



Interplay between chemical structure and ageing on mechanical and electric relaxations in poly(ether-*block*-amide)s

Silvia Todros^a, Arturo N. Natali^a, Matteo Piga^b, Guinevere A. Giffin^{b,1}, Giuseppe Pace^{b,c}, Vito Di Noto^{b,*}

^aCentre of Mechanics of Biological Materials, Department of Industrial Engineering, University of Padova, Viale G. Colombo 3, I-35131 Padova, Italy

^bDepartment of Chemical Sciences, University of Padova, Via Marzolo 1, I-35131 Padova, Italy

^cIstituto di Scienze e Tecnologie Molecolari ISTM-CNR & INSTM, via Marzolo 1, I-35131 Padova, Italy

ARTICLE INFO

Article history:

Received 22 October 2012

Received in revised form

19 March 2013

Accepted 21 March 2013

Available online 26 March 2013

Keywords:

PEBAs

Block copolymer

Broadband Electrical Spectroscopy

Molecular relaxation

Polymer degradation

ABSTRACT

The molecular relaxations of two poly(ether-*block*-amides) with different polyamide/polyether ratios were studied to evaluate the effect of the chemical structure on the mechanical and electrical properties and to investigate the modification of these properties by an ageing process at high relative humidity. A specific treatment is designed to simulate an accelerated degradation of the material to evaluate the effect of freezing and melting thermal cycles of residual adsorbed water. The effects of the polyamide/polyether ratio on the polymer properties and the consequences of the degradation treatment are studied by correlating the results of FT-IR, TGA, DSC, DMA and BES.

The analysis of DMA and BES data highlights the presence of various relaxation events: α_{PA} , α_{PE} , β_{PA} , β_{PE} and γ , assigned respectively to polyamide (α_{PA}) and polyether (α_{PE}) glass transitions, local fluctuations of the dipole associated with the polyamide (β_{PA}) and the polyether (β_{PE}) chains and local fluctuations of the CH_2 groups (γ) along the polymer chains.

The ageing treatment results in an increased crystallinity in PEBAs with a high polyamide content due to the transition of the polyamide chains from a parallel to anti-parallel β -sheet conformation which forms a stronger hydrogen bonding network. In contrast in PEBAs with high polyether content, the ageing treatment induces the transition of polyamide chains from a parallel β -sheet to an α -helix conformation resulting in the formation of weaker inter-chain interactions.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Poly(ether-*block*-amides) (PEBAs) are thermoplastic elastomers which offer a broad range of performances in terms of mechanical and chemical properties and can be easily diversified in a controlled manner by varying the copolymers' block lengths. For this reason, they are finding extensive technological application in the fields of sports equipment, biomedical devices and automotive and telecommunication components [1]. Despite the widespread diffusion of commercial PEBAs, their application is not always accompanied by a deep comprehension of their molecular dynamics under operating conditions and a reasonable prediction of the effect of such conditions on the materials performance. In particular, when PEBAs are used for competitive sports equipment in extreme atmospheric conditions, i.e. snow and cold temperatures, safety is a

crucial point and understanding the effects of ageing on mechanical, thermal and chemical properties is of vital importance.

PEBAs are segmented block copolymers consisting of linear chains of hard polyamide (PA) blocks bridged by flexible polyether (PE) blocks. The connections between the different blocks are ester groups, as shown in Fig. 1. Such covalently bonded chain segments are incompatible due to the different types of intermolecular interactions occurring in the PA and PE domains. The PA chains, which are characterized by a higher permittivity, are reticulated via inter-chain hydrogen bonding interactions and result in harder domains. The real part of the relative permittivity of polyamide 12 is 3.1 at 105 Hz at 30 °C [2]. In contrast, the PE chains that have a lower relative permittivity ($\epsilon_{\infty} = 2.5$) [3] interact via weaker dipole–dipole interactions to give domains that are more flexible. These differences in the inter-chain interactions can produce segregated micro-phase domain morphologies [1]. However, the PA domains act as junctions of physical cross-linking for the flexible PE domains [4].

The mechanical properties of these polymers are expected to respond to modifications in either the hard blocks or soft segments

* Corresponding author. Tel./fax: +39 (0)498275229.

E-mail address: vito.dinoto@unipd.it (V. Di Noto).

¹ Present address: MEET Battery Research Center, Institute of Physical Chemistry, University of Muenster, Corrensstrasse 28/30, 48149 Münster, Germany.

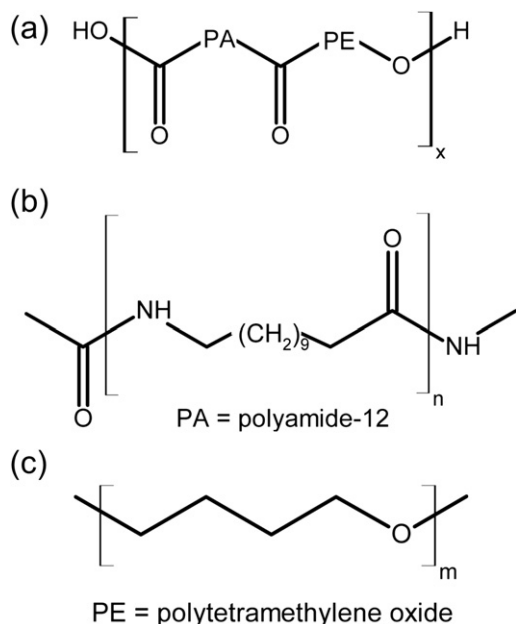


Fig. 1. Structure of poly(ether-block-amides) (a), where polyamide 12 is the PA block (b) and polytetramethylene oxide is the PE block (c).

[5]. The lower temperature region, generally below -50°C , seems to be primarily influenced by the degree of flexibility of the PE segments, while the higher temperature relaxation region, between -50 and 175°C , is controlled mainly by the length of the rigid PA segments. At temperatures higher than ca. 175°C , the PA domains begin to melt and mechanical properties gradually decline [1].

PEBAs were introduced in the early 1980s by Atochem, with the trade name of PEBAX[®] [6]. Various polyamides (such as nylon 6, nylon 11 and nylon 12) have been used as the PA block, while polytetramethylene oxide (PTMO), polypropylene oxide or polyethylene oxide have been used in the PE block. Polyamide 12 and PTMO are used in PEBAX[®] xx33 series, where xx represents the shore *D* harness of the material [7].

The solid state structure and properties of the PEBAX[®] xx33 series have been extensively studied [8,9] through various characterization techniques to reveal the morphological features of the series. Sheth et al. [8] found a micro-phase separated morphology that is strongly influenced by the PA/PE ratio over a broad temperature range. Ghosh et al. [10] studied the thermal and thermo-oxidative degradation of PEBAs with different hard and soft block lengths at different times and temperatures. They also addressed the electric properties of PEBAs with different PA/PE ratios through electrical spectroscopy but only over a small frequency range (10^3 – 10^5 Hz) [11]. Their results revealed three different transitions in the $\tan \delta$ spectra as a function of temperature, which they assigned as α , β and γ . The α transition was related to PA segment glass transition, the β transition was believed to be a combination of the glass transition of PE segments and the dipole relaxation of the amorphous PA domains, while the γ transition was attributed to the motion of the $-\text{CH}_2-$ units present in both the PA and PE blocks. The α and β transitions were found to shift with the PA/PE ratio, while the γ transition remained unaltered. The electrical properties of PEBAs, in correlation with dynamic mechanical analysis (DMA) and thermal analysis, have never been extensively investigated. Moreover, the functional properties of PEBAs under operating conditions and the effect of such conditions on the materials performances have not been evaluated.

In many cases, especially in the field of winter sports equipment, PEBAs materials are intended to operate in conditions of low temperature and to come into contact with water in a solid–liquid state (i.e. snow). In a wet environment, water can diffuse into the bulk polymer as an adsorbed molecule where it interacts with polymer chains via dipole–dipole or hydrogen bonding interactions. Repeated thermal cycling, i.e. freezing and melting of the adsorbed water, can significantly deteriorate the crystalline structure of the amide block, and consequently, the mechanical properties of the material. Thermal cycling processes frequently occur in equipment for winter sport applications such as ski boots.

It is essential to achieve a deep comprehension of the mechanical and electrical properties of PEBAs under operating conditions and to consider the effect of intensive use in extreme atmospheric conditions such as cold temperatures and in the presence of snow. Understanding the molecular relaxations characterizing the molecular dynamics of PEBAs will permit the design of materials that are tailored to the functional properties required for each specific application.

The aim of this work is to analyse in detail the assignment of the thermal, mechanical and electrical relaxation events of PEBAs over a broad range of temperatures. Moreover, the effect of the environmental conditions on materials stability is evaluated, particularly the role of water on the structure and properties of PEBAs with different PA/PE ratios. For this purpose, a specific ageing treatment was designed to simulate accelerated degradation of the material under high humidity conditions, causing water adsorption and evaluating the effect of freezing and melting thermal cycles of residual adsorbed water.

The high temperature ageing of PEBAs has been previously studied by some authors [10,12,13]. Ghosh et al. [10] treated PEBAs with varying block lengths for different times (24–72 h) and temperatures (100 – 130°C) in air: they concluded that polymers with high PA contents were less susceptible to ageing than PEBAs with a high PE amount since oxidative degradation generally affects the PE blocks first. In contrast, Dixon and Boyd [12] aged a single PEBA of the xx33 series at temperatures between 18 and 85°C for times equivalent to about 48 weeks at room temperature: they found an increased crystalline degree in the aged samples and oxidative damage leading to chain scission primarily in the PA segments.

The effect of high temperature ageing on polyamides has been widely reported in literature [14–16]. It is well established that under severe conditions or at elevated temperatures polyamides react with oxygen, which abstracts a hydrogen atom from the methylene group vicinal to the NH and results in the scission of alkyl-amide N–C or vicinal C–C bond [14]. Moreover, polyamides are known to be particularly affected by water uptake, due to the hydrophilic character of the amide functionality, where the moisture causes plasticization and has a profound effect on the mechanical properties of the polymer [17,18]. However, the effect of freezing and melting thermal cycles of residual adsorbed water on the mechanical and electrical properties PEBAs, which is of crucial importance for the application of this material in ski boots, has never been investigated before.

In this work, degradation effects were studied by correlating the results of different techniques, such as FT-IR, TGA, DSC, DMA and Broadband Electrical Spectroscopy (BES). BES has proven to be a powerful technique to study the dynamic properties of materials, primarily due to the wide frequency range that can be explored. Electrical studies combined with structural characterization and dynamical mechanical analysis significantly contribute to the elucidation of the structure–property relationships and highlight the molecular dynamics of PEBAs with different chemical structures over a wide range of temperatures.

Download English Version:

<https://daneshyari.com/en/article/5202126>

Download Persian Version:

<https://daneshyari.com/article/5202126>

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