

Research Progress of Semi-Aromatic Copolyamides: Structure-Property Relationship



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Abstract

Semi-aromatic copolyamides owing to both possessing the machinability of aliphatic polyamides and the high temperature resistance of aromatic polyamides, were widely used in automotive and electronic fields. To better summarize the research on the structure-property relationship of semi-aromatic copolyamides, the review was carried out from three aspects: synthesis, structure characterization and structure-property relationship. The study of structure-property relationship can be applied to the modification process of semi-aromatic copolyamides, and it can shed light on the design and actual production process.

Keywords: Copolyamides; Solution Polycondensation; Sequence structure; Structure-Property Relationship

Introduction

Semi-aromatic copolyamides contain both aliphatic and aromatic segments, therefore possess some unique properties, such as high mechanical strength, high temperature resistance, chemical corrosion resistance and excellent processing performance, etc., and were widely used in automobile and electronic industry. Researchers have done a lot to improve the properties of semi-aromatic copolyamides like widen the melt processing window, enhance mechanical strength and heat resistance, so that the product can be used in harsher working environment [1,2]. The structure of semi-aromatic copolyamides has an important effect on its properties, and so changing the chain structure has become one of the important methods to improve the properties of copolyamides, and the nuclear magnetic resonance (NMR) is an important means to characterize the sequence structure [3]. In recent years, semi-aromatic copolyamides exhibit great advantages in the field of special engineering plastics, and the microstructure design of copolyamides was widely used to enhance the product performance [4].

Discussion

Synthesis Method

The mainly synthesis method of semi-aromatic copolyamides is solution polycondensation method, which is beneficial to enhance the heat and mass transfer in the polymerization process, and the

reaction is highly controllable. The solution polycondensation method can be divided into low temperature and high temperature according to the polymerization temperature. The high temperature solution polycondensation method adopts nylon salt solution for polymerization, and the production process is mature and stable [5,6]. However, due to the serious chain exchange and chain transfer in high temperature polycondensation process, it is difficult to synthesize copolyamides with specific sequence structure. Low temperature solution polycondensation method uses highly active acyl chloride and diamines dissolved in organic solvent, the reaction rate is fast and generates a lot of heat, in order to avoid side reactions, it is necessary to react in low temperature without oxygen [7].

Characterization Method

NMR is the main method to characterize the sequence structure of copolyamides. Geert et al. [8] dissolved polyamides in solvents such as D₂SO₄, TFA and HFIP etc., and used ¹H-NMR to distinguish various homopolyamides qualitatively. ¹³C-NMR analysis was used to obtain the peak position of methylene of a series of homopolyamides in the above solvents. ¹³C-NMR and ¹⁵N-NMR can distinguish the mixture of homopolyamides, and the different sequence structure of copolyamides. However, due to the occurrence of chain exchange and chain transfer in the polycondensation process, the synthesized copolyamides

commonly contain random chain segments, and the poor solubility of the copolyamides result in the unclear NMR peak [9,10].

Structure-property Relationship

The microstructure of chain segment of semi-aromatic copolyamides determines the properties of the product, and the design of the molecular structure is conducive to obtaining the corresponding target product. The regularity of the aliphatic segments on the main chain has a great influence on the crystallization properties, and chain segments containing the cis conformation unit are arranged more closely and the degree of crystallinity is better. So that the thermal stability and melt flow properties of the copolyamides with the cis conformation unit are better than those with the trans unit conformation [11]. The benzene ring in the chain segment plays a role in improving the heat resistance and reducing the crystallization property of the copolyamides. Therefore, by increasing the amount of terephthalic acid in the reaction process, the crystallization degree of the copolyamides is reduced, which is conducive to obtaining transparent copolyamides with better mechanical strength [12]. The terephthalic acid units in the chain segment will reduce the processing performance of the copolyamides. Adding asymmetric isophthalic acid units to the chain segment can obtain amorphous segments and improve the melt flow performance of the copolyamides [13].

Conclusion

As a copolycondensation product of aliphatic polyamides and aromatic polyamides, semi-aromatic copolyamides have the characteristics of both. The study of structure-property relationship has inspiring significance for the design on the microstructure of the chain segment and was widely used in the study of the modification process of semi-aromatic copolyamides. The segment design was mostly realized by introducing monomers with specific structure, which has strong controllability. However, due to the severe side reactions in the polymerization process, it is difficult to achieve industrial production of semi-aromatic copolyamides with specific sequence structure. In the foreseeable future, the improvement of synthesis methods and the enhancement of detection technology will facilitate the in-depth study of the structure-property relationship of semi-aromatic copolyamides and deepen the understanding of the micro-design of high-performance composite materials.

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