive dyes, thus obtaining a more optimized dyeing method. Currently, there is no research on dyeing nylon 56 with reactive dyes. In respect of dyeing performance, there is still no accurate method for dyeing bio-based nylon 56, and the research is not deep enough. It is an urgent problem to be solved on how to control the dyeing rate of bio-based nylon 56 by using existing enzymes and other substances without affecting its performance. Meanwhile, the color fastness of bio-based nylon 56 fabric after dyeing is relatively poor, and the staining of nylon fiber and cotton fiber lining is relatively serious. How to fix the color, especially for medium and dark color products, also needs more research.

3. Main Applications

Used as fabric. Clothes made of bio-based nylon 56 worn are not brittle or hard in alpine and high altitude areas. They can be used in cross-country, mountaineering, exploration, scientific research and other equipment and clothing. As for military clothing and equipment, on account of its low density and good moisture absorption and permeability, equipment made of bio-based nylon 56 material can be widely used in military combat protective clothing, tents, parachutes and other fields, which can not merely tremendously decrease the load of soldiers and make their range of activities wider, but perform field alpine and high altitude tasks. When making socks, underwear, shirts and jerseys, the bio-based nylon 56 is blended with fibers such as cotton, wool and viscose, which can make the blended fabric possess fairly good wear resistance. Apart from that, the current study discovers that bio-based nylon 56 is of certain antibacterial properties and can be applied to underwear and garment fabrics [9].

Used as plastic. Nylon is used as engineering plastic, and the most widely used field is automobile. In today's society, people's awareness of environmental protection is gradually raised, nylon materials, such as nylon 6 and nylon 66, have been used to replace various non-ferrous metals and alloy steels, which are widely used in the automotive field. Nylon is principally used in engines, electrics, car bodies and drive controllers, among which engine components[10] are used in large quantities. The application of bio-based nylon 56 instead of nylon 66 in industry, especially in the field of automobiles, requires not merely excellent mechanical properties, but a series of properties such as long-term high temperature resistance, hydrolysis resistance, chemical corrosion resistance, oil resistance, etc. The physical properties of bio-based nylon 56 are similar to nylon 66, which renders it possible to replace nylon 66. The results of Ye Shibing's research [11] turn out that the long-term high temperature resistance, high temperature resistance, chemical resistance, heat and oxygen aging resistance and oil resistance of bio-based nylon 56 are equivalent to those of nylon 6 and nylon 66, which can meet the application requirements in the field of automobiles, especially in the peripheral parts of automobile engines. However, the bio-based nylon 56 is not suitable to replace nylon 66 in the field of automobiles at present because of its good hygroscopicity, large changes in wet properties, poor hydrolysis (alcoholysis) resistance and low retention rate of tensile strength and flexural modulus. It is an urgent problem to be solved on how to solve the hygroscopicity of bio-based nylon 56 through processing, synthesis and modification.

4. Conclusion

As a new material, bio-based nylon 56 is in possession of multiple excellent properties such as good hygroscopicity and mechanical strength, low glass-transition temperature and strong antistatic ability, and it is currently principally used as fabric material. Through processing and modification, it is expected to be used in the field of automobile manufacturing in the future.

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