



Transamidation determination and mechanism of long chain-based aliphatic polyamide alloys with excellent interface miscibility



Lili Wang, Xia Dong^{*}, Yunyun Gao, Miaoming Huang, Charles C. Han, Shannong Zhu, Dujin Wang

Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

ARTICLE INFO

Article history:

Received 12 October 2014
Received in revised form
13 December 2014
Accepted 24 December 2014
Available online 6 January 2015

Keywords:

Transamidation
Interface miscibility
Polyamide alloys

ABSTRACT

Transamidation between PA1012 and PA612 was investigated with combination techniques including differential scanning calorimetry (DSC), rheometry, nuclear magnetic resonance (NMR) and variable-temperature Fourier transform infrared spectroscopy (VT-FTIR). Based on the increase of storage modulus with sweep time, the presence of reactive chain ends were proved, promoting chain growth in either polyamide and interchange reaction in binary blend at high temperature. NMR and VT-FTIR testing signals sufficiently convinced the expected interchange reaction. Quantitative data analysis of DSC and NMR provided direct evidences for evaluating the exchange degree. Various experimental parameters were systematically considered, including reaction temperature and time, blending composition and categories of polyamides. Raising the reaction temperature or prolonging the reaction time would accelerate the transamidation rate and degree. The interfacial miscibility between two LCPA components could be improved by the formation of copolyamides. This work provides a quantitative evaluating method to detect the transamidation extent between two aliphatic LCPAs that overcomes the traditional characterization limitation which is only feasible for whose polyamide component chain is with large volume structure like benzene ring.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Polyamide, presented excellent mechanical and thermal properties, had become a classic important engineering thermoplastic, among which, aliphatic polyamide was generally named as nylon which firstly realized industrialization by DuPont in 1939 last century. In principle, any polyamide having more than 10 repeat units in the main chain was considered as long chain polyamide (LCPA). Due to relatively low density of hydrogen bonds in recurring amide groups, LCPA not only provided a combination of toughness, rigidity and lubrication-free performance but also possessed lower water absorption and better dimensional stability [1–3]. Consequently, based on higher aliphatic portions, it offered more benefits than common polyamide which had high level of absorbed water and hence decreased mechanical properties seriously [4,5]. Thus LCPA provided multiple potential applications in a wide range, such

as automobile manufacturing, aerospace engineering and electronic appliances [6].

Even-even LCPA is the condensation polymerization product of dicarboxylic acids with diamines, where diamines are converted by dicarboxylic acids. Usually dibasic acid currently could be obtained either by chemical synthesis method using non-renewable petrochemical feedstock which produced unwanted hazardous by-products, or by biological fermentation method using enzymes in microbial cell as catalyst to transform n-alkanes into long chain dibasic acid, which was an environmental friendly conversion process with biobased materials and mild condition [7]. Synthesis of LCPA using biological fermentation based monomers had attracted particular interest in recent years and many commercial polyamides produced in this method were available. In this article, both monomers of PA1012 and PA612 were prepared by biological fermentation method.

More recently, the application of pure polyamide was so limited considering its properties and costs, and preparation of polymer alloys had become an economic and efficient alternative to traditional synthesis of novel polymeric material, which made it

^{*} Corresponding author. Tel./fax: +86 10 82618533.
E-mail address: xiadong@iccas.ac.cn (X. Dong).

possible to add both advantages [8,9]. As far as polymer alloys are concerned, the key issue, determining success in obtaining better comprehensive properties, is miscibility of two components [10–13]. In general, polymer alloys tend to present poor thermal and mechanical properties caused by thermodynamic immiscibility and thus much emphasis should be put on the studying of the specific interaction between two components as well as corresponding improvement program [14]. In the past years, great effort has been made by researchers to study the compatibility of blends which can be manipulated by some strategies concerning about physical or chemical means. In the case of physical methods, Pang et al. [15,16] extensively studied interaction of isotactic polypropylene/polyethylene-octene copolymer (iPP/PEOc), in which, tailored mechanical properties can be obtained by controlling phase separation and crystallization processes. To compatibilize the ternary immiscible polypropylene/polystyrene/polyamide (PP/PS/PA), a polyolefin-based component PP-g-(MAH-co-St) was produced with maleic anhydride (MAH) and styrene (St) by Xie's group [17]. This multiphase component provided a novel and effective way to achieve good compatibilization. These mentioned modification methods were all without chemical structure change and could effectively improve the components miscibility. Another commonly used method, which was defined as chemical strategies, including ester–ester [18,19], ester–amide [20] and amide–amide exchange reactions, was collectively referred to as effective reactive compatibilization and had an increasing research trend. A lot of polymer alloys were involved in this research like polyamide/styrene-acrylonitrile (PA/SAN) [21], poly(butylene terephthalate)/polycarbonate (PBT/PBS) [22], and polyamide/polyamide (PA/PA) [23–27]. Among polyamide alloys, researches based on semi-crystalline aliphatic polyamide and amorphous aromatic polyamide blends are mainly performed. G. Groeninckx et al. systematically studied the transamidation occurring in polyamide-4,6/polyhexamethylene isophthalamide (PA46/PA6I) blends under molten state. According to the theory developed for polyesters that in all triads the substitution on the left of a central unit does not influence the substitution on the right, number-average block length and degree of transamidation were calculated [23–25]. In order to determine the chain architecture in exchange reactions of polyamide mixtures, different measurements were used. According to that NMR signals have great sensitivity to aromatic polyamide structure with large volume sturture [28], Eersels et al. characterized structure change and degree of randomness by means of high resolution carbon nuclear magnetic resonance (^{13}C NMR) and gradient elution chromatography (GEC) [23–25]. By means of proton NMR (^1H NMR), Micaela Vannini et al. distinguished the various sequences in copolyamide efficiently and simply [26]. As reported by Giorgio Montaudo et al., thanks to matrix-assisted laser desorption ionization-time-of-flight (MALDI-TOF) MS, copolymer formed in situ and its block length in polyamide alloys were accurately analyzed [29,30].

However, since the primary structure of aliphatic polyamide, particularly for LCPA, is mainly composed of methylene units and insoluble in most common solvents, traditional characterization methods like NMR and MALDI-TOF are difficult to distinguish aliphatic copolyamides in exchange reactions. Under this condition, little information is available in previous reports for elucidation of chemical interaction for aliphatic polyamide alloys in molten state. In the present paper, to obtain polyamide alloys with high performance, fundamental understanding of chemical interactions and corresponding effect on miscibility of long chain-based polyamides is required, in which polymer blending was adopted to manufacture mixtures. Moreover, particular attention was given for polyamides of PA1012/612. To overcome the characterization limitation, DSC, NMR, and variable-temperature FTIR were combined to

comprehensively analyze factors influencing interactions of two polyamides, giving quantitative information about exchange reaction. Simultaneously, mechanisms of improved interface miscibility in aliphatic LCPA alloys were put forward.

2. Experimental

2.1. Materials and sample preparation

Polyamide 612 (PA612, $-\text{[HN(CH}_2)_6\text{NHCO(CH}_2)_{10}\text{CO]}_n-$) and polyamide 1012 (PA1012, $-\text{[HN(CH}_2)_{10}\text{NHCO(CH}_2)_{10}\text{CO]}_n-$) were synthesized from hexamethylene diamine, decamethylene diamine and dodecanedioic acid whose monomers were produced with microorganism fermentation method. The chemical structures of two polyamides were given in Scheme 1 from which it could be obviously seen that PA1012 owns longer diamine chain than PA612. Fundamental physical characterization of four polyamides (PA66, PA610, PA612, PA1012) mentioned in this work was shown in Table 1. All long chain polyamides were commercial grade supplied by Shandong Guangyin New Materials Co., Ltd.

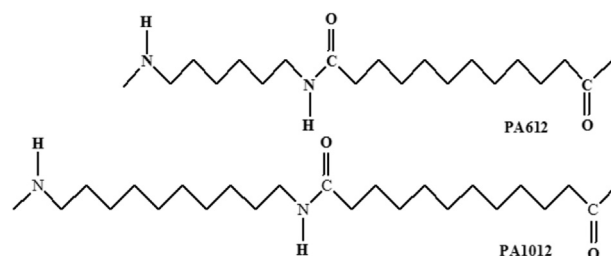
Dissolution-precipitation method was used to prepare various polyamide alloys. In this process, trifluoroacetic acid (TFA) and deionized water were used as a common solvent and a poor solvent respectively. Two polyamides were added into TFA vigorously stirring for 10 h, followed by slowly pouring the solvent into deionized water. After precipitation, the blends were intensively washed with deionized water for several times and subsequently dried under vacuum at 60 °C for 72 h until a constant weight was reached. The pure PA612 and PA1012 undergone the similar treatments stated above so that all materials kept the same initial state. In this paper, the weight ratio of polyamide alloys was used to express blend composition. (PA1012/612 50/50 denotes weight fraction of PA1012 is 50% in polyamide mixtures.)

2.2. Measurements

Thermal behaviors of polyamide alloys were measured by Differential Scanning Calorimeter (TA Q2000) which was calibrated in indium standard. Each specimen of about 7 mg sealed in an aluminum pan was tested under N_2 atmosphere at a constant flow rate. All the measurements recorded the first cooling and the second heating runs.

The glass transition of polyamide was determined by a Dynamic Mechanical Analyzer (DMA Q800). The specimens with the dimensions of 6 mm \times 4 mm \times 0.1 mm (length \times width \times thickness) were held by vertical clamps subjected to tensile modes. Measurements were conducted over a range of -100 °C to 150 °C with a heating rate of 3 °C/min under a constant frequency of 1 Hz.

The ^1H NMR spectra were collected on a Bruker DMX 300 instrument equipped with a BBO double-resonance probe at ambient temperature. The samples were dissolved into trifluoroacetic acid (20 mg/ml) which served as solvent and locking agent. The spectra were acquired after accumulating 128 scans with a digital



Scheme 1. Chemical structure of repeat units for PA612 and PA1012.

Download English Version:

<https://daneshyari.com/en/article/5180537>

Download Persian Version:

<https://daneshyari.com/article/5180537>

[Daneshyari.com](https://daneshyari.com)