



Chain extension of polyamide 6 using multifunctional chain extenders and reactive extrusion for melt foaming

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ARTICLE INFO

Keywords:

PA6
Chain extension
Rheology
Thermal properties
Foamability

ABSTRACT

We used the reactive extrusion method to modify virgin polyamides 6 (PA6) for melt foaming. The reactive extrusion was performed with a Haake melt mixer, and the following modifiers were used: 1,1'-isophthaloyl-bis-caprolactam (IBC), 2,2'-bis(2-oxazoline) (BOZ) and an epoxy-type chain extender KL-E4370 (EP) as well as an IBC and BOZ combination. The chain extender's effects on the reactive modification were characterized through the PA6 chain's rheological properties, including the storage modulus, the loss modulus, and the dynamic complex viscosity. The EP-modified PA6 was shown to have the highest viscoelasticity; that is, the highest melt strength. The PA6's melting and crystallization properties were also investigated. A high-pressure differential scanning calorimeter (DSC) under compressed CO₂ was used to evaluate the foaming temperature windows. Finally, the foamability of the modified PA6 was verified by our batch melt foaming experiments, where supercritical CO₂ was used as the blowing agent. The EP-modified PA6 with the highest melt strength had the widest foaming window and the biggest expansion ratio.

1. Introduction

Polyamide (PA), also known as Nylon, is used worldwide in fiber, film, packaging, and molding applications [1]. It is one of the most important commercial engineering plastics [2] because it offers an attractive combination of good processability, excellent mechanical properties, and desirable chemical resistance [3]. However, due to its molecular weight and/or molecular weight distribution limitations, industrially produced PA6 is unsuitable for use in the melt foaming process because it cannot produce foams with a high expansion ratio. Such foams require a high melt viscosity/melt strength. The standard industrial polymerization processes can only produce a limited molecular weight. Therefore, solid-state polycondensation (SSP) is often employed to overcome this problem. Nevertheless, SSP is too slow, and it requires special equipment for large-scale operations [4–6]. Because of these challenges, use of a chain extender(s) is a practical option. The chain extenders are generally multifunctional compounds that are thermally stable, and non-volatile at the polymer's melting temperature. They can also react rapidly within the polymer chains' terminal groups to join two or more chains. In this way, they can change the polymer's macromolecular structure and increase its molecular weight [7,8]. Chain extenders have been widely used for the modification of such polymers as poly(ethylene terephthalate)

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<http://dx.doi.org/10.1016/j.eurpolymj.2017.09.012>

Received 6 July 2017; Received in revised form 18 August 2017; Accepted 8 September 2017

Available online 09 September 2017

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(PET), poly(butylene terephthalate) (PBT), and polyurethane (PU) [9–11]. Polyamides 6 (PA6) is also a good material for use in polymer modification because of its inherent chemical functionality [12–14].

Polymeric foams have attracted significant attention from the polymer community due to their outstanding properties. These include their light weight, thermal and acoustic insulation as well as their improved energy-absorption performance, which has given rise to the development of various microcellular foaming techniques. These techniques have been applied to such processes as batch foaming, extrusion foaming, and foaming injection moulding [15]. Turng et al. [16–21] investigated the foaming of commercial grades of modified PA6 and PA6-based composites, with the addition of fibers or nanomaterials, by using microcellular injection moulding. They found that the melt volume of the shot size greatly influenced the products' tensile strength, cell size, and density. In addition to a lower supercritical fluid content, a higher injection speed and a lower melting temperature, a moderate addition of nanomaterials helped to fabricate products with a desirable cell structure. However, the expansion ratio of the microcellular-foamed injection-molded nylon was lower than 2.

PA6 is a linear polymer made up of amide (-CONH-) repeating units. These chemical units are polymerized by the ring opening polymerization (ROP) of the caprolactam (CPL). The amino and carboxyl groups existing in the PA's molecular chain are both reactive under certain conditions. Thus, all the bi- or multi-functional compounds, which are capable of reacting with the amino group and/or carboxyl group can theoretically be chain extenders for the PA. These would include phosphides [22], bisoxazolinones [23], bisoxazolines [24–26], bisoxazines [27], and bisepoxides [28]. The PA's chain extension can be classified as either condensation-type or addition-type reaction. The addition-type chain extenders, which generate no by-products, are preferable, and these can be further classified into the amino-addition-type, the carboxyl- addition-type or a combination of the two, depending on the PA functional terminal group to which they react.

In recent years, certain chemical treatment approaches have been used to modify polyamide [29]. Loontjens et al. [30] studied the action of 1,3-phenylene bis(2-oxazoline-2) (PBO-1) and isophthaloyl biscaprolactamate on poly(ethylene terephthalate) and PA6. They found that the viscosity increase was modest when only one chain extender was used, but there was a strong increase in the molecular weight when two types of chain extenders were used. Schacker et al. [31] investigated the difference between linear chain extension with bisoxazoline and chain bundling by grafting onto the maleinated polystyrene (SMA) of the PA. They concluded that the PA's melt viscosity was greatly improved by grafting onto the SMA. This proved to be better than using the modest linear chain extension with bisoxazoline. Qian et al. [32,33] performed a detailed investigation on the chain extension of PA1010 by using 2,2'-bis-(2-oxazoline) (BOZ) and 1,4-phenylene bis(2-oxazoline-2) (PBO-2) as the modifiers. Their results suggested that the BOZ's coupling effect was superior to the PBO-2's due to the differences in their reactivity and diffusivity. Jakisch et al. [34] applied a new bifunctional coupling agent that had one oxazoline group and one oxazinone group for the chain extension of PA. They showed that the reactions of the oxazoline and the oxazinone groups with the carboxyl and amino groups, respectively, acted independent of each other and with a high selectivity. This greatly increased the PA's molecular weight. Buccella et al. [35–37] investigated the effects of 1,1'-carbonyl-bis-caprolactam and PBO-1 individually as well as in combination on the chain extension behavior and thermo-mechanical properties of the resultant PA6 materials. Lu et al. [38–40] made detailed studies of the PA6's chemical modification by chain extension using BOZ, PBO, and terephthaloyl-biscaprolactam (TBC) both separately and in combination. There was an optimal dosage for only one of the chain extenders used. A shortage of this chain extender caused incomplete chain extension and an excess of it led to more blocked reactions. The molecular weight was larger when both of two types of chain extenders were used. The thermal and mechanical properties of chain-extended products have also been investigated. Interestingly, the epoxide group experienced a relatively high reactivity with both the amino and carboxyl end-groups of the PA6 [41]. A styrene-acrylic oligomeric polyepoxide Joncryl-ADR-4368 has been used as a productive chain extender in engineering plastics. A small addition of Joncryl-ADR-4368 increases the PA6's tensile strength and melt viscosity [42]. Likewise, Alvianto et al. [43] found that the PA6's melting torque, when modified by mixing for 2.5 min with 1.5 wt% bis(glycidyl)oxy phenylphosphine oxide (BGPPPO), was about seven times higher than that of the unmodified PA6. BGPPPO includes two epoxide groups and a phosphorus-oxygen double bond, as a forceful electron-withdrawing group, which caused the two epoxide residues to connect with it [44]. On the other hand, the BGPPPO's low molecular weight (270 g mol⁻¹) might have diffused in the high viscosity polymer melt quickly. Thus, a higher than expected level of chain extension resulted [45]. However, all of these studies had focused on obtaining a PA6 with a high molecular weight, and only a few of them had tried to prepare a modified PA6 with a high melt strength for use in the foaming process.

In this study, modified PA6 with high melt strength by screening out excellent chain extenders was successfully fabricated and then was used for foaming with CO₂ as the foaming agent. The following three types of multifunctional compounds for use was chosen as chain extenders to improve the PA6's melt strength: 1,1'-isophthaloyl-bis-caprolactam (IBC), BOZ, and commercial KL-E4370 (EP). The branched samples were prepared using a Haake melt mixer. The mixer's melt torque for the PA6 and the chain extenders were recorded. A Haake Mars III was used to characterize the PA6's rheological properties so as to evaluate the amount of chain extension. In addition, we studied the non-isothermal crystallization behaviors of the modified PA6 with different kinds of chain extenders under atmospheric N₂ and compressed CO₂ by using a differential scanning calorimeter (DSC). The foamability of the chain-extended PA6 was evaluated through batch melt foaming experiments with CO₂ as the blowing agent.

2. Experimental

2.1. Materials

PA6 flakes (Ultramid® B3S grades) was purchased from the BASF chemical company, with a density of 1.13 g/cm³ and a 220 °C melting point. Three different types of chain extenders: IBC, BOZ, and EP, were purchased from the Tianjin Heowns Biochemical

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