Polymer Degradation and Stability 137 (2017) 109–121

Contents lists available at ScienceDirect

Polymer Degradation and Stability

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

Aging of plasticized polyvinyl chloride in heritage collections: The impact of conditioning and cleaning treatments

Adeline Royaux [a, b, c], Isabelle Fabre-Francke [a], Nathalie Balcar [b], Gilles Barabant [b], Clémentine Bollard [d], Bertrand Lavédrine [c], Sophie Cantin [a, *]

[a] *Laboratoire de Physicochimie des Polymères et des Interfaces (LPPI), Institut des Matériaux, Université de Cergy-Pontoise, 5 mail Gay-Lussac Neuville-sur-Oise, 95031 Cergy-Pontoise Cedex, France*

[b] *Centre de Recherche et de Restauration des Musées de France (C2RMF), Département Restauration, Filière XXe - Art Contemporain, 2 Avenue Rockefeller, 78000 Versailles, France*

[c] *Centre de Recherche sur la Conservation (CRC), Muséum National d'Histoire Naturelle, Ministère de la Culture et de la Communication, Sorbonne Université, USR CNRS 3224, 36 Rue Geoffroy St Hilaire, 75005 Paris, France*

[d] *Atelier Curial, 12 Rue Labois Rouillon, 75019 Paris, France*

A R T I C L E   I N F O

Article history:
Received 7 October 2016
Received in revised form
25 November 2016
Accepted 17 January 2017
Available online 19 January 2017

Keywords:
PVC
Plasticizer migration
Artificial aging
Storage
Cleaning

A B S T R A C T

The degradation kinetics of plasticized PVC films naturally aged for about 30 years old in museum conditions and displaying surface exudates was studied during an artificial aging treatment consisting in a temperature cycle (2 days at 80 °C/1 day at 25 °C) and under controlled relative humidity (65%). The role of the enclosure was investigated by placing the films either in a closed vessel or by freely hanging them in the climatic chamber, while the effect of a preliminary mechanical surface cleaning to remove the exudates was also studied. Plasticizer migration and PVC degradations were characterized every week by coupling thermo-gravimetric analysis, gas chromatography, dynamic mechanical thermal analysis, infrared and UV–visible spectroscopy, atomic force microscopy and contact angle measurements. The results show that there is a significant slowing down of PVC aging in a closed container with respect to an open environment. Plasticizer loss and thus changes in mechanical properties are thus strongly delayed in a closed environment while PVC dehydrochlorination leading to sample yellowing also evolves at a slower pace. Concerning the effect of the preliminary PVC surface cleaning, it appears effective and has no effect on the kinetics of further PVC degradation. In particular, the removal of the exudates does not accelerate the further plasticizer loss. This study brings significant insights for conservation strategies. Indeed, the lifetime of soiled PVC-base heritage artifacts can be extended through a soft mechanical cleaning of the surface allowing retaining their visual appearance. Moreover, preservation of PVC artifacts in a closed container is preferable to slow their degradation process.

1. Introduction

Plasticized polyvinyl chloride (PVC) is a material widely present in heritage collections however its state of preservation is often considered as poor [1]. The most commonly observed degradations are sweating, loss of flexibility and soiling which can sometimes be spectacular. These degradations are related to the progressive migration of the plasticizer towards the surface of the material. This migration does not only lead to a gradual loss of the material mechanical properties such as flexibility but also alter the visual appearance of the object. Indeed, plasticizer migration may induce surface exudate formation promoting soiling. Material aging is also accompanied by a dehydrochlorination process of PVC chains leading to the formation of conjugated polyene sequences and thus material yellowing. Studies of thermal degradation of plasticized PVC show that the dehydrochlorination is delayed in presence of plasticizer and all the more so its amount is important [2–4].

Phthalate plasticizers, such as di-(2-ethylhexyl)phthalate (DEHP) and dioctylphthalate (DOP), are common plasticizers widely used to improve the flexibility and processing of PVC. Their weight concentration can reach 50% of the final weight of the material. These low molecular weight compounds not covalently bonded to the polymer are often released from the PVC matrix over

* Corresponding author.
E-mail address: sophie.cantin-riviere@u-cergy.fr (S. Cantin).

http://dx.doi.org/10.1016/j.polymdegradstab.2017.01.011

time.

In order to extend the lifetime of plasticized PVC used in a variety of products, extensive experimental research has been carried out to understand the thermal or photochemical degradation of these materials [3–11]. Most literature related to thermal aging under artificial tests deals with the effect of the aging temperature on the degradation mechanisms, most often at quite high temperature (90–200 °C range) and in relatively dry air. Less attention has been paid to thermal artificial aging at moderate temperatures and relatively high relative humidity that could be more representative conditions of museum environment [12]. In addition, the main issue regarding the state of preservation of PVC-based heritage objects resides in the reduction as far as possible of the material aging through the implementation of the most appropriate methods of both preservation and surface cleaning. This requires a better understanding of the impact of exhibition or storage environment on the degradation mechanisms of plasticized PVC as well as of the exudate release through cleaning processes on the subsequent evolution of the material.

Relatively little work has been devoted to the role of the environment on the kinetics of plasticized PVC degradation. In particular, Y.R. Shashoua investigated the degradation at 70 °C during 65 days of model plasticized PVC stored in various environments reproducing museum conditions [2]. The weight loss attributed to plasticizer diffusion towards the surface as well as the discoloration was found to be strongly reduced in a non-absorbent closed environment such as a glass flask while considerably enhanced in low density polyethylene bags or open environment. M. Ekelund et al. also reported a slowing down of the aging process of the core insulation of plasticized PVC cables with respect to the jacketing material which was attributed to the fact that this part is aging in a closed environment [13]. Linde et al. also showed that the kinetics of degradation of plasticized PVC samples was dependent on the air flow rate during thermal aging, and slowed under stagnant air atmosphere [11].

Until now, cleaning of naturally or manually soiled plasticized PVC has been studied mainly in terms of efficiency and immediate physical or chemical modifications [14]. In particular, C. Morales Muñoz studied the influence of different dry cleaning methods on naturally soiled plasticized PVC [15]. Cleaning efficiency was shown to depend on the type of cloth and in some cases, mechanical action was observed to induce plasticizer migration. PEL-cloth™ containing 70% polyester and 30% polyamide was found to be the most efficient without any significant alteration of material properties provided the cleaning time is shorter than 100s. Määttä et al. evidenced that the cleaning efficiency of plasticized PVC covered with model soils and cleaned using a microfiber cloth was enhanced for samples with a lower plasticizer content [16]. However, to our knowledge, cleaning of degraded aged plasticized PVC has not been studied and above all, the effect of surface cleaning on the long-term kinetics of subsequent plasticizer migration has not been addressed.

This study aims to better assess degradation mechanisms and preservation strategies for plasticized PVC-based heritage objects. Several physico-chemical analysis techniques have been coupled to deepen the understanding of thermal aging mechanisms of plasticized PVC at both macroscopic and molecular levels, including a better understanding of the impact of conditioning and of the effect of cleaning on the further plasticizer migration.

This work was carried out on plasticized PVC naturally aged for about 30 years in museum conditions and displaying surface exudates. These samples were selected as they spent a long time in a museum environment and display degradations commonly observed for PVC artworks in collections. The presence of exudates associated to plasticizer migration thus enables an investigation of the effect of surface cleaning on the further evolution of the material. In addition, the availability and possibility of sampling the material in a destructive way complement our choice of this material. Plasticizer content and nature were first determined using Gas Chromatography combined to Mass Spectrometry (GC-MS). Plasticizer migration and PVC degradation were then characterized every week during a thermal artificial aging treatment in a climatic chamber. A temperature cycle (2 days at 80 °C/1 day at 25 °C) under controlled relative humidity (65%) was chosen to mimic the impact of fluctuation in temperature that happens during storage of heritage objects. In order to examine the effect of both conditioning and surface cleaning on the kinetics of material degradation, PVC samples were placed either in an open or a closed container and whether or not submitted to a preliminary mechanical cleaning treatment using a microfiber cloth.

During artificial aging, weight loss and sample yellowing were measured weekly. Plasticizer content was also determined by coupling Thermo-Gravimetric Analysis (TGA) and GC-MS while mechanical properties were investigated by measuring the mechanical α-relaxation temperature using Dynamic Mechanical thermal Analysis (DMA). Material aging was followed using infrared and UV–visible spectroscopy measurements. Changes in surface topography were probed by optical microscopy and Atomic Force Microscopy (AFM) while surface wettability was characterized by water advancing contact angle measurements.

2. Experimental section

2.1. Materials

The studied plasticized PVC films were used as protective covers for about 30 years in a museum environment (Versailles Palace). These films were naturally aged away from direct sunlight. The studied samples arise from two protective covers with the dimensions of 45 × 45 cm^2 and a thickness of 250 μm. Their homogeneity was checked by analyzing, before artificial aging, both plasticizer content, PVC degradations and surface properties on about 20 samples collected at different places of the two protective covers.

Unplasticized PVC powder was provided by Griffine Enduction and used as received.

Cyclohexane (Merck, SupraSolv®), tetrahydrofurane (THF) (VWR, HiperSolv®), dibutylphthalate (DBP) (Sigma-Aldrich, > 99.5%), dimethylazelate (DMZ) (TCI, > 98%), dioctylphthalate (DOP, > 98%) (Sigma-Aldrich) and diethylhexylazelate (DEHZ) (Emery Oleochemichal, Edenol®) were used as received.

2.2. Cleaning of the PVC films

The commercial cloth used for the PVC cleaning was one of those recommended for plastic artifacts in museum collections: spectacles cloth (EverClean, Braüner), made of polyester and polyamide [15]. Cleaning was performed unidirectionally on each 4 cm^2 surface for 10 s by face, and by applying a moderate pressure.

2.3. Artificial aging test

An accelerated aging test with a temperature cycle consisted in 2 days at 80 °C then 1 day at 25 °C under a relative humidity of 65± 3% was carried out in a Vötsch, VC0020 climatic chamber with forced convection. In order to compare the aging in an open or a closed container, the PVC samples were either freely hung in the climatic chamber, or placed in closed glass Petri dishes. In order to check the reproducibility of the results for each of the aging environment, a series of samples with the dimensions of 3 × 1.5 cm^2