European Polymer Journal 220 (2024) 113503

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Computer-aided design of thermosetting benzoxazoles containing bis-endoalkynyl groups: Low melting points and high thermal stability

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ARTICLE INFO

Keywords:
Thermosetting benzoxazole
Screen method
Thermal stability
Processability
Dielectric property

ABSTRACT

High-temperature-resistant polybenzoxazoles (PBOs) have recently become a prominent research area due to their potential applications in aviation and aerospace. However, achieving a balance between thermal stability and processability remains a significant challenge. In this study, a computer-aided method to develop PBOs with high thermal stability and processability is explored. First, thermoset benzoxazoles (CPBOs) are designed using a material genomic approach. Subsequently, their zero shear viscosity, temperature at 50 % thermal weight loss, dielectric constant and dielectric loss are predicted using a computer-aided method. Finally, two screened thermosetting benzoxazoles, CPBO-1 and CPBO-6, are synthesized and experimentally validated. The experiments indicate that their melting points are below 100 °C, with the lowest melt viscosities being 0.5 Pa•s and 1.5 Pa•s, respectively. The corresponding polymers, pCPBO-1 and pCPBO-6, feature high thermal stability. The 5 % weight loss temperature of pCPBO-1 in N_2 is 618.9 °C, while the dielectric constant and dielectric loss are 3.1 and 0.0063, respectively. These are excellent values for thermosetting resins. This computer-aided screening method is more efficient and cost-effective compared to conventional trial-and-error methods.

1. Introduction

Polybenzoxazole (PBO) is widely used in aerospace [1–3], defence/military [4–6], and integrated circuits [7–10]. However, PBO lacks a melting point and shows poor solubility (it can only be dissolved in strong protonated acids), which limits its applications.

In general, solubility and meltability are crucial criteria for polymers to exhibit good processing properties [11–13]. However, most currently reported PBOs either lack melting points or have very high melting points. Consequently, previous studies have focused on enhancing their solubility in common solvents by modifying the molecular structure. For example, modifications have included introducing flexible alkyl chain segments, non-coplanar or bulky side groups (e.g., straight-chained olefins), thickened cycloaromatic hydrocarbons, ether bonds, and fluorine-containing groups to the PBO main chains[14–20]. A variety of crank-twisted non-coplanar structures and novel PBOs containing ether bonds were systematically studied and prepared by Yoshio et al. [21]. They demonstrated that introducing flexible groups can improve the solubility of PBO. Qian Fu et al. improved the solubility of PBO without seriously affecting its thermal stability by introducing soft bonds and rigid pendant groups [22]. Our research group suggested a new route: thermoset benzoxazoles (CPBO) instead of linear PBOs. The crosslinked groups of CPBO include alkynyl and cyano groups. In previous reports, we synthesized a series of CPBOs [23,24], which are soluble in low-boiling solvents such as tetrahydrofuran, and the corresponding crosslinked polymer (pCPBO) showed good thermal stability. However, the above thermosetting benzoxazoles lacked a melting point and could only be processed using solvent methods.

In this study, we aimed to develop new thermoset benzoxazoles that do not lack melting points while ensuring their thermal stability would not be significantly reduced. Since the alkynyl group can crosslink and form a benzene ring, which has high thermal stability, alkynyl was chosen as the cross-linkable group. In terms of molecular structure design, the traditional method involves designing molecules based on experience and then synthesising all the designed structures for verification. However, this approach is time-consuming and inefficient. The Materials Genome Approach (MGA) is based on high-throughput molecular structure design and screening. The MGA method differs from the conventional experimental trial-and-error method by emphasizing the combination of theoretical calculation and experimental validation. This integrated approach significantly enhances the efficiency of materials development and reduces resource waste[25–28]. This method has

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https://doi.org/10.1016/j.eurpolymj.2024.113503
Received 15 August 2024; Received in revised form 6 October 2024; Accepted 10 October 2024
Available online 12 October 2024