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Hydrolytic and photochemical aging studies of a Kevlar®-PBI blend

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ABSTRACT

The focus of this work is the study of the hydrolytic and photochemical aging behavior of a Kevlar®-PBI blend fabric. Tensile tests carried out on yarns extracted from this fabric after either irradiation with UV light or exposure to high humidity indicated a continuous decrease of the breaking force with exposure time. ATR-FTIR analyses of photo-chemically aged samples showed evidence of a photo-oxidative reaction initiated by the cleavage of the amide bond of Kevlar. The overlapping of the breaking-force curves that was observed as the irradiance level was increased at constant temperature is believed to be caused by a "screen" effect produced by Photo-Fries products. The fact that at constant temperature the breaking force was unaffected by the variation of the relative humidity suggests that the absorption of water is not the rate-controlling step in the degradation kinetics. ATR-FTIR analyses revealed the presence of a new absorption band ascribed to carboxylic acid end groups produced during the hydrolysis of the amide linkage that occurred after humidity aging. The relative intensity of the –COOH band tended to a constant value as exposure times increased, suggesting that in addition to the hydrolysis, a competing recombination reaction takes place during degradation. A kinetic model for the hydrolytic degradation process was formulated and solved.

1. Introduction

Within the broader scope of studying the degradation of a Kevlar®-PBI blend fabric exposed to a multi-stress environment, our group has already presented two studies concerning the thermal aging of this blend [1,2]. The focus of the present work is to investigate the detrimental effects on the properties of this material (mechanical properties in particular) under the action of two other aging factors: humidity and light radiation. The material studied here is currently used in the manufacturing of fire-fighting garments. The reliability of this protective gear after extended use is of vital importance to insure adequate protection against fires to the person wearing it, and, while the blend is composed of high performance fibers specially selected to withstand severe environmental stresses, their long-term aging behavior is still poorly understood. Therefore, evaluating the consequences of prolonged use of this material in the harsh conditions met by fire fighters is a worthwhile endeavor.

As a polyamide synthesized by condensation, Kevlar®, poly(p-phenylene terephthalamide) (PPTA) shown in Fig. 1, is prone to undergo a hydrolysis reaction catalyzed either by an acid or a base, which attacks the amide linkage causing a chain scission process [3,4]. The hydrolysis of polyamides, its effect on molecular weight, and the mathematical models of the reaction have been thoroughly studied and are well documented [4–7]. However, while some publications address the issue of the absorption of water by Kevlar® and its influence on the tensile and creep properties [8–10], the literature is still lacking an in-depth study on the hydrolysis of Kevlar® itself. Indeed, the high crystallinity exhibited by Kevlar® [11,12] sets it apart from the other polyamides and may constitute a hindering factor for the hydrolysis reaction, since most of the polymer interactions with water occur within the amorphous phase [3,9]. In addition to Kevlar's high crystallinity, another factor that may prevent the hydrolysis reaction is the need for an acid or basic catalyst to initiate the reaction [4,13] as the hydrolysis will not proceed in a neutral pH environment like the one usually found in climatic (natural) aging. Apart from being vulnerable to hydrolysis, Kevlar® exhibits a strong intrinsic absorbance in the near UV (wavelength between 300 and 400 nm), making it susceptible to photo-chemical aging as well [4]. Exposure to light radiation in air results in a yellowish coloration, a fast decrease of the molecular weight at the outer layers of the polymer and the formation of carboxylic acid end groups. Photo-chemically aged Kevlar is also prone to undergo a Photo-Fries bond rearrangement process involving caged free radicals produced during the initial light-induced amide bond scission [4,14] according to the mechanism illustrated in Fig. 2. This mechanism has also been observed in the

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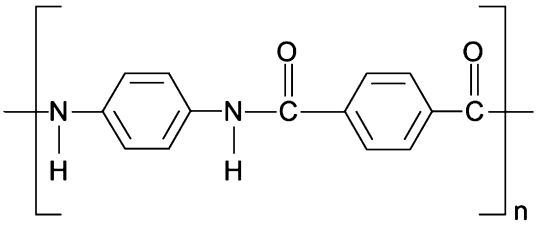

Fig. 1. Chemical structure of Kevlar.

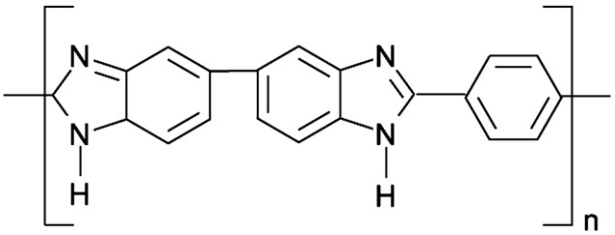

Fig. 3. Chemical structure of PBI.

Photo-Fries rearrangement of polycarbonates [15]. It has been reported that the Photo-Fries products of molecules containing aromatic amides possess a strong UV absorbance that may enable them to act as stabilizers upon irradiation with UV light [16]. On the other hand, the remaining component of the fabric blend, namely PBI (polybenzimidazole), possesses an entirely aromatic structure (shown in Fig. 3) which provides excellent thermal and chemical stability [17]; therefore PBI is expected to be practically impervious to hydrolysis and photo-chemical aging.

As opposed to non-oriented, non-crosslinked polymers, in which mechanical failure may be considered primarily the result of disentanglements between polymer chains whose molecular weight (MW) has decreased beyond a certain critical value, thus showing a clear, quantifiable relation between mechanical failure and MW, the relation between MW and mechanical failure for oriented polymers such as fibers has not been entirely established [18]. While it is accepted that an important number of chemical bonds are broken before a macroscopic rupture, their exact magnitude remains a topic of debate [19–22]. The only fact in which authors seem to concur is that the ends of broken polymer chains act as defects and thus where failure is initiated [13,21,22]. It is therefore expected that any process resulting in the cleavage of chemical bonds, such as hydrolytic or photo-chemical aging, will have an impact on the mechanical properties of the material, especially on ultimate properties such as rupture [23]. Under this premise, the tensile breaking force of yarns will be the variable used to assess the aging progress.

In this paper, we study the individual effect of humidity and light radiation on a Kevlar-PBI blend by evaluating their influence on the tensile breaking force of yarns pulled from fabric samples. The mechanisms of degradation as well as the evolution of the chemical structure throughout the photochemical and humidity aging processes were followed by ATR-FTIR analyses. Energy dispersive X-ray spectroscopy (XDS) was also used to characterize the physical and chemical changes that ensue from the degradation process.

2. Materials and experimental

2.1. Materials

The material used in this study is a fabric whose yarns are composed of a 60-40 wt. % blend of Kevlar® and PBI staple fibers reinforced with Kevlar® continuous filaments. Samples of this fabric, distributed commercially under the trade name Gemini®, were provided by Innotex (Richmond, QC, Canada).

2.2. Humidity aging treatments

Pieces of the Kevlar®-PBI blend fabric were placed in a BURNSCO BTH-1.3P environmental testing chamber equipped with a PID controller for the relative humidity that has a precision of ±5% RH. Three temperatures (80, 60 and 50 °C) and two levels of relative humidity (80 and 60% RH) were chosen to conduct the aging treatments. The fabric samples were aged for different periods ranging from 4 to 31 days. Demineralized water was used throughout the whole duration of treatments in order to insure the neutrality of the environment.

2.3. Light radiation aging treatments

Light radiation accelerated aging treatments were carried out in a Q-LAB QUV Accelerated Weathering Tester. Pieces of fabric (2.5 cm × 22 cm) were placed in sample holders and exposed to radiation from UVA lamps (wavelength 340 nm) at a given combination of temperature and irradiance for periods of time ranging from 4 to 35 days. Four temperatures (50, 60, 70 and 80 °C) and different levels of irradiance (ranging from 0.35 to 1.55 W/m^2) were selected for the aging treatments. The main goal when choosing the irradiance levels was not to simulate the radiation emitted by the sun (for example, the irradiance of the light during a midsummer noon is approximately 0.68 W/m^2) but to obtain several sets of data in a relatively short amount of time in order to predict the behavior of the material for a wide domain of radiation conditions.

2.4. Breaking-force tests

Breaking-force tests were performed on Kevlar-PBI yarns pulled from the aged fabric samples according to a modified version of ASTM D 2256-02 test method [24]. An MTS Alliance tensile testing machine in combination with automated data acquisition software was used for the data collection. The test speed was 100 mm/min, the distance between the grips was 10 cm and the ends of the yarn

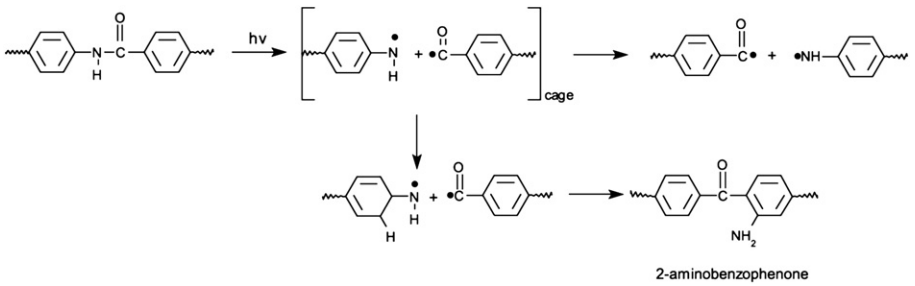

Fig. 2. Mechanism of Photo-Fries rearrangement for Kevlar®.