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Material behaviour

Moisture sorption in polyamide 6.6: Experimental investigation and comparison to four physical-based models

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ABSTRACT

Water sorption in polyamide 6.6 has been characterized for a wide range of temperature (25°C to 80°C) and various water activities using a Dynamic Vapor Sorption testing machine. Complex sorption mechanisms govern the water uptake in the material. The competition between two main temperature dependant mechanisms has been observed: a Henry's sorption mechanism that mainly governs the sorption curve at low water activities, and a second mechanism at high water activities that could be related to the formation of water clusters. It is observed that the temperature dependency can mainly be attributed to the Henry's contribution. Four physically based models are then used and identified thanks to the extended experimental database. It is shown that a simple Flory-Huggins model is not able to capture the experimental observations at very high water activities for all the temperatures tested. The ENSIC model is a better choice, but good prediction for very high water activity cannot be obtained. Both modified Park and GAB models can accurately predict the volume fraction of water for the whole ranges of water activity and temperature, although the modified Park model should be preferred considering the number of parameters and the mathematical simplicity.

1. Introduction

In order to reduce CO_2 emission and fuel consumption, the automotive industry wishes to reduce the mass of vehicles. Short glass fiber reinforced polyamide 6.6 composites are appropriate candidates because they combine an affordable price and a reasonable stiffness thanks to the complex shapes allowed by the injection molding process. These materials are not new in the automotive industry, they have been used for a long time for parts submitted to limited thermo-mechanical loading. They are nowadays increasingly used for structural applications such as engine mounts or clutch pedals (Fig. 1) that are submitted to complex cyclic movements. Furthermore, important variations of the temperature and relative humidity can be induced by the service conditions (under-bonnet temperature and climatic variations) [1]. Both temperature and relative humidity are known to have a strong impact on the mechanical properties of polyamide [2–5].

The strong influence of the relative humidity on the mechanical response is especially high for polyamide because of the hydrophilic nature of the amide functional group [6]. In the case of unfilled polyamide 6.6, saturation

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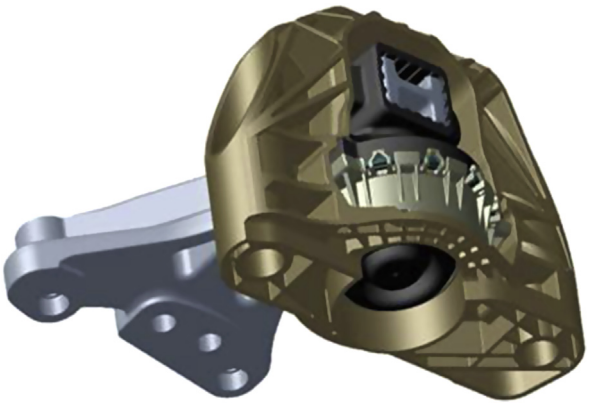

Fig. 1. TrelleborgVibracoustic engine mount with PA6.6 50%wtGF housing for PSA.

values of water absorption up to 8.5% at 23°C and relative humidity of 100% are commonly found in the literature [7]. The absorption of water in the polyamide leads to at least three consequences. The first is modification of the matrix behavior: the ultimate strain increases and the material stiffness decreases [2,5]. The second is the reduction of the glass temperature transition T_g with the increase of water content. A reduction of nearly 60°C when the relative humidity ratio is increased from 0 to 80% (T_g varies from 320K to 260K) is, for example, reported [7]. The last consequence is swelling of the structure that induces dimensional changes that can be problematic for the integration of the structure in its environment [8]. Moreover, in many industrial parts submitted to demanding loading, the concentration of water in the material is not homogeneous. Thus, understanding of the water gradient and the consequences on the mechanical and physical properties variations with time, but also with position, is mandatory to predict the thermo-mechanical response needed to get a reliable design.

The classical way to investigate the water sorption consists of monitoring the global mass uptake using gravimetric analysis. Two main quantities can be defined from these experiments: the equilibrium mass uptake (*i.e.* the maximum water content absorbed by the polymer) and the time needed to reach this saturation state characterized by the diffusion coefficient. In this paper, we choose to focus only on the equilibrium mass uptake; the analysis of the diffusion coefficient will be discussed in a forthcoming paper. Dealing with equilibrium water content, the early studies performed by Barrie in 1968 [9], highlighted the diversity of sorption mechanisms. The amount of sorbed water at equilibrium increased almost linearly over a wide range of water activities obeying Henry's law isotherm, except for at low and high relative humidity. The deviation at low relative humidity classically appears as a “shoulder” and is typical of type “II” isotherms [10] classically modeled with a Langmuir type sorption. At high water activities, the equilibrium water uptake rises sharply, which could be related to water clustering [11]. For water absorption in PA6.6, several studies have already noted that the Langmuir type sorption is absent [6,12,13], and the water sorption isotherm is composed of only two zones: that following Henry's law at low activities and Flory-Huggins type sorption.

Indeed, the experimental databases found in the literature are usually restricted to a limited range of temperatures and water activities, not consistent with the ranges seen by industrial structures, especially automotive structures. Therefore, the first aim of this paper is to build an experimental database as thorough as possible covering a wide range of temperature and humidity ratio. The literature provides a wide range of models, so the other aim of the paper is to challenge the experimental database and compare the predictability of four physically-based models classically found in the literature (Flory Huggins [14,15], ENSIC [16], Park [17] and GAB [18–20]). The restriction to physically based models is motivated by the idea that the extrapolation to a wider range of temperature of such models is more reasonable as long as the underlying hypotheses of this model are known, which is usually not the case for empirical models.

The paper is divided into 5 sections. First, the material and experimental used to build the database are briefly detailed. It should be pointed out that we chose to focus in this paper on polyamide 6.6 matrix only. The investigation of the influence of fibers on the ability of the material to absorb water is considered as a perspective of this work. Moreover, in order to limit as much as possible the time needed to build an extended database, the measurements were performed on thin films, rather than on thick plates, as classically done in the literature. The experimental results are then presented and the key points are highlighted. Various models are then presented and their ability to capture the specificities of the experimental database is then discussed. Finally, conclusions are proposed.

2. Materials and methods

2.1. Materials and samples

The material used is a polyamide 6.6 matrix provided by Solvay® (A218nat) with a density of 1.14 g/cm^3, and a molecular weight of 16 500g/mol. The glass transition temperature of the polymer in the dry state has been evaluated at 56 ± 1°C with classical DMTA tests using the three tangents method on the storage modulus E'. Thin films of 100μm thickness were cut from injected plates using a Leica microtome.

2.2. Gravimetric experiments and construction of the sorption curves

The gravimetric experiments were performed using a Dynamic Vapor Sorption (DVS) Q5000SA, TA Instruments, equipped with a high-accuracy micro-balance (0.1μg ± 1%). The accuracy of the system is ±1% for the RH over a range of 0–98% and ±0.1°C for the temperature stability. During a DVS measurement, the sample can be subjected to varying humidity and temperature conditions, and the mass of the sample is measured continuously during the test. To simplify the interpretation of our measurements, the temperature remained fixed whereas the humidity ratio