European Polymer Journal xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

European Polymer Journal

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

Nanostructure of thermally aged thermoplastic polyurethane and its evolution under strain

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ARTICLE INFO

Article history:
Received 25 October 2015
Received in revised form 22 November 2015
Accepted 23 November 2015
Available online xxxx

Keywords:
Polyurethane
Thermal ageing
Tensile testing
SAXS monitoring
Structure evolution
Hard domains

ABSTRACT

A polyether based thermoplastic polyurethane (TPU) containing 43 wt.% hard domains is aged in air at 150 °C for 15 and 36 days, respectively. Straining of the samples (0 d, 15 d, 36 d) is monitored by small-angle X-ray scattering (SAXS). Visual inspection of the chord distribution functions (CDFs) guides to a model for the fitting of the longitudinal projection of the fiber scattering. This model comprises two components: isolated hard domains (solos) and hard domains which are arranged with respect to a next neighbor (duos). Aging increases the average size of the hard domains (HD) (0 d:5, 15 d:8, 36 d:7 nm) and the average distance between them (0 d:3, 15 d:6, 36 d:9 nm). It decreases the volume fraction of HD considerably. The probable mechanism is selective degradation of the smaller hard domains. With increasing strain the relative loss of HD is the same for all samples. Aging softens the HDs. Softened HDs lengthen when the sample is stretched. They are destroyed before the rigid ones. HD-lengthening is identical for sample 15 d and 36 d. Only with the aged materials small strain causes HDs to migrate from the random to the arranged component – and back at higher strain. Sample 36 d breaks at strain 1.5, whereas sample 15 d resists. Here the soft-domain height doubles suddenly at strain 1.2. The indicated mechanism is disruption of each second HD.

1. Introduction

1.1. General

Polyurethanes (PUs) are prevalently used both in industry and in everyday life. Thus it is not surprising that the relationship between structure and properties is widely discussed in the literature, and that there are many studies on the effects of thermal aging.

Thermoplastic polyurethanes (TPUs) are a subcategory of the polyurethane elastomers (PUE), namely the portion which can be melted and processed. Elastic are these materials due to their two-phase morphology. A soft phase makes the TPUs deformable. Embedded hard domains act as physical crosslinks. The combination of these characteristics provides the materials elastomeric properties. With PUs the topology is usually much more distorted than with comparable other

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http://dx.doi.org/10.1016/j.eurpolymj.2015.11.027
0014-3057/

polymers. For example, the shape of the hard domains cannot generally be described by simple bodies (lamella, cylinder, sphere). Microscopic images often show only a grained [1] morphology. An arrangement of these grains can be guessed at most. The small-angle scattering, however, shows a wide long-period peak. Thus some rudimentary order exists. The respective topology may be quantified by fitting the scattering data to an appropriate morphological model.

Thermal aging tests are most frequently carried out in air at elevated temperature. They are used to assess lifetime or a loss of the functionality of the material. Closely related to aging is annealing. It is carried out in vacuum or in an inert atmosphere. The goal of annealing is, in general, a maturation of the morphological structure.

It is not a simple task to quantify the effect of aging on an already blurred morphology. This may be the reason that there are not so many reports on the influence of aging on the two-phase morphology of PU. Comparing their number with the number papers on the general subject of aging of polyurethanes, the quantification of morphological modifications appears as a field in which there are still some gaps to be closed. In particular, we have found no studies in which both the morphology of the TPU and its response to mechanical load are characterized as a function of aging duration. The corresponding effects are in the focus of our present study.

1.2. Reviews

A comprehensive review [2] is devoted to the question as how to increase the thermal stability of PU materials. The authors conclude that the thermal decomposition of PU affects the hard domains first, because their building blocks, the hard segments, are attacked early. Yong He et al.[3] present a review on the structure and morphology of polyurethanes. They write that the hard domains do not only act as reinforcing fillers, but also improve the thermal performance of the material. Other reviews consider aging under biological conditions [4] or focus on the optimization of morphology and thermal stability by tailoring of the chemistry [5,6].

1.3. Annealing studies in original literature

Kazmierczak et al. [7] anneal TPUs for 2 d in vacuum between 80 °C and 167 °C and study the morphology by SAXS. They cannot detect significant effects on the topology. Martin et al. [8] anneal TPUs under nitrogen atmosphere for 10 h between 80 °C and 170 °C and carry out a SAXS study. At 150 °C and 170 °C some thermal degradation is already observed. Temperatures between 80 °C and 100 °C appear to be the best choice for a maturation of the two-phase morphology. Castagna et al. [9] anneal polyureas for 8 h under vacuum at 120, 150, and 170 °C and study the isotropic materials by atomic force microscopy (AFM) and scattering methods. From the 120 °C experiment they conclude that the maturation transition happens above 70 °C and demonstrate that it is not only temperature dependent, but also a function of time. Yanagihara et al. [10] anneal a TPU with a hard-segment content of 43 wt.% in vacuum for 16 h between 40 and 160 °C and study the isotropic material by scattering methods. They fit the SAXS curve by a Percus–Yevick [11] model assuming hard domains of ellipsoidal shape in order to be able to draw conclusions on the hard-domain growth direction. In the Percus–Yevick model the domains are placed almost at random, and in the model the observed long-period peak is imprinted by an interaction potential. Yanagihara et al. find that the additional consideration of a domain-size distribution overstrains the fit and spoils the significance of determined parameters.

1.4. Thermal aging in original literature

Tang et al. [12] age a TPU at low temperature (40–70 °C) for up to 300 days. Its composition is quite similar to that of the original material of our present study. They report that the phase separation decreases with increasing duration of the aging. On the other hand, Gibson et al. [13] report increased phase separation and an increase of the domain sizes. They age similar materials at high temperature (90 °C and 150 °C), study the morphology by small-angle X-ray scattering (SAXS) and analyze their data by means of the general [14] correlation function approach.

Huitron-Rattinger et al. [15] study a TPU of completely different composition compared to ours. They subject the material to 7 temperature cycles (oscillation between 20 °C and 180 °C). The morphology of the aged material is studied by SAXS. The authors find domain enlargement.

Madkour and Mohamed [16] age a series of TPUs at 100 °C for intervals between 2 days (2 d) and 14 d and study the resulting morphology by SAXS. SAXS curves of the isotropic materials are fitted by various models. The best-fitting model is defined by almost random arrangement of spherical hard domains according to Percus–Yevick [11]. The aging alters the morphology, but not the thermal stability. The hard domains grow.

Tian et al. [17] study isotropic TPU (Estane 5703) aged at 70 °C for 60 d in dry and wet air, respectively, by means of small-angle neutron scattering (SANS). Several models are fitted to the curve. The best fit is obtained by the Percus–Yevick [11] model of spherical hard domains under consideration of a diameter distribution. The analysis returns a growth of the hard-domain size from 2.3 to 3.8 nm, and a growth of the next-neighbor distance from 8.4 to 10.6 nm.

Two papers [18,19] find that the first stage of thermal degradation affects the hard segments. Mass loss and degradation of the mechanical properties are observed in the second stage, when the soft segments degrade.

Boubakri et al. [20] age a TPU in air for up to 270 d at 70 and 90 °C. They carry out tensile tests and find that aging increases the rigidity of the material.

Please cite this article in press as: X. Li et al., Nanostructure of thermally aged thermoplastic polyurethane and its evolution under strain, Eur. Polym. J. (2015), http://dx.doi.org/10.1016/j.eurpolymj.2015.11.027