The Effects of Cleaning on Plasticizer Migration in Plasticized Polyvinyl Chloride (PVC)
Research Proposal and Literature Review

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Introduction

Plastics permeate museum collections just as they permeate our daily life. From fine art museum to local archive, nearly any cultural heritage collection will include some example. As cultural significance or historicity drives museum acquisition rather than material, plastics enter collections as part of cultural significant objects, either as a wholly plastic object or as a component of a larger structure. Additionally, modern and contemporary artists have taken advantage of the polymer's range of material properties and incorporated synthetic polymers into their artwork.

Despite their prevalence, conservation has only begun to understand the longevity and material properties of synthetic plastics. Materials meant to last for only several uses—certainly no more than a few decades—will degrade on a faster timeline than these institutions operate. We are currently faced with a question: how do you preserve a disposable object?

This question is exemplified in a transparent polyvinyl chloride dress in the collection of the Philadelphia Museum of Art which serves as a case study and inspiration for this project (Acc. # 1969-54-10**,** Fig. 1). Designed by Parisian designer Daniel Hechter in 1966, the dress stems from the twin 1960s fads of disposable clothes and space-age fashion. While it was originally meant to be worn only a handful of times and then discarded, the dress has been permanently accessioned into the PMA's collection. Today, it conveys this original function along with added layers of meaning such as history of French fashion design, the 1960s "youthquake", and the rise of the plastic industry. However, the blue polyvinyl chloride (PVC) that comprises the dress has deteriorated to such as a degree that the garment no longer reflects Hechter's original design and cannot be exhibited without further damage to the plastic.

Fig. 1: Overall of the front of Hechter's transparent polyvinyl chloride (PVC) mini dress.
In the collection of the Philadelphia Museum of Art, Acc. # 1969-54-10
Before Treatment, Normal Illumination

Hechter's PVC mini dress and objects like it render the conservation of plastics the upmost priority for the field. Given the pervasiveness of plastics in collections, the cultural importance of plastic objects, and the dramatic speed of their degradation, the field requires active research into practical conservation treatments.

This study seeks to contribute to this research by examining the long-term effects of cleaning polyvinyl chloride, one of the most common plastics in museum collections, and one of the most challenging to clean. Specifically, this study hopes to ascertain if aqueous cleaning of plasticizer from the surface of degraded PVC cases more plasticizer to leach from the polymer matrix.

PVC in Museum Collections

Synthesized in the latter 1930s, polyvinyl chloride production drastically increased in the 1940s when the second World War required a replacement for natural rubbers (Waentig and Verlag 2008). Production skyrocketed after the war, and the polymer was produced for synthetic leather and textiles, building materials, children's toys, food packaging, and a myriad of other industries.

Today, PVC is one of the most common plastics found in museum collections (Shashoua 2001). It appears in cultural heritage objects of nearly every variety, in nearly every type of institution. Libraries and archives house irreplaceable photographs, film, or vinyl records containing or house in PVC. It is a significant component in textiles (such as Hechter's dress) including elements in the Apollo spacesuits, garments by the fashion designer Elsa Schiaparelli (1890–1973), or the synthetic leather upholstery in the iconic mid-century modern furniture. The polymer appears in modern and contemporary fine art collections, whether the artwork is created directly from PVC as with Chinese artist Wang Jin's PVC garments, or as part of larger assemblages such as in the work of Bruce Connor (1933-2008) or Robert Raushcenberg (1925-2008).

In the field of collections care, PVC is one of the infamous "malignant" plastics whose autocatalytic deterioration mechanism will damage both the object itself and those stored with it (Shashoua 2008, Waentig and Verlag 2008). This deterioration has been shown to occur within five to ten years of an object entering a museum collection, making conservation an upmost priority.

PVC Degradation, Plasticizer, and Plasticizer Migration

Raw PVC is brittle and inflexible and requires additives or modifiers to act as light stabilizers, antioxidants, or opacifiers to alter its material properties. Plasticizer is the most common, added to rigid PVC to make the material more flexible, soft, or extendable and lower the material's Tg. PVC can contain 15-50% plasticizer, with the plasticizer concentration dictating the material properties and future use in manufacture (Shashoua 2008). These plasticizers are commonly phthalates[1] (Wypychn 2017), again exemplified in the Daniel Hechter dress where the plasticizer in the blue PVC is 2-Ethylhexyl phthalate, or DEHP (Fig. 2) (Peterson 2019), the single most highly produced plasticizer since the 1950s, and therefore present in many museum plastics (Shashoua 2001).

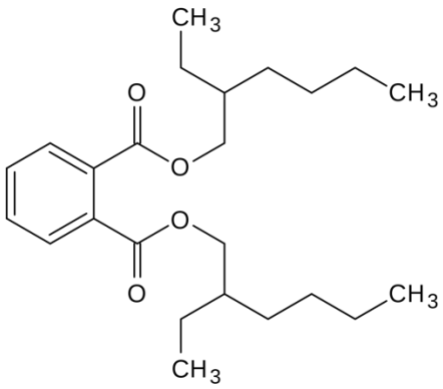

Fig. 2: Chemical Structure of the bis 2-Ethylhexyl phthalate (DEHP) plasticizer

While pure PVC is relatively stable, plasticizers –and other additives – contribute to the speed of the degradation and cause the majority of condition issues seen in museum plastics.[2] While a homogenous mixture, the plasticizer is not chemically bound with the PVC polymer. Rather, the plasticizer molecules are physically dispersed between the polymer chains, accumulating in

[1] The most common plasticizers of PVC are di (2-ethylhexyl) phthalate (DEHP), di-isononyl phthalate (DINP) and di-isodecyl phthalate (DIDP) (Shashoua 2008).

[2] In addition to plasticizers, PVC commonly contains UV inhibitors, fillers, flame retardants, lubricants, and other additives (Quye and Williamson 1999, Shashuoa 2008, Wypychn 2017, Waentig and Verlag 2008).

areas where the polymer is more loosely orientated and held in place with van der Waals forces (Shashuoa 2008). It is this increased space between the polymer chains that allows for the flexibility of the final plasticized PVC; the more plasticizer, the greater movement between chains and higher flexibility.

While the polymer and plasticizer degrade in separate mechanisms, the combined reactions between polymer and plasticizer affect how an object degrades. PVC polymer degradation is complex. The main mechanism is dehydrochlorination, which produces hydrogen chloride gas when the polymer is exposed to heat, light, and oxygen creating an acidic environment. The loss of the chlorine atom creates double bonds between carbon and oxygen, creating a conjugated polyene system which discolor the object and crosslink the polymer. Plasticizer may actually stabilize the polymer. The chemical stability of the DEHP has been shown to actually stabilize the PVC polymer by preventing the formation of the conjugated polyene (Beltran and Marchilla 1997), and the aging of PVC is dependent on the quantity of plasticizer rather than the type of plasticizer present (Waentig and Verlag 2008).

However, plasticizers such as DEHP are susceptible to hydrolysis in acidic environments and the degradation of the PVC may cause the degradation of the DEHP. Additionally, plasticizer often migrates out of the polymer matrix as physical forces overcome the week Van der Waals forces holding it in place, removing any stabilization affect it may have. Deteriorated plasticized PVC often exhibits a tacky surface, where the plasticizer has leached from the polymeric matrix and deposited on the surface. This tacky layer alters the original texture, attracts dust, and makes handling, exhibition, and storage highly problematic if not damaging to the object. There are often variations in the layer between two objects of the same type (Tonkin 2017) or in different areas within a single object. The amount of plasticizer, type of plasticizer, polymerization technique, and environmental history the object may all affect the rate or migration (Waentig and Verlag 2008). Studies suggest that greater air circulation may minimize the migration, and the offgassing of hydrochloric acid from the PVC may alter to the rate of migration (Royaux et al 2017).

Accelerated Aging of Plastics

As described above, plasticizer migration and other significant condition issues arise as plastic ages. Since plastics have their origins in the latter 20th century, many objects have only begun to show significant signs of age in the last few decades. Therefore, conservators are in the early stages of understanding how these materials change over time and are seeking ways of understanding the existing degradation and anticipating future changes. Yvonne Shashoua described how this research only began circa 1992 initially focused on identifying types of plastics and their degradation processes, and research into interventive treatment began a decade ago, circa 2008 (Shashoua 2016).

The majority of the research into the aging of plastics comes from the plastics industry, where the research deals with the mechanical properties of the material, or environmental science, which is concerned with sustainability or long-term environmental effects (Shashoua 2016). However, neither field is focused in the preservation of plastics. Rather, environmental research looks into the degradation products and alternative materials, while the plastics industry assumes old plastic will be discarded and replaced. Therefore, conservation studies into plastics degradation often necessitate “artificial” or “accelerated” aging to illuminate the degradation processes and material properties of plastic in within the decades-long (if not centuries-long) timeline of museum collections. These accelerated aging studies seek to “speed up” the aging of a material, replicating the conditions encountered in nature or the museum environment and thereby approximate the degradation conservators can expect. To achieve

this, samples are placed in an artificial aging chamber that cycles through different visible and ultraviolet light, humidity, and temperature levels, or a subset or combination of these factors (Feller 1994).

As previously described, the degradation mechanisms of PVC and phthalate plasticizers are complex, interrelated, and dependent on a variety of environmental factors. As many of these factors as possible should be address for an accelerated aging study to provide helpful data. Light and dark cycles that include ultraviolet light will exacerbate discoloration, and even the orientation of the sample will alter the exposure to radiation and affect the degradation process (Waentig and Verlag 2008). In combination with oxygen, this energy contributes to the dehydrochlorination and formation of conjugation resulting in the chromophores responsible for the yellowed appearance, as well as crosslinking causing the embrittlement of the polymer (Quye and Williamson 1999). Cycles of humidity in the accelerated aging chamber, combined with the acidic environment from the degradation of PVC will, in turn, contribute to the hydrolysis of the phthalate plasticizer. Finally, PVC will soften upon warming, and changes in temperature place physical strain on the PVC and plasticizer. Combined, these factors affect plasticizer migration.

Critiques of artificial aging discuss the inherent inaccuracy of the protocol (Feller 1994). While temperature, light, UV, and humidity certainly cause dehydrochlorination and hydrolysis within the polymer, the exact combination of these factors, their duration, and myriad of other conditions will affect the chemical mechanism occurring in the sample. Essentially, artificial conditions can not accurately replicate the sheer variety of conditions that occur in the real environment, and therefore may not accurately replicate how a material will age. Nevertheless, artificial aging is currently the only method conservators have to replicate material aging on the long-term time scale on which conservation operates. Therefore, many studies will include accelerated aging to approximate any long-term effects.

Cleaning Plasticized Polyvinyl Chloride

As discussed above, treatment of soiled and degraded PVC often requires surface cleaning. However, there is a theory in the field that plasticizer deposited on the PVC surface creates a “stable equilibrium” with the polymer matrix of the object, protecting further deterioration. If this is the case, removing plasticizer from the surface may cause additional migration of the plasticizer to reform this equilibrium (Royaux et al 2017, Waentig and Verlag 2008). Further migration would increase embrittlement, so removing plasticizer could actually exacerbate the damage to the object in the long-term.

The number of studies around cleaning plastics has increased as plastics deterioration becomes increasingly prevalent in museum collections. Typically, cleaning studies will test a variety of solvents and applications that are commonly used in conservation. In 2012, the EU-funded project Preservation Of Plastics ARTefacts (POPART) in museum collections was the first to investigate specific issues regarding cleaning plastics. POPART included testing of the materials commonly used by conservators, thus providing as an excellent base for future studies. POPART considered variations in plastics and soiling types and tested twenty-three materials typically used, encompassing both aqueous and solvent cleaning methods. POPART’s method of analysis was limited to visual examination, gloss, percentages of area scratching, and contact angle (POPART 2012). While the project was thorough, it was by no means comprehensive and did not employ accelerated aging or examine long-term effects.

Since plastics are sensitive to polar solvents, conservators (and therefore cleaning studies) employ aqueous methods that include surfactants[3], alkaline solutions buffered with KOH, chelators such as tri-ammonium citrate, or synthetic saliva (POPART 2012). Similarly, the application method tested are chosen to minimize surface scratching or disruptions[4], with rolled cotton swabs as the most common (POPART 2012, Morales Muñoz, C. 2014, Laganà et al 2014). Choices of cleaning reagent is dependent of the type of soling on the surface, such as plasticizer, sebum, dust, etc.

Currently, very few studies have been published that explore cleaning plasticizer from plasticized PVC specifically, and none that attempt to quantitatively assess if removing plasticizer from degraded PVC will increase plasticizer migration.

Analysis of PVC: Common Analytical Methods

For the purposes of this study, analysis will be essential in determining the specific composition of the polymer and plasticizer, and the quantity of plasticizer present in the sample.

Researchers have used a variety of methods to analyze the components of PVC. Fourier transform infrared spectroscopy (FTIR) and pyrolysis Gas Chromatography – Mass Spectroscopy (py-GC-MS) are routinely used to identify polymers, plasticizers, and other additives (Tikka et al 2014, Tonkin 2017, Gumargalieva et al 1995, including others). Especially when combined with Evolved Gas Analysis (EGA), py-GC-MS allows for specific identification of the polymer and additives.

Studies quantify plasticizer content and migration with a variety of methods. Thermogravimetric analysis (TGA) proves especially helpful in polymer matrixes with additives, extenders, or plasticizers. The sample is continuously weighed during consistent heating, and volatile compounds (such as plasticizer) may be tracked by the temperature they volatilize, identifying the material and degradation process (Quye 1995). Royaux et al's 2017 study utilized TGA to determine the percentage of plasticizer content by comparing the weight loss of the samples to that of unplasticized PVC, where differences in mass percentage were assumed to be plasticizer loss. Other methods examine weight change with an analytical balance, assuming that a decrease in weight corresponds to increased plasticizer migration (Royaux et al's 2017**).** However, this method does not account for other physical changes in the plastic that may alter the weight, nor consider the location of the plasticizer. Finally, previous studies have quantified the plasticizer within a sample by comparing the increase of the carbonyl groups in ATR-FTIR before and after cleaning, creating a percentage of plasticizer loss before and after aging (Morales Muñoz, C. 2014, sourcing Mantuana and Kamden 2002 and Stark and Mantuana 2004). This method allows for a comparable, quantitative measure of the entirety of plasticizer in a sample but relies on the accuracy of the ATR-FTIR spectra.

[3] The surfactants tested in the POPART study included Dehypon LS45 (1% w/w in distilled water, non-ionic detergent, cloud point 22°C, fatty alcohol C12-C14, critical micelle concentration 0.0598 g/l), Judith Hofenk de Graaff detergent (textile detergent, 1% w/w in distilled water, non-ionic detergent, concentrated included 50g sodium dodecylnzenesulphonate, 50g tri-sodium citrate and 50g sodium carboxymethylcellulos in 1000mL distilled water), Orvus WA paste (1% w/w in distilled water, anionic detergent, sodium lauryl sulfate, critical micelle concentration 0.29 g/l) (POPART 2012)..

[4] For example, POPART tested twenty-four application materials in total and found different methods appropriate for different polymers (POPART 2012). Cleaning of PVC was carried out using cotton swabs, PVA sponges, cotton cloths, leather chamois, spectacles cloth, and microfiber cloths. Royaux et al 2017 utilized spectacles cloth EverClean, Braüner both made of polyester and polyamide (Royaux et al 2017).

These methods have been used to examine the efficacy of cleaning methods for different soil types (Morales Muñoz, 2010) including the extent of scratching (Laganà et al 2014) or the migration of the cleaning agent into the plastic (Morales Muñoz, 2014). Adeline Royaux et al's 2017 study incorporated plasticizer migration in examining the effects of aging cleaned plasticized PVC in open and controlled containers (Royaux et al 2017). Their study incorporated cleaning tests and examined plasticizer migration as part of the final analysis on the impact of the enclosures. They determined that non-enclosed samples had far higher plasticizer loss than contained samples, and cleaning with this method had no effect on migration. Additionally, Morales Muñoz et al's 2014 article evaluated the efficacy of cleaning methods on artificially aged PVC, examining plasticizer leaching caused by the cleaning reagent with ATR-FTIR as part of the analysis.

Research Question

This study will examine the following the effects of cleaning the plasticizer from the surface of degraded plasticized PVC affect future plasticizer migration. Specifically, does removing the plasticizer cause more plasticizer to leach from the polymer matrix?

Materials

This study will be conducted using samples of degraded PVC that is already exhibiting plasticizer migration. These samples will be sources from the Winterthur study collection.

The use of aged PVC presents several variables. The environmental conditions that caused the samples' current condition will be unknown, and information on the manufacture date or methods will be unknown. For this reason, existing studies have either tested new plastic samples (POPART 2012), subjected new sampled to accelerated aging (Morales Muñoz et al 2014) or compared natural aged plastic with artificially aged samples (Gumargalieva et al 1995). While this reduced the variables, the variations in the manufacturing process for plastics and variables from pre-accelerating aging still makes reproducibility problematic. By using already degraded PVC, this study would more closely replicate conditions and treatment of museum plastics and therefore be more useful to the field. Plastics already include a myriad of chemical compositions, copolymers, additives, and degradation pattern, that no single study can inform the conservation of all plastics. Moreover, new PVC may not give enough information about the migration since the plasticizer is stable and bound with the polymer. Lastly, all samples will be analyzed before the experiment begins so the polymer and plasticizer can be identified (discussed in the following sections).

Methods for Analysis

The following analytical methods are listed in order of priority for the experiment and sequence in which they will be performed:

1. Fourier Transform Infrared Radiography (FTIR)

FTIR will provide a broad analysis of the polymer and plasticizer that will be supported by the more specific results obtained py-GC-MS and TGA (discussed below). This initial analysis would allow for more targeted – and therefore more informative – subsequent analysis.

2. Pyrolysis-Gas Chromatography-Mass Spectrometry (py-GC-MS)

   Py-GC-MS would allow us to specifically identify the type of plasticizer within the plasticized PVC samples. Plasticizers and other additives readily volatilize, and by pyrolyzing the sample the polymer may be broken down into smaller components without pretreatment. Additionally, gas-born chromatography has larger, more reliable reference libraries available (compared to liquid chromatography) and is preferable for polymers, as polymers are not readily soluble in a liquid injection and readily volatize.

   This step is essential to characterize chemical compounds present in order to correctly interpret any conclusions. Py-GC-MS may show changes in the plasticizer or PVC, indicating chemical decomposition from cleaning or accelerated aging. If possible, EGA-MS should be conducted first. EGA-MS would give a general identification of the material and a specific temperature at which each component volatilizes. These temperatures regions could be analyzed in more detail with py-GC-MS, and a more targeted analysis would yield more specific, helpful results.

3. Thermogravimetric analysis (TGA)

   TGA assesses the quantity of plasticizer and how the plasticizer leaves the polymer matrix. This method may indicate the extent to which the plasticizer has deteriorated or migrated, the rate of migration, and the time at which migration occurs (Royaux et al 2017). This analysis will be conducted at the University of Delaware's Advanced Materials Characterization Laboratory (AMCL).

4. Attenuated Total Reflection - Fourier Transform Infrared Radiography (ATR-FTIR)

   Since ATR-FTIR is a surface technique, the presence of absorption bands associated with plasticizers – or their degradation products – will indicate if they are present on the surface (Morales Muñoz, et al 2014). Changes to the spectra may indicate the presence of degradation products after aging and increases or decreases in the carbonyl bands to the plasticizer after cleaning and accelerated aging may indicate changes to the concentration of the plasticizer (Morales Muñoz, et al 2014). This technique may also show detergent residues remaining on the sample surfaces.

5. Visual Examination Under Magnification

   While subjective, visual examination under a stereomicroscope should accompany the analytical methods listed above. Detailed visual examination is often the only way conservators have of assess PVC degradation, and comparing physical characteristics of color, surface texture, or gloss will inform the analytical results obtained through other methods.

Procedure

The following experiment will be conducted in January-May of 2020 at the Scientific Research and Analytical Laboratory (SRAL) at the Winterthur Museum and Gardens and the Advanced Materials Characterization Laboratory (AMCL) at the University of Delaware.

1. Examine the samples using the methods described above in Methods for Analysis.

2. Clean the plasticizer from the surface of the samples
   i. Solvents:
      Control/no cleaning – (x3 samples)
      Dei-ionized water – (x3 samples)
      Surfactant – 0.4% Ecosurf EH-9[5] in deionized water (x3 samples)

      Ecosurf EH-9 was selected based on the cleaning tests on the transparent Daniel Hechter dress in the collection of the Philadelphia Museum of Art, (Acc. Acc. # 1969-54-10). This surfactant appears to the be most effective at remove the surfacing dust and debris and will be the likely choice for surface cleaning the soiled PVC. Therefore, there is value in testing this surfactant's future effects on the plastic. Additionally, Ecosurf EH-9 is readily available in American labs, has no known environmental or health risks, and has a similar critical micelle concentration as surfactants previously tested by POPART and other studies.

   ii. Application method:
      Commercial swabs may be applied in circular motions to an area approximately 1 x 1 inch square for 10 seconds. The commercial swabs will reduce the variations of hand-rolled swabs, and the area and time reproduces cleaning methods commonly used by conservators (Morales Munoz et al 2014). All samples should be cleaned in the same space of time at room temperature.

      The samples cleaned with the surfactant should be rinsed following the cleaning to replicate typical lab practices that avoid leaving residue on the surface. The procedure for rinsing will follow the same time and application as the cleaning, described above.

3. Accelerate Aging of the samples
   Place all samples in an accelerated aging chamber following the ASTM standard D4459-99 for Xenon-Arc Exposure of Plastics Intended for Indoor Application (ATSM 1999, Laganà 2014) for 400 hours. 400 hours in accelerated aging corresponds to 40 years of museum lighting at 200 lux (Laganà 2014, Van Oosten and Laganà 2011).

4. Examine the samples using the same procedure as Step 1, described in Methods for Analysis.

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