Plasticized Polyvinyl Chloride

Subjects: Polymer Science
Contributor: Paula Gassmann, Carolin Bohlmann, Valentina Pintus

Plasticized polyvinyl chloride (p-PVC)—widely present in modern and contemporary art collections as objects, clothing and footwear, furniture and upholstery, and housewares and toys—is known to deteriorate very rapidly in museum collections. The tendency of colorless p-PVC-based objects to yellowing-browning in combination with stickiness and cracking are the main issues of this important plastic material, which require the attention of conservation scientists in cooperation with conservators, engineers, curators, and art historians.

Keywords: PVC ; plasticizer migration ; DEHP ; TCP ; artificial aging

1. “*PO^{E}METRIE*” by Dieter Roth—Challenges in the Preservation of Modern Polymeric Materials Combined with Natural Organic Fats

The preservation and conservation of contemporary art are especially challenging for conservators and conservation scientists because the artistic intention is far less clear than it might be for more traditional fields of art and needs to be questioned in far more detail. With some artworks, the idea as such is the core of the work; with others, it is the appearance or the materiality. Some artworks are supposed to look exactly the same as when they were produced, while others are allowed to undergo specific forms of decay. The list of ways contemporary artwork should be referred to is as long as the possible materiality or their combination can be made of. This can vary from inorganics to natural organics, synthetic organics, or even a mixture of all of them. Especially the combination of different kinds of material and how they were used (not always in the sense the material was supposed to be used from a manufacturing point of view) is making the preservation and conservation of contemporary art extremely complex.

Dieter Roth (1930–1998) in particular is no exception, but perhaps even one of the most extreme examples. The use of food as artistic material and sometimes the explicit intention of decay is bringing conservators partly to ethical conflicts but also to quite unique technical challenges.

The Artwork *PO^{E}METRIE* (1968) (**Figure 1**) is a special edition of Dieter Roth’s *POETRIE* Series, which he published between 1966 and 1969 as a biannual magazine. Next to the “normally printed” versions on paper, each volume was published additionally in the form of one or two special editions, which only vaguely reminded of a book in the conventional sense.

Figure 1. *PO^{E}METRIE* (1968) by Dieter Roth, (**a**) sticky brownish surface layer on the bags and agglomeration of droplets towards the edges, and (**b**) text interspersed with exudates under magnification (raking light).

In the case of the following copy, Dieter Roth used a yellowish-translucent plate made of plasticized polyvinyl chloride (p-PVC) as the book’s cover, and transparent p-PVC bags are mounted on it as pages. The text of the 4th *POETRIE* volume is printed on the outside of the bags, while the bags themselves are stuffed with minced mutton (**Figure 1**). Over time, a sticky-brownish surface film formed on the bags’ outer surface (**Figure 1**a), in which not only dust and dirt particles could accumulate but also put the printed text at massive risk of being lost (**Figure 1**b). Although the discussion on artistic intention is cropped short here, the loss of the text would massively undermine the readability and the artwork as a book, and especially its characteristics as a special edition of the 4th edition of the *POETRIE* series. In several interviews and publications, Dieter Roth described himself primarily as a writer rather than an artist [1], giving his books and texts a special position in his oeuvre. The loss of the text therefore cannot be seen as intended by the artist, and conservation treatment appears reasonable. Since the combination of p-PVC and minced mutton is also rather unusual for contemporary art, several material-based questions need to be answered in more detail before a conservation concept can be established.

2. Plasticized Polyvinyl Chloride Properties and Issues

Polyvinyl Chloride (PVC) is obtained through the polymerization of the vinyl chloride monomer (C_2H_3Cl), which is usually produced from the reaction of ethene, chlorine, and oxygen. During polymerization, the polarity of the C-Cl bond increases the attraction of the individual polymer chains, resulting in a rigid and brittle material without additional components such as plasticizers. The properties of PVC can be greatly varied by the use of additives, making this material partially suitable for other uses. This diversity is also the reason for the widespread use of PVC. Additives for PVC include, above all, plasticizers, but also stabilizers, lubricants, pigments, fillers, blowing agents, fungicides, etc., which all have a significant influence on the chemical and physical properties of the resulting material. The exact recipes differ depending on the processing method and area of application of the later product [2][3][4].

In order to obtain a softer and more flexible product, the distance between the individual PVC polymer chains must be increased. This can be done by copolymerization with other polymers, e.g., polyvinyl acetate (PVAc) (called internal plasticizer), but also by simply mixing plasticizers with the PVC granulate (called external plasticizer). Over time, many different substances have been used as plasticizers, and for a long time, bis(2-ethylhexyl) phthalate (DEHP) has dominated the market. Next to DEHP, other plasticizers were used as well, including other alkyl phthalates, phosphates like tricresyl phosphate (TCP) or triphenyl phosphate (TPP), different polyesters, sebacates, and chlorinated hydrocarbons [2][4]. These external plasticizers are held in the polymer structure by secondary valency forces, which, however, also leads to a separation of the two substances over time and thus to the plasticizers being displaced from the polymer structure, which is widely known and described as plasticizer migration. The plasticizer migration takes place because, during aging, PVC and plasticizer become increasingly incompatible with each other, leading to the segregation and displacement of the plasticizer from the bulk material to the outer surface [2][3][4]. The loss of phthalate plasticizers as semi-volatile organic compounds (SVOCs) such as DEHP depends mainly on the temperature and air-flow conditions [5]. Room temperature and low air flow rates above the surface influence their evaporation from the surface, while higher temperatures and airflows promote diffusion from the bulk. DEHP has a boiling point of 386 °C and is prone to evaporate slowly from the surface under ambient conditions [6].

Other issues with PVC in terms of aging and degradation are related to the influence of light and heat, accelerated by the presence of oxygen. Compared with other synthetic polymers, PVC is less prone to photochemical degradation, so most of the decomposition phenomena are of thermal origin [2]. The heat-activated degradation starts at 83.6 kJ/mol, which is comparatively low energy (e.g., PE 192.5 kJ/mol, PS 230 kJ/mol, PP 272 kJ/mol) [2]. The thermal instability is due to structural irregularities in the material, particularly the -C=C- bonds at the chain ends. Tertiary carbon atoms, oxygen-containing compounds, and residues of catalyst from polymerization also play their part and reduce the resistance to thermal decomposition processes. Irregularities in the material with low binding energy (such as oxygen-containing groups, branching, or head-to-head connections) are easy targets where material degradation sets in first [2]. Cleavage of these low-energy bonds leads to radicalization of the polymer chain and the eventual elimination of HCl molecules. The splitting of a Cl atom not only leads to the formation of hydrochloric acid but also to a displacement of the electrons; as a result, conjugated double bonds are formed [2]. As soon as one HCl molecule is split off, further HCl molecules are separated like a zipper, meaning that this reaction continues autocatalytically [2]. From a number of 5 to 7 conjugated double bonds, the PVC shifts in color (from transparent to yellow, through red to brown, and finally turns black) [2][7]. The formation of these conjugated sequences can also lead to the formation of carbenium salts, which in turn lead to an intensification of the color depth (halochromic). This is particularly noticeable with PVC, which has already been thermally stressed [7]. However, in the context of the lifespan of p-PVC in indoor conditions, HCl elimination of the p-PVC takes place later than plasticizer migration, which will appear as the first issue in museum objects [5]. Investigations into the stability and degradation of PVC plasticized with DEHP highlight the impact of environmental conditions, and museum objects should be stored in closed environments, frozen, or kept at high relative humidity to prevent the loss of plasticizers [2]. Contact with materials like low-density polyethylene (LDPE) should be avoided due to the strong contact migration and diffusion of DEHP [2].

While all involved additives make the resulting plastic material a perfect fit for its intended industrial purpose, p-PVC as an artistic material has often been misused in its application. The same applies to the object on which this research is based. Most plasticizers are well soluble in fats, and studies from the food packaging industry point out that plasticizers especially diffuse from the packaging into fatty foodstuffs [8][9][10][11]. Since diffusion is a bidirectional mechanism, this process also applies the other way around, and fatty components from foodstuffs will therefore also diffuse in and through the p-PVC. Next to plasticizer migration, fat diffusion needs to be seen as an essential part of the following case study and investigation. In addition to these two physical phenomena, the possibility of the bags leaking at the weld seams cannot be ruled out and appears to be a very likely additional factor that aggravates the problem.

According to the authors' knowledge, so far, there have been no studies on plasticizer migration and fat diffusion in p-PVC associated with the fields of art and conservation. The only studies in this direction come from the food packaging industry, although the issue is viewed from exactly the other direction (the migration of packaging components into the food) [8][9][10][11]. Additionally, those studies refer to shorter periods of time, from a few days to a maximum of months, but nowhere near 60 years, as in the present artwork. Within the field of art and conservation, several different studies have been performed into the aging behavior of p-PVC [2][3][6][12], as well as on the impact of environmental [13] and storage conditions [14], or the cleaning of degraded p-PVC [14][15]. A recent review on PVC in plastic heritage collections reports the different degradation pathways and properties of PVC relevant to conservation, also highlighting several still existing gaps in understanding of PVC degradation, such as surface accumulation of plasticizers, degradation at temperatures below T_g, etc. [5]. A number of different analytical techniques have been used to study plasticizer migration and degradation of p-PVC in art and conservation contexts [2][3][12][13][14][15][16] as well as for industrial purposes [17][18][19][20]. Degradation factors such as the yellowing of PVC in relation to dehydrochlorination and the length of the polyene sequence in PVC have been investigated by UV/Vis [12][21][22] and Raman spectroscopy [22][23][24], which have been considered suitable techniques for detecting polyenes and characterizing the current state of the material. The presence of phthalate in p-PVC has been investigated by Raman spectroscopy but also by Fourier Transform Infrared in Attenuated Total Reflection (FTIR-ATR), but the similarity of the di-alkyl phthalate spectra makes the exact identification challenging. On the other hand, FTIR-ATR represents, especially for art and conservation purposes, one of the widest-spread techniques. It is also one of the quickest but at the same time most informative ones for the identification of the major compounds and functional groups, as well as for the identification of specific surface phenomena [2][13][14][15][16]. It is generally complemented by Pyrolysis—Gas Chromatography/Mass Spectrometry (Py-GC/MS) for the precise identification and characterization of plasticizers and other additives [15][25][26].

3. Relevance to Other *PO^E^METRIE* Copies

Five further copies of the edition *PO^E^METRIE* could be visually examined during this research (Dieter Roth Foundation, Hamburg, Germany; LWL Münster, Münster, Germany; Staatsgalerie, Stuttgart, Germany; Kunstbibliothek, Berlin, Germany; Zucker Art Books, NY City, USA; and this copy, private ownership and permanent loan at Belvedere Wien, Vienna, Austria). The individual copies showed extensive similarities, but also individual differences. All copies have in common the format, the p-PVC components, and the text, but deviations can sometimes be found not only in the design of the book's cover but also in the bag's filling. Despite the minced meat commonly found in all copies, one copy seems to contain additional portions of fat (optically reminiscent of clarified butter) [27], while another copy appears to contain a higher content of blood in addition to the meaty component [28]. However, no analysis of the bag filling was performed, neither in this research nor for one of the other copies, because this would have required an opening of the bags for sampling. Therefore, it is unclear whether the bags are really stuffed with minced mutton or if Dieter Roth just claims that minced meat of another origin was used. In the present case, it does not appear as if blood was added, but differences in the fat concentration cannot be ruled out, also because natural products, especially those of animal origin, generally vary in exact composition. However, the differences mentioned did not necessarily lead to different material behavior, although the individual copies are in different states of preservation, and while some are still in good condition, others showed similar degradation patterns like those described here in more detail.

References

1. Dobke, D. Melancholischer Nippes: Dieter Roths frühe Objekte und Materialbilder (1960–1975). Ph.D. Thesis, Universität Hamburg, Hamburg, Germany, 1997. Available online: https://ediss.sub.uni-hamburg.de/bitstream/ediss/163/1/Dissertation_gesamt.pdf (accessed on 26 November 2023).
2. Shashoua, Y.R.R. Inhibition the Deterioration of Plasticized Poly (Vinyl Chloride)—A Museum Perspective. Ph.D. Thesis, The Technical University of Denmark, Lyngby, Denmark, 2001. Available online: http://www.cwaller.de/didaktik_teil4/shashoua_2001.pdf (accessed on 26 November 2023).
3. Ryf, S. Weichmacherverlust Bei Objekten Aus Weich-PVC Am Beispiel Einiger Multiples Von Joseph Beuys, Semesterarbeit; Hochschule der Künste Bern: Bern, Switzerland, 2005.
4. Waentig, F. Kunststoffe in Der Kunst: Eine Studie Unter Konservatorischen Gesichtspunkten; Petersberg: Imhof, Germany, 2004; pp. 239–248.
5. Rijavec, T.; Strlič, M.; Cigić, I.K. Plastics in Heritage Collections: Poly(vinyl chloride) Degradation and Characterization. Acta Chim. Slov. 2020, 67, 993–1013.
6. Shashoua, Y.R. Conservation of Plastics Materials Science Degradation Preservation. Butterworth-Heinemann. In Conservation of Plastics; Routledge: London, UK, 2008.
7. Ehrenstein, G.W.; Pongratz, S. Beständigkeit Von Kunststoffen—Bd. 1; Carl Hansen Verlag: Munich, Germany, 2007; pp. 362–363.
8. Cruz, R.M.S.; Rico, B.P.M.; Vieira, M.C. 9—Food packaging and migration. In Food Quality and Shelf Life; Galanakis, C.M., Ed.; Academic Press: Cambridge, MA, USA, 2019; pp. 281–301.

9. Ardıç, M.; Kahve, H.; Duran, A. Chemical Migration in Food Technology. Acad. J. Sci. 2015, 4, 163–166. Available online: https://www.researchgate.net/publication/290429224_CHEMICAL_MIGRATION_IN_FOOD_TECHNOLOGY (accessed on 26 November 2023).
10. Bhunia, K.; Sablani, S.S.; Tang, J.; Rasco, B. Migration of Chemical Compounds from Packaging Polymers during Microwave, Conventional Heat Treatment, and Storage. Compr. Rev. Food Sci. Food Saf. 2013, 12, 523–545.
11. Fiigge, K. Migration of Components from Plastics-Packaging Materials into Packed Goods-Test Methods and Diffusion Models. Prog. Polym. Sci. 1980, 6, 187–252.
12. Rijavec, T.; Strlič, M.; Cigić, I.K. Damage function for poly(vinyl chloride) in heritage collections. Polym. Degrad. Stab. 2023, 211, 110329.
13. Klempová, S.; Oravec, M.; Vizárová, K. Analysis of thermally and UV–Vis aged plasticized PVC using UV–Vis, ATR-FTIR and Raman spectroscopy. Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 2023, 294, 122541.
14. Royaux, A.; Fabre-Francke, I.; Balcar, N.; Barabant, G.; Bollard, C.; Lavédrine, B.; Cantin, S. Aging of plasticized polyvinyl chloride in heritage collections: The impact of conditioning and cleaning treatments. Polym. Degrad. Stab. 2017, 137, 109–121.
15. Morales Muñoz, C.; Egsgaard, H.; Sanz-Landaluze, J.; Dietz, C. A model approach for finding cleaning solutions for plasticized poly(vinyl chloride) surfaces of collections objects. J. Am. Inst. Conserv. 2014, 53, 236–251.
16. Rijavec, T.; Ribar, D.; Markelj, J.; Strlič, M.; Cigić, I.K. Machine learning-assisted non-destructive plasticizer identification and quantification in historical PVC objects based on IR spectroscopy. Sci. Rep. 2022, 12, 5017.
17. Dutta, P.K.; Graf, K.R. Migration of Plasticizer in Vinyl Resins: An Infrared Spectroscopic Study. J. Appl. Polym. Sci. 1984, 29, 2247–2250. Available online: https://onlinelibrary.wiley.co (accessed on 26 November 2023).
18. Petre, A.; Budrugeac, P.; Segal, E. Thermal Degradation of Polyvinyl Chloride. J. Therm. Anal. Calorim. 1999, 56, 1065–1070. Available online: https://www.academia.edu/6225326/Thermal_Degradation_of_Polyvinyl_Chloride?email_work_card=view-paper (accessed on 26 November 2023).
19. Jakubowicz, I.; Yarahmadi, N.; Gevert, T. Effects of accelerated and natural ageing on plasticized polyvinyl chloride (PVC). Polym. Degrad. Stab. 1999, 66, 415–421.
20. Ito, M.; Nagai, K. Analysis of degradation mechanism of plasticized PVC under artificial aging conditions. Polym. Degrad. Stab. 2007, 92, 260–270.
21. Braun, D.; Sonderhof, D. Assignment of UV-absorption maxima of degraded PVC. Polym. Bull. 1985, 14, 39–43.
22. Al-Dossary, A.K.; Gilbert, M.; Hitt, D. Evaluating PVC degradation using UV and Raman spectroscopies. Adv. Mater. Res. 2010, 83–86, 923–930.
23. Baruya, A.; Gerrard, D.L.; Maddams, W.F. Resonance Raman spectrum of degraded poly (vinyl chloride). 4. determination of conjugated polyene sequence lengths. Macromolecules 1983, 16, 578–580.
24. Kip, B.J.; van Aaken, S.M.; Meier, R.J.; Kenneth, P.J.W.; Gerrard, D.L. Considerations for Raman Spectroscopic Determination of Polyene Length Distribution in Degraded Poly(vinyl chloride). Macromolecules 1992, 25, 4290–4296.
25. Fumitaka, M.; Fujimaki, S.; Sakamoto, Y.; Kudo, Y.; Miyagawa, H. Screening of Phthalates in Polymer Materials by Pyrolysis-GC-MS. Anal. Sci. 2015, 31, 3–5.
26. Akoueson, F.; Chbib, C.; Monchy, S.; Paul-Pont, I.; Doyen, P.; Dehaut, A.; Duflos, G. Identification and quantification of plastic additives using pyrolysis-GC/MS: A review. Sci. Total Environ. 2021, 773, 145073.
27. Landesmuseum Westfalen-Lippe (LWL), Dieter Roth, POEMETRIE (1968). Available online: https://www.lwl.org/323sc-download/LWL/Kultur/stiftung-cremer/popups/roth-poetry/index.html (accessed on 16 September 2023).
28. Zucker Art Books, New York, Dieter Roth, POEMETRIE (1968). Available online: https://www.zuckerartbooks.com/inc/scripts/image_pdf.php?file_id=20562&caption=Dieter%20Roth%2C%20%3Ci%3EPoemetry%2C%20Deluxe%20Edition%20No.4%20of%20the%20review%20%EBK%2C%20Price%20Upon%20Request (accessed on 16 September 2023).