Diffusion-limited oxidation of polyamide: Three stages of fracture behavior

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ABSTRACT

Polyamides (PAs) frequently experience diffusion-limited oxidation (DLO) under elevated temperatures due to their combination of relatively high oxygen barrier properties and high susceptibility to, and rate of, oxidation; under DLO conditions, oxidation is uneven and limited to a thin surface layer. In this study, the reduced extensibility/embrittlement of unstabilized PA6 under DLO conditions was understood by revealing DLO-induced fracture behavior. The DLO was induced by thermally ageing PA6 samples at 180 °C; the built-up of the thin oxidized layer by ageing was revealed by infrared microscopy. Notably, the formation of the thin oxidized layer significantly reduced the strain-at-break. Depending on whether the oxidized layer was brittle, two types of surface behavior (voiding and cracking) occurred during the tensile tests, which in turn lead to three types (stages) of tensile fracture behavior. In particular, in the early stage (Stage I) of ageing, the fracture was caused by a long crack formed by the coalescence of adjacent surface voids, leading to a decrease in the strain-at-break from 300% to 30%. In Stage II, multiple surface cracks, which initiated in the oxidized layer, was arrested by the interface between the oxidized and unoxidized material, leading to an almost constant strain-at-break (at or close to the necking strain). Maximum brittleness occurred in Stage III, where a more extensive oxidation of the oxidized layer initiated cracks with high propagation rate, causing the interface to be unable to arrest the cracks.

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1. Introduction

Thermal oxidation has always been a major concern for polymers used in long-term applications because it ultimately leads to brittleness and failure [1–6]. Oxidation-induced chain scission, causing a molar mass decrease below a critical value, leads to embrittlement [7,8]. In semi-crystalline polymers chain scission is particularly critical when it occurs in tie molecules and trapped entanglements, since this has an important impact on the covalent continuity between the adjacent crystallites. Another important effect of solid-state oxidation is chemi-crystallization, which leads to an increase in crystallinity and crystal thickness [9,10].

Oxidation of polymers is often uneven and limited to a thin surface layer due to diffusion-limited oxidation (DLO) [11–14]. DLO occurs when the oxygen consumption rate exceeds the oxygen diffusion rate (oxygen supply rate). The oxygen, permeating into polymers from the surrounding phase, is primarily consumed in the oxidation of the surface layer and does not reach the interior of the sample under DLO conditions, resulting in surface-dominated oxidation [8]. DLO has been commonly observed after ageing under various conditions (e.g., high temperature, and UV– and gamma-radiation) for many types of polymeric materials [15–17]. Generally, the degree of DLO depends strongly on temperature, becoming more pronounced at elevated temperatures [18]. The DLO behavior is a key contributor to the divergence between high temperature accelerated testing (for predictive purposes) and the ageing behavior with a more spatially even oxidation under service conditions (at lower temperatures) [8,19,20].

Samples aged under DLO conditions show a brittle oxidized surface layer, whereas the bulk of the material remains ductile. The

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mechanical performance, particularly the fracture behavior, of the skin-core structure formed under DLO conditions has so far not been thoroughly studied. In practice, the oxidized "skin" can be very thin. For instance, Hu et al. [21] reported that after 4200 h of ageing at 100 °C, the oxidized layer in polydicyclopentadiene was 120 μm, corresponding to 1.5% of the sample thickness. On the other hand, Pourmand et al. [22] showed that the oxidized layer, for ethylene propylene diene monomer rubber seals aged at 170 °C for 100 h, was 1.5 mm thick, accounting for 7.5% of the sample thickness. It should be noted that reported DLO thicknesses depend on how DLO is measured and how the oxidation border is defined.

Polyamides (PAs), a group of engineering polymers commonly used in textiles and vehicles, are intrinsically susceptible to oxidation due to weak carbon-hydrogen bonds of the methylene group next to the nitrogen [23]. Polyamides with high content of the amide group (e.g. PA6) are also relatively good oxygen barriers. Hydrogen bonds, frequently occurring in PA6, act as obstacles for diffusion of gas molecules [24]; the oxygen permeability coefficient of PA6, polypropylene and low-density polyethylene, at 30 °C, is $\sim 0.028 \times 10^{-10}$, 2.3×10^{-10} and 5.5×10^{-10} cm^3 cm/(cm^2 s cm Hg), respectively [25]. Due to the incorporation of polar/hydrogen bonding groups (carbonyl groups) and a crystallinity increase (chemi-crystallization) during oxidation, it is likely that the gas permeability of the oxidized layer decreases with increasing ageing time. As a result, DLO is commonly observed for PAs under various service and accelerated ageing conditions [18,23]. Gijsman et al. [18] reported that PA6 showed DLO at a wide range of temperatures (120−180 °C). In a previous study, DLO was observed in the PA6 inner layer of a fuel pipe when exposed to mixtures of biodiesel and diesel [26]. However, there are only a small number of articles focusing on the DLO of PAs, and they do not reveal the mechanical property effects of the formed oxidized layer on the polyamide samples [18,27,28].

In this study, we investigated the surface-induced embrittlement process of PA6 under DLO conditions. Practically, it would correspond to thermally accelerated testing or service under a limited high-temperature exposure under unloaded conditions. To reduce the complexity of oxidation in the presence of antioxidants, pure thermal ageing was considered for an antioxidant-free PA6. Oxidation profiles were obtained by infrared (IR) microscopy, which confirmed that the unstabilized PA6 experienced a pronounced DLO under thermal ageing at 180 °C, leading to the formation of a thin oxidized layer. The influence of the thin oxidized layer on the strain-at-break followed a scheme of three stages of fracture behavior, depending on the core-skin structure and the brittleness (degree of oxidation) of the skin layer. This investigation provides new insight into the embrittlement process of PAs under DLO conditions.

2. Experimental section

2.1. Materials and sample preparation

Unstabilized polyamide 6 (PA6), having a trademark of Akulon F136 and a density of 1130 kg/m^3, was supplied by DSM Engineering Plastics, the Netherlands. The polymer was molded into type 1BA tensile bars (ISO527-2-1BA) with a thickness of 2 mm using an injection molding machine (Boy XS V, Boy Machines, Postfach, Germany) with temperatures of 285 and 290 °C in the screw zone and nozzle, respectively. Prior to injection molding, the PA6 material was dried at 100 °C for 12 h under vacuum. After the injection molding, the obtained tensile bars were further dried at 100 °C for 24 h under vacuum, where the samples were protected from oxidation. The dried specimens were kept in a desiccator containing silica gel at room temperature before ageing.

2.2. Oven ageing

The dried tensile bars were hung on aluminum stands and aged in dry air (<1% relative humidity (RH)) in an ULE-600 ventilated oven (volume = 256 L; Memmert GmbH & Co., Germany) at 180 ± 1 °C for different periods of time, up to 48 h. The samples were positioned to avoid direct airflow from the gas inlet. The linear airflow rate was ca. 1 m s^{-1}, and the air replacement rate was 10000 L h^{-1}, corresponding to an oven volume replacement of 40 times each hour [22].

2.3. IR microscopy

The degree of oxidation at different depths in the aged samples was determined using a Perkin-Elmer Spotlight 400 FTIR imaging system equipped with a liquid-nitrogen-cooled mercury-cadmium-telluride detector. Thin slices were prepared by cutting along the cross-section of the aged tensile bars. Using double-sided adhesive tape, the thin slices of the aged samples were fixed on a metal microscopy slide, which was placed on the stage of the IR microscope. ATR image data were acquired with a pixel size of 6.25 μm at a resolution of 8 cm^{-1}, with eight consecutive scans at a wavenumber range of 4000 to 700 cm^{-1}. The area of the sample was imaged over 400×100 μm^2, where 400 μm is the length of the images parallel to the sample depth direction (ATR imaging mode). Acquisition of an image consisting of 1024 spectra took 7 min. For comparison, the unaged sample was also assessed under the same conditions.

The IR absorption bands in the 1690-1760 cm^{-1} region are due to carbonyl groups formed during the ageing (oxidation products, i.e., carboxylic acids at 1756 and 1711 cm^{-1} and imides at 1734 cm^{-1}) [29]. The carbonyl index (CI) was determined as the ratio of the integrated oxidation band between 1695 and 1760 cm^{-1} and the reference band at 1193 cm^{-1} (between 1220 and 1182 cm^{-1}), which was found to be insensitive to oxidation [27,30]. One example of the CI calculation is presented in Fig. S1.

2.4. Gel fraction measurements

The gel fraction of the aged PA6 samples was determined by gravimetry. PA6 blocks of ca. 150 mg, evenly cut along the cross-section from the middle part of the aged tensile bars, were dissolved in m-cresol and then filtered through a polypropylene filter (pore size of 45 μm). The filter was washed with pure m-cresol and acetone, and weighed after being dried for 48 h at 70 °C in a vacuum oven. The gel fraction was calculated as the ratio of the sample mass of the dried insoluble sample collected on the filter and the initial sample mass.

2.5. Differential scanning calorimetry (DSC)

The change in crystallinity by ageing was assessed using a Mettler-Toledo DSC 1. Pieces were evenly cut along the cross-section of the specimen and placed in a 40 μL aluminum cup. The sample was heated from 20 to 250 °C at a rate of 10 °C min^{-1}. All measurements were carried out in dry nitrogen with a gas flow rate of 50 mL min^{-1}. The degree of crystallinity was calculated by dividing the melting enthalpy with the melting enthalpy of 100% crystalline PA6 (190 J g^{-1}) [31,32]. For the measurement of the glass transition temperature, samples were heated between −40 and 120 °C at 10 °C min^{-1}.

2.6. Weight measurements (thermogravimetry (TGA) and balance)

The weight of the sample during the 180 °C ageing was made on a balance (XR205-DR, Precisa) by intermittently removing the