Polymer Degradation and Stability 110 (2014) 457–463

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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

Long term aging of LLDPE based multi-layer film by exposure to light hydrocarbons

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ARTICLE INFO

Article history:
Received 20 August 2014
Received in revised form
8 October 2014
Accepted 13 October 2014
Available online 19 October 2014

Keywords:
Polyethylene
Aging
LLDPE
Polyamide

ABSTRACT

This study focuses on the stability of a polymeric Linear Low Density Polyethylene/Polyamide/Linear Low Density Polyethylene multi-layered container during long-term aging by exposure to light hydrocarbons in aviation gasoline. The containers examined and tested for this work were stored and used for different service periods, the longest of which is 10 years. During the containers' service periods, the inner LLDPE layer is exposed to avgas (aviation gasoline), and the outer LLDPE layer – to air. The aging process caused by the film interaction with avgas was examined by a variety of methods. Pb line-scan and IR spectroscopy show no evidence for the presence of small organic carbohydrate molecules originating from the avgas in the LLDPE. The viscoelastic and thermo-mechanical properties of the material were not significantly changed after 10 years. Nevertheless, DSC-OIT analysis shows a remarkable rise in oxidation rate as samples get older, presumably, as a result of antioxidants leaching out or being used up. The SEM results show the polymer to be much more prone to cracking, indicating a rise in crystallinity, as further substantiated by the results from DSC 1st heating cycle enthalpy evaluation. The 2nd DSC heating cycle results, which show no differences between samples, indicate the difference seen in the 1st heating cycle is affected by intermolecular rearrangements. Macro-mechanical properties show a remarkable stability for at least a decade, negating the aging phenomena discussed. Polyamide, as the load baring layer in the film, is probably responsible for the dampening seen in these results. In years to come, apparent oxidation will begin – most prominently in the outer layer – but probably would not compromise the structural strength of the bag, as both polyethylene layers are not the main load bearing layers.

1. Introduction

Containers from flexible polymer films had become commonplace replacements for storage tanks made of traditional engineering materials, such as metal, glass, etc. These containers offer many advantages such as low weight, chemical resistance, gas and light impermeability and low manufacturing costs. Moreover, the container's ability to adjust its size to fit the volume of the stored liquid eliminates the air head above the liquid, which in turn reduces evaporation and prevents air penetration. Polymeric containers are being used in diverse fields – from the food industry ("Bag in Box" method is used for beverage storage) to medicine (IV bags).

Mechanical properties of polymeric materials depend on various parameters, including molecular weight, crystallinity, branching and crosslinking [1,2]. Changes to these fundamental parameters are the result of the aging process, caused by natural weathering [3,4] and accelerated mainly by oxidation [5,6], exposure to radiation (UV particularly) [4,7–13] and chemicals [14]. Elevated temperatures tend to enhance the rate of these aging processes [1,2,15–20]. Other common causes of polymer materials degradation include: erosion [16], friction and abrasion [14,21], presence in electrical systems [22], and fatigue [23]. Incorporating antioxidants [24] and other additives [25] is an accepted practice for inhibiting or decelerating [26,27] polymer aging and degradation. However, it is the basic chemistry of the polymer that dictates its general resistance to chemical exposure [28].

Understanding the aging mechanisms of polymers may enable prediction of products' service life. Kondo et al. [29] reported changes in the mechanical properties of various commercial

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http://dx.doi.org/10.1016/j.polymdegradstab.2014.10.011
0141-3910/

polymer compounds that had been stored for sixteen years in a temperature-controlled environment. But, service life of polymeric materials often exposes them to ever-changing sometimes extreme, circumstances. Exposure of polymeric materials to hydrocarbon based fuels causes undesirable effects, such as swelling and extraction of additives, especially plasticizers. Intermittent exposure to fuel accelerates the degradation of polymeric substances, and causes crazing and cracking of the surface since emptying and refilling cycles cause fuel to be absorbed and desorbed repeatedly [30,31]. Briassoulis et al. [21] presented an extensive work on the degradation characteristics of agricultural Low Density Polyethylene (LDPE) films, which exemplifies factor isolation. In their research, external factors (radiation, temperature, humidity, etc.) and inherent properties of the polymer (degree of crystallinity, molecular weight and its distribution, branching, etc.) were studied separately for their influence on aging and degradation. Kamal et al. [32] studied oxygen and humidity permeability in polyethylene/polyamide (PE/PA) films as a function of the relative amount of the PA component. Changes in the microscopic structure of the layer were observed after being subjected to different levels of exposure to oxygen and humidity.

More recent studies present the effect of fuels and fuel blends on polymer based components [31,33–35]. Most of these works note changes in some mechanical, physical and chemical parameters of containers made of High Density Polyethylene (HDPE), mainly as a result of full immersion of the samples in liquid for up to about a year [36]. Nevertheless, a study of multi-layered films involved in multiple adsorption and desorption cycles, lasting up to 10 years, common service life-time for these products, had yet to be presented.

Methods employed in previous studies concerning polymeric film aging include mechanical tests [2]; physical properties tests [36]; thermal analyses (DMA, DSC, TGA); rheology [37–42] and permeability of gases and humidity tests. In addition, spectral analyses (e.g., FTIR analysis results that give evidence of oxidation processes by changes of the carboxylic peak); fractography and study of the changes on the surface and in microstructure (SEM/TEM) have also been reported [43].

This study focuses on the stability of a polymeric Linear Low Density Polyethylene/Polyamide/Linear Low Density Polyethylene (LLDPE/PA/LLDPE) multi-layered container during long-term aging, not only by storage, but also by exposure to light hydrocarbons in aviation gasoline ("avgas"). The containers examined and tested for this work were stored and used for different service periods, the longest of which is 10 years. During the containers' service periods, the inner LLDPE layer is exposed to avgas, and the outer LLDPE layer - to air. The combination of multiple layers of different polymeric sheets required attention to the mutual influence of the different layers on each other. Various mechanical, analytical and microscopic methods were utilized in order to obtain new insight into chemical and physical phenomena, in order to explain the change in each layer's properties after long-term service periods to improve the understanding of aging mechanisms of multi-layer films.

2. Materials and methods

Original flexible bags were manufactured by Aran Packaging, Israel. The polymeric film from which the bags are made is manufactured by co-extrusion by Plastopil Hazorea, Israel. The film is made of five different layers: the two outer layers (40 μm each) are made of LLDPE (Dowflex NG 5056, Dow Chemical, USA) adhered with approximately 1 μm of a maleic anhydride modified PE (OREVAC C306, Atofina, France) to a single middle layer of 20 μm PA 6 (Ultramid B40 L, BASF, Germany). These bags have been fabricated from the same batch of the multi-layered film throughout ten years and had been in service ever since. Its usage involves storing Aviation Gasoline (Avgas 100LL, ASTM D910). Two types of reference materials were used: margin area behind the welding seam of the bags were considered as reference materials for aging of the bags without further chemical interference (since they were not in direct contact with the fuel) and the raw materials of the bags' layers were considered as reference materials. It should be noted that neither the bags, nor the multi-layered film were exposed to sunlight. Samples will be referred to by these designations: (1) Old sample – 10-year-old sample, after exposure to avgas; (2) Old reference – 10-year-old sample, no exposure to avgas; (3) New sample – 2-year-old sample, after exposure to avgas; (4) New reference – 2-year-old sample, no exposure to avgas.

2.1. FTIR measurements

2.1.1. Transmission FTIR

The IR spectra were obtained with a FTIR spectrometer (Magna-IR Spectrometer 550 model, Nicolet) by collecting and averaging 64 samples, at a resolution of 4 cm^{-1}. Transmission FTIR had been used because of their uniform thickness that is suitable for this method (~100 μm).

2.1.2. Diamond ATR-FTIR

The IR spectra were obtained with a FTIR spectrometer (Vertex 70 model, Bruker), using single-bounce ATR with a diamond crystal, by collecting and averaging 32 samples, at a resolution of 4 cm^{-1}.

2.2. Thermal analyses

2.2.1. DSC

Calorimetric data was obtained with DSC (DSC Q100 model, TA Instruments). Samples were cut to uniform circles and placed into a standard aluminum crucible with a pierced lid. Enthalpy and peak temperature measurements were obtained from recording of the heat flow as a function of temperature using a linear integration at fixed temperatures. The sample underwent the following thermal procedure: Ambient gas: nitrogen; Equilibrate at −30 °C; Isothermal for 2 min; Temperature was increased to 200 °C at a rate of 10 °C/min; Isothermal for 2 min; Temperature was decreased to −28 °C at a rate of 10 °C/min; Isothermal for 2 min; Temperature was increased to 200 °C at a rate of 10 °C/min; Isothermal for 2 min; Temperature was decreased to −20 °C at a rate of 10 °C/min.

2.2.2. DSC-OIT

Oxidative induction time measurements were obtained with a DSC (DSC Q100 model, TA Instruments) by cutting a sample and placing it into a standard open aluminum pan. The measurements were modeled after ASTM D3895-03, with minor adjustments to better replicate real time exposure. The procedure the sample went through was as follows: Ambient gas: nitrogen; Equilibrate at 40 °C; Isothermal for 5 min; the temperature was increased to 185 °C at a rate of 20 °C/min; (Measurement zero point) Isothermal for 5 min; ambient gas: air, 50 mL/min. Isothermal for 120 min, max. The measurement was stopped as soon as oxidation was apparent.

2.2.3. DMA

Dynamic Mechanical Analysis was made with a DMA (DMA Q800 model, TA Instruments). 1 Hz, 10 mN, 25.0 μm, 120%, heating rate 3 °C/min in the temperature range: (−150 °C)–(+200 °C); sample dimensions: 5 × 17 × 0.1 mm^3.