Yield stress changes induced by water in polyamide 6: Characterization and modeling

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ABSTRACT

This paper considers the effect of water content on mechanical properties of polyamide 6 when used in a humid environment. First an experimental section presents the tensile behavior of polyamide with different amounts of water, with and without a through-thickness water gradient. Water profiles are introduced by immersion in sea water at 25 °C. The effect of testing temperature is also investigated in order to consider the influence of macromolecular chain mobility on the mechanical behavior. Then, in a second section, modeling of yield stress is proposed based on physical considerations. This can be used for life time prediction of PA6 in humid environment when plasticization is the main degradation mechanism.

1. Introduction

Polyamides are widely used due to their intrinsic properties such as processability, repairability, and low cost [1—3]. Despite this extensive use, polyamide 6 (PA6) undergoes different types of degradation that lead to large modifications of its mechanical properties during service. For example, PA can become brittle due to oxidation [4,5]. Considering now humid environment, two main types of degradation can occur; first, plasticization of the polymer occurs due to water diffusion from the external environment into the polymer. This physical degradation induces a large decrease in mechanical properties such as stress at yield or modulus [6—8]. The second mechanism is the hydrolysis of the molecular backbone in PA. This chemical degradation leads to chain scission in the polymer and also results in significant changes in mechanical properties [9—11], but this degradation mechanism will not be considered in this paper. In fact, ageing times are short enough here to avoid any hydrolysis of the polymer, in order to focus only on plasticization [9,10].

The presence of water in PA6 leads to a large modification of mechanical properties induced by an increase in the mobility of macromolecular chains. This increase in mobility leads to a decrease in both Young's modulus and yield stress, whereas elongation at break is increased. For example, Silva et al. found a decrease of 80% in modulus when PA6 was saturated with water at 20 °C. Despite this large change in mechanical properties induced by the presence of water, the use of polyamide 6 in a marine environment is still attractive, provided that we are able to predict the long term decrease in yield strength. This is especially important when structures are thick, with heterogeneous water content through their thickness.

In a previous paper [12] a new model to describe water absorption was proposed. It was shown that water absorption in PA6 cannot be described by a simple Fickian behavior due to changes in water diffusivity with water activity when the polymer goes from the glassy to the rubbery state; this behavior is known as case II diffusion [13]. The proposed model involves a step by step process; first the local water content in the polymer is described. Then, an evaluation of the local T_g is made based on the Sihma-Boyer equation [14,15]. And, finally the local diffusivity of water is calculated as follows: When the polymer is in the glassy state, water diffusion depends only on temperature and can be described using an Arrhenius expression [16]. Whereas when the polymer is in the rubbery state water diffusion depends on both temperature and water activity, in this case diffusivity is successfully described by the free volume theory [17—20]. The proposed model has been validated using comparison with water absorption measurements on 2 mm thick samples immersed in sea water at temperatures

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Table 1
Main physical characteristics of the PA 6 studied here.

Properties	Values
Density	1130 kg m^{-3}
T$_g$ (Dry)	66 °C
Crystallinity	38%
M$_n$	48 kg mol^{-1}
Modulus (Dry)	2.3 GPa

Table 2
Water content in the PA6 as a function of conditioning parameters.

Environmental conditions	Homogeneous water content (%)
80 °C, 20% RH, 48 h	0.7
80 °C, 30% RH, 48 h	1.1
80 °C, 40% RH, 48 h	1.7
80 °C, 50% RH, 48 h	2.4
80 °C, sea water, 48 h	9.3

from 15 to 60 °C. This model was the first step towards prediction of properties when PA6 samples are immersed in sea water. The present paper is the second step, and consists of characterizing, understanding and describing the relationship between water content and mechanical properties.

This paper will describe the changes in mechanical performance induced by immersion in sea water. First, experimental results will be presented with special attention paid to changes in tensile behavior induced by mobility in the PA6. Then, these results will be discussed and a relationship between water content and yield stress will be proposed based on physical considerations. Finally, using this relationship coupled with the diffusion model, a prediction of property changes will be made. This prediction will be validated by comparison with other experimental data.

2. Material and methods

2.1. Material

The polymer used in this study is a commercial Polyamide 6 in the form of 2 mm thick sheet supplied as the reference AM303020 by Goodfellow. The main characteristics are reported in Table 1. All samples tested here were cut using a high-pressure water jet machine, then dried at 40 °C in a desiccator until a constant mass was reached. The sheet is processed by compression molding so the polymer is considered to be isotropic.

2.2. Method

2.2.1. Ageing

Two kinds of ageing were considered here. The first one is immersion in natural and renewed sea water that comes directly from the Brest estuary. In this case the temperature is 25 ± 1 °C. Samples were tested directly after removal from the ageing tank in order to limit water evaporation. The second one aims to obtain samples at different water contents with no water profile through thickness. To do so, samples are conditioned for 48 h at 80 °C at several humidity levels (see Table 2) using a Servathin conditioning chamber. The water content in the polymer was determined based on the weight gain of samples after exposure. For each condition, 3 samples were tested. Samples fully saturated in sea water were dried at 25 ± 1 °C in a desiccator maintained at 0% RH. The tensile samples were dried at 80 °C for 48 h in order to reduce drying time. The water content in samples was determined by weight measurements.

2.2.2. Size exclusion chromatography (SEC)

Molar mass was determined by SEC made by the PeakExpert Compagny according to the Laun and al. method [21] and used in Ref. [4]. Samples of 25 mg were dissolved in 10 ml of 1,1,1,3,3,3-hexafluoroisopropan-2-ol (HFiP) the dissolution was performed for 24 h at room temperature. Samples were injected in the chromatograph (Waters 2695) after a filtration on PTFE 0.2 μm. The separation was performed using a pre-column and two columns packed with 7-μm PFG particles, and 1000 Å and 100 Å pore size, the dimension of columns was 8 mm ID × 300 mm length. The mobile phase was a mixture of HFiP +0.05 mol l^{-1} potassium trifluoroacetate (KTFAc), flow rate was 1 ml min^{-1} and injection volume was 50 μl. The detection was performed using a Waters 2414 differential refractive index detector and data treated with PSS WinGPC unity v7.5 SEC software. The calibration was built using poly(methyl methacrylate) standards supplied by PSS GmbH Mainz, Germany, with molar mass ranging between 800 and 1,600,000 g mol^{-1} and calibration curve was adjusted with an order 5 polynomial. Calculations are conventional and average molecular weights are expressed in PMMA equivalent.

2.2.3. Tensile tests

Tensile tests were performed using a 10 kN capacity Instron machine with a load cell of 10 kN. Samples were tested under displacement control at a rate of 6 mm/min. The strain was measured by digital image correlation based on the displacement of two marker points on the specimen, using in-house software. For
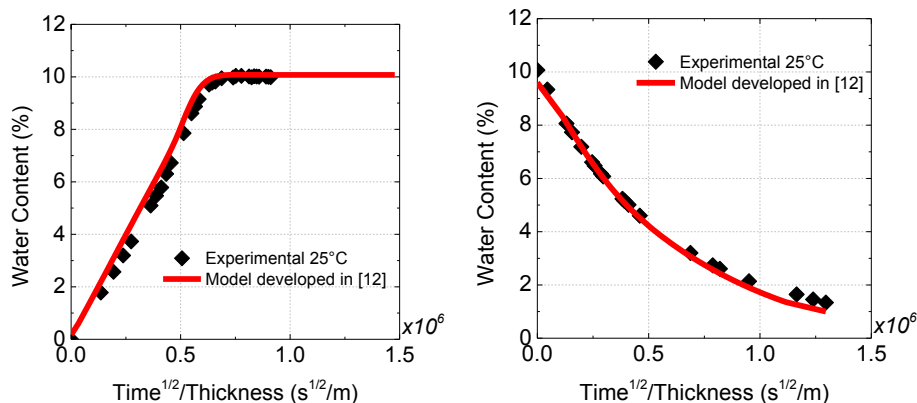

Fig. 1. Water absorption when immersed in sea water (left) and desorption at 0%RH (right) in 2 mm thick PA6 samples (dots are experimental data and lines show the model developed in Ref. [12]).