

# CONSERVATION AND RESTORATION OF WORKS OF ART AND MUSEUM ARTIFACTS MADE FROM POLYMER MATERIALS – FIELD OF CLOSE CONNECTION OF SCIENCE AND ART: OVERVIEW OF CURRENT PRACTICE

**Radmila B. DAMJANOVIĆ**

*University of Belgrade, Faculty of Technology and Metallurgy  
– Department of Materials Engineering; University of Arts in Belgrade,  
Faculty of Applied Arts – Department of Conservation and Restoration,  
Belgrade, Serbia*

**Mina Lj. JOVIĆ**

*University of Arts in Belgrade, Faculty of Applied Arts  
– Department of Conservation and Restoration, Belgrade, Serbia*

**Radmila M. JANČIĆ-HEINEMANN**

*University of Belgrade, Faculty of Technology and Metallurgy  
– Department of Materials Engineering, Belgrade, Serbia*

**Irena D. ŽIVKOVIĆ**

*University of Arts in Belgrade, Faculty of Applied Arts  
– Department of Conservation and Restoration, Belgrade, Serbia*

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**Abstract:** Decorative, functional, and artistic objects made from polymer materials, as witnesses of creative development of humankind, gained their place in museums and collections. Being organic, polymers are more prone to degradation than inorganic materials. Depending on the physical, chemical, and biological degradation factors, fabrication, composition and the presence of additives in a polymer material, artifacts and works of art made from polymers possess different levels of stability and endurance to external conditions, whether in close or in open. An overview of current practice in the field of conservation and restoration of works of art and museum artifacts made from polymer materials, presented in this paper, is based on the analysis of gathered available scientific-professional literature. The main properties of polymer classes, typical degradation factors and processes, examples of conservation-restoration treatments based on scientific methods, and storage recommendations are given. The materials that the analyzed objects are made from include natural polymers like amber, tortoiseshell, horn, natural rubber, as well as synthetic polymers like synthetic rubber, cellulose nitrate, cellulose acetate, casein-formaldehyde, Bakelite, poly(methyl methacrylate), poly(vinyl chloride), polystyrene, polyurethane, polyethylene, phenol-formaldehyde, thermore-

active polyesters and epoxies. Based on the analyzed literature it can be observed that conservation and restoration of works of art and museum artifacts made from synthetic polymer materials is a new area of conservation-restoration research, still in development. The fact that precise methodologies have not yet been specified for many polymer materials contributes to this. It is also a field of close cooperation of scientific-technological and conservation-restoration approaches, where they intertwine and complement each other.

**Keywords:** polymers, plastics, conservation, restoration, degradation

## INTRODUCTION

Polymers, both natural and synthetic, are present in museum collections, either as a constitutive material of works of art and museum artifacts or as a substance/material used for conservation and restoration treatments.<sup>1,2,3</sup> Regarding objects made from polymers, the term ‘plastics’ is often used. It refers to polymer-based materials modified with additives and sometimes reinforcing materials and shaped into dimensionally stable forms.<sup>4,5</sup> Polymers, as organic materials, decay faster than inorganic ones. However, within polymer materials there are variations in the speed of decay.<sup>6</sup> It should be noted that, when it comes to works of art and museum artifacts made from polymer materials, degradation is not only attributed to physical and chemical changes, but also to loss in function, form, and significance of the object. Degradation of objects made from synthetic polymers is generally observed by appearance, odor or feel within the period of 5 to 25 years of collection.<sup>7</sup> The research in the field of conservation and restoration of works of art and artifacts made from synthetic polymer materials and related polymer degradation has only been recognized since the last decade of the 20th century. There have been a number of conferences and projects covering this topic,<sup>8</sup> including POPART: Preservation Of Plastics ARTefacts, research project with focus on establishing protocols for analyzing, examining and conserving plastic artifacts.<sup>9</sup>

The aim of this article is to provide a brief general overview of literature on the current practice in the field of conservation and restoration of works of art and museum

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1 M. T. Baker, “Polymers in museums”, in: *Historic Textiles, Papers, and Polymers in Museums*, eds. J. M. Cardamone et M. T. Baker, Washington, DC, 2001, 128.

2 C. V., Horie, *Materials for conservation: organic consolidants, adhesives and coatings*, 2nd Edition, 2010, Preface ix–x

3 M. Lazzari et D. Reggio, “What Fate for Plastics in Artworks? An Overview of Their Identification and Degradative Behaviour”, *Polymers*, Vol. 13, 2021, 883–884.

4 Y. Shashoua, *Conservation of Plastics: Materials Science, Degradation and Preservation*, Oxford, 2008, 1

5 *ibid.*, 115.

6 F. Waentig, *Plastics in Art: A Study from the Conservation Point of View*, Petersberg, 2008, 148.

7 Y. Shashoua, 2008, *op. cit.*, 151–152.

8 *ibid.*, 11–13.

9 POPART: Preservation Of Plastics ARTefacts research project, <https://popart-highlights.mnhn.fr/>

artifacts made from polymer materials, specifically connected to the application of scientific and technological methods. It addresses only 3D works of art and museum artifacts, not paints, textiles and photographic films. The article is divided in three sections covering the following: a short overview of general degradation factors and processes for polymer materials (Section 2), general information on conservation-restoration methodology of works of art and museum artifacts made from polymer materials (Section 3), and information about main properties of characteristic polymer classes, their typical degradation factors and mechanisms, and examples of conservation-restoration treatments, based on the analysis of the found available scientific-professional literature, along with storage recommendations (Section 4).

## DEGRADATION OF POLYMER MATERIALS

The term 'degradation' of a material refers to long-term physical and chemical processes that cause damage to a material.<sup>10</sup> Another common term used in terms of degradation is 'aging' and it generally refers to long-time changes of material properties caused by weathering.<sup>11</sup> Polymer degradation is possible throughout the lifecycle of existence.<sup>12</sup> In the case of synthetic polymers, it starts from fabrication because reactions of polymerization along with additives and forming processes all have impact on the physical and chemical properties of polymer materials, on their lifetime and degradation pathways.<sup>13</sup> Once the degradation has started it is almost impossible to stop or reverse it.<sup>14,15</sup> The factors that cause degradation are divided in the following three groups:

**Physical factors.** They can be classified by degradation due to a) mechanical use of plastics, resulting in stress, fatigue and mechanical damage, b) physical interaction with surroundings, which relates to permeability of polymers to liquids, vapors, and gases, and to dimensional and flexibility changes due to temperature variations and c) migration and loss of additives, which can cause brittleness and shrinkage, oily or solid bloom on the surface.<sup>16,17</sup> Physical aging is connected to reorganization of extant molecules and depends on internal factors (like molecular weight, molecule structure and form, intermolecular forces, and presence of plasticizers) and external factors (like temperature changes and mechanical stresses).<sup>18</sup>

**Chemical factors.** They refer to chemical reactions of polymers with water, oxygen, ozone, radiation (visible light, ultraviolet, UV, light and heat), metals,<sup>19</sup> chemical agents during usage, exhibition, storage, and conservation-restoration treatments.<sup>20</sup>

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10 I. Živković et R. Aleksić, *OSNOVE POZNAVANJA MATERIJALA za studente primenjene umetnosti*, Beograd, 2012, 242.

11 Y. Shashoua, 2008, *op. cit.*, 151.

12 I. Živković et R. Aleksić, 2012, *op. cit.*, 290.

13 Y. Shashoua, 2008, *op. cit.*, 39.

14 F. Waentig, *op. cit.*, 148.

15 A. Holländer, "Aging of plastics – What can we do about it?", in: *FUTURE TALKS 2009: The Conservation of Modern Materials in Applied Arts and Design; papers from the conference held at the Pinakothek der Moderne. Munich 22–23 October 2009*, ed. T. Bechthold, Munich, 2011, 30.

16 Y. Shashoua, 2008, *op. cit.*, 153–161.

17 E. Martuscelli, *The Chemistry of Degradation and Conservation of Plastic Artefacts of Pre-synthetic "era" Based on Natural Or Artificial Polymers*, Firenze, 2010, 88–89.

18 O. Chiantore et A. Rava, *Conserving Contemporary Art Issues, Methods, Materials, and Research*, The Los Angeles, 2012, 76.

19 Y. Shashoua, 2008, *op. cit.*, 162.

20 E. Martuscelli, *op. cit.*, 89.

Due to the activity of this group of factors, the main transformation processes that can occur in polymers are the following: photo degradation (light), thermal degradation (heat) and oxidative processes: photo-oxidation (light and oxygen) and thermo-oxidation (heat and oxygen).<sup>21</sup> Chemical factors can cause the following changes in structure of polymers: chain scission, cross-linking,<sup>22</sup> development of chromophores and development of polar groups.<sup>23</sup>

**Biological factors.** Activity of microorganisms can lead to degradation of natural and synthetic polymers,<sup>24</sup> causing structural, functional<sup>25</sup> and aesthetical damage. Production of acids and enzymes by microorganisms can lead to polymer deterioration and components leaching.<sup>26</sup> Biofilm is considered the main cause of deterioration.<sup>27</sup> It is formed due to microbial growth and can occur on surface as well as in the cracks of polymer material.<sup>28</sup>

Besides these external degradation factors, harmful phenomena to polymer materials are caused by internal factors, i.e., composition, structure, form, internal stresses, structure defects, surface condition etc.<sup>29</sup> Since polymers are macromolecules, their properties are in relation to their high molecular weight. Change in molecular weight of a polymer causes alteration of properties, which can be of two types: physical (decrease in molecular weight, tensile strength, impact strength, elongation at break, loss of gloss, surface erosion), and chemical (chemical structure changes: formation of functional groups).<sup>30</sup>

## BRIEF OVERVIEW OF THE METHODOLOGY OF CONSERVATION AND RESTORATION OF WORKS OF ART AND MUSEUM ARTIFACTS MADE FROM POLYMER MATERIALS

The first step prior to any analysis and treatment is an assessment of the condition of preservation of works of art and artifacts. A description of damage categories of polymer objects can be found in the literature.<sup>31,32,33,34</sup> To plan an adequate conser-

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21 *ibid.*

22 I. Živković et R. Aleksić, 2012, *op. cit.*, 290.

23 Y. Shashoua, 2008, *op. cit.*, 164.

24 V. M. Pathak et Navneet, "Review on the current status of polymer degradation: a microbial approach", *Bioresources and Bioprocessing*, Vol. 4, 2017, 15–45.

25 F. Cappitelli et C. Sorlini, "Microorganisms Attack Synthetic Polymers in Items Representing Our Cultural Heritage", *Applied and Environmental Biology*, Vol. 74 (3), 2008, 564.

26 C. McNamara et al., "Microbial Deterioration of Cultural Heritage Materials", in: *Environmental Microbiology*, eds. R. Mitchell, J. D. Gu, Hoboken (NJ), 2010, 142.

27 F. Cappitelli, P. Principi et C. Sorlini, "Biodeterioration of modern materials in contemporary collections: can biotechnology help?", *TRENDS in Biotechnology*, Vol. 24 (8), 2006, 350–354.

28 F. Cappitelli et F. Villa, "Modern materials and contemporary art", in: *Biodeterioration and Preservation in Art, Archaeology and Architecture*, eds. R. Mitchell et J. Clifford, London, 2018, 80–81.

29 I. Živković et R. Aleksić, 2012, *op. cit.*, 240.

30 N. S. Allen et M. Edge, *Fundamentals of Polymer Degradation and Stabilization*, London, 1992, 2–3.

31 B. Keneghan, "A Survey of Synthetic Plastic and Rubber Objects in the Collections of the Victoria and Albert Museum", *Museum Management and Curatorship*, Vol. 19 (3), 2001, 330–331.

32 Y. Shashoua, 2008, *op. cit.*, 271–274.

33 F. Waentig, *op. cit.*, 156–161.

34 A. Quye, et B. Keneghan, "Degradation", in: *Plastics: Collecting and Conserving*, eds. A. Quye et C. Williamson, Edinburgh, 1999, 111–121.

vation-restoration treatment a necessary condition is identification of the polymer type(s) that works of art/artifacts contain. It includes simple tests and instrumental techniques. Simple tests, used for rough qualitative assessment, are divided in non-destructive (examination of appearance and odor) and destructive (determination of density and hardness, heat tests).<sup>35</sup> Instrumental analyses include a range of techniques like Fourier transform Infrared (FTIR) spectroscopy, Raman spectroscopy, near-infrared (NIR) spectroscopy, pyrolysis gas chromatography-mass spectrometry (py-GC-MS), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), energy dispersive X-ray analysis (EDAX, EDX or EDS), X-ray fluorescence (XRF), nuclear magnetic resonance (NMR), dynamic thermal mechanical analysis (DTMA), etc.<sup>36,37,38</sup> There are two general approaches to conservation treatments: preventive and interventive conservation. This classification is also applicable for works of art and museum artifacts made from polymer materials. The goal of preventive conservation is to limit the rate and extent of materials degradation by minimizing exposure to degradation factors, along with the provision of stable environmental conditions (during storage, exhibition, packaging and transporting). It can be performed by using adsorbents, by enclosing objects and by low temperature storage. Interventive conservation relates to invasive treatments on objects with the purpose of stabilizing and strengthening degraded materials, limiting further degradation, and preserving their significance. It involves cleaning (mechanical and chemical), consolidation, adhering broken fragments and filling losses.<sup>39</sup> Regarding the literature for conservation-restoration of works of art and museum artifacts made from polymer materials, the topic on preventive conservation is more present than on the interventive conservation and restoration.<sup>40</sup>

### OVERVIEW OF LITERATURE ON CONSERVATION AND RESTORATION OF WORKS OF ART AND MUSEUM ARTIFACTS MADE FROM POLYMER MATERIALS BY SPECIFIC POLYMER TYPES

As an additional supplement for the overview given in the following section, a fact sheet with the gathered data on conservation-restoration of works of art and artifacts made of listed polymer types is presented (not included within the text of the following section). It provides the information on specific substances for cleaning, consolidation, joining, and gap-filling, which are used on original objects. This information is provided in Table 1 at the end of the paper text.

#### Amber

Amber, a natural polymer, is a fossilized resin that has amorphous structure and conchoidal shaped fracture. It is insoluble in water and variably soluble in common organic solvents.<sup>41</sup> Negative charge and attraction of lightweight particles is caused

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35 Y. Shashoua, 2008, *op. cit.*, 116–129.

36 *ibid.*, 133–147.

37 M. Lazzari et D. Reggio, *op. cit.*, 885–889.

38 E. Martuscelli, *op. cit.*, 298.

39 Y. Shashoua, 2008, *op. cit.*, 193–207.

40 *ibid.*, 230.

41 G. Pastorelli, *Archaeological Baltic Amber Degradation Mechanisms and Conservation Measures* (PhD thesis), Bologna University, 2009, 1–2.

when friction is applied to amber.<sup>42</sup> The main degradation factor for amber is oxygen; degradation leads to darkening, loss of polish and craquelures formation, which causes opacity and brittleness.<sup>43</sup> Oxidation is considered to be a surface phenomenon due to low amber porosity and slow gas diffusion.<sup>44,45</sup> Light and heat can accelerate oxidation.<sup>46</sup> UV light can cause rapid degradation.<sup>47</sup> A doctoral thesis reports on conducted artificial aging tests used for degradation examination and the application of results for planning a preventive conservation strategy.<sup>48</sup> Degradation is slower for higher relative humidity (RH) values.<sup>49</sup> A paper about the conservation of Baltic amber artifacts from the British Museum collection investigated choices for resin and solvent mixtures for the consolidation of amber, and improved methods for storage and display. It also provides a review of past conservation treatments of amber. Two types of physical changes caused by oxidation are described: surface crazing and surface powdering, both having as a result weakening and loss of material. Prior to any conservation-restoration treatment it is advised to provenance amber so that there is no interference with the future analysis of amber.<sup>50</sup> Another research was focused on the identification and treatment of a particular amber piece of jewelry with the intention of mitigating the opaque bloom, along with brief overview of methods for amber identification.<sup>51</sup> Recommended general storage conditions are: temperature 17–25 °C, relative humidity (RH) 45–55%, exclusion on UV radiation in storage and 50 µW/lm for display.<sup>52</sup>

### Tortoiseshell

Tortoiseshell is a natural thermoplastic polymer and can be formed into desired shapes using heat and pressure.<sup>53</sup> It is composed mainly of structural protein keratin.<sup>54</sup> Due to the presence of disulfide bonds<sup>55</sup> keratin is insoluble in solvents like water, aqueous acidic and basic solutions, and organic solvents, and has high mechanical strength.<sup>56</sup> A paper on the conservation of an archaeological lyre, apart from providing information on biochemistry, structure, and decay of tortoiseshell, deals

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- 42 F. Causey, *Ancient Carved Ambers in the J. Paul Getty Museum*, Los Angeles, 2019, 18.
- 43 K. W. Beck, "Authentication and conservation of amber: conflict of interests", *Studies in Conservation*, Vol. 27, Sup. 1, 2016, 105.
- 44 G. Pastorelli, J. Richter et Y. Shashoua, "Evidence concerning oxidation as a surface reaction in Baltic amber", *Spectrochimica Acta Part A*, Vol. 89, 2008, 268.
- 45 Y. Shashoua, M.L. Degn Berthelsen et O.F. Nielsen, "Raman and ATR-FTIR spectroscopies applied to the conservation of archaeological Baltic amber", *Journal of Raman Spectroscopy*, Vol. 37, 2006b, 1227.
- 46 K. W. Beck, *op. cit.*, 105.
- 47 D. Thickett, P. Cruckshank et C. Ward., "The conservation of Amber", *Studies in Conservation*, Vol. 40 (4), 1995, 224.
- 48 G. Pastorelli, *op. cit.*
- 49 Y. Shashoua 2006b, *op. cit.*, 1227.
- 50 D. Thickett, P. Cruckshank et C. Ward., *op. cit.*, 218.
- 51 N. Caldararo et al., "The Analysis, Identification and Treatment of an Amber Artifact", *Archaeomatica*, No. 2, 2013, 46–49.
- 52 D. Thickett, P. Cruckshank et C. Ward., *op. cit.*, 224.
- 53 T. Hainschwang, et L. Leggio, "The Characterization of Tortoise Shell and its Imitations", *Gems and Gemology*, Vol. 42 (1), 2006, 39.
- 54 A. Pereira et al., "Tortoiseshell or Polymer? Spectroscopic Analysis to Redefine a Purported Tortoiseshell Box with Gold Decorations as a Plastic Box with Brass", *Applied Spectroscopy*, Vol. 70 (1), 2016, 68.
- 55 J. S. Mills et R. White, *The Organic Chemistry of Museum Objects*, Oxford, 1987, 75.
- 56 M. C. Tanzi, S. Farè et G. Candiani, *Foundations of biomaterials engineering*, London, 2019, 235.

with practical conservation treatments including cleaning, consolidation and assembly. Aging of tortoiseshell causes brittleness, desiccation, and microscopic separation of keratin layers which leads to loss of translucency. Keratin decay pathways include chemical – and biodegradation, the latter being the major cause. Despite insolubility in water, hydrogen bonds exist between some keratin polypeptide chains, so water can penetrate it causing swelling and dimensional change. When in contact with corroding metals in burial ground keratin structure is invaded by corrosion products, which enables protection of organic matrix up to some level. Temperature, moisture content and pH of burial environment influence the chemical deterioration rate. Keratin is better preserved in anaerobic conditions. Recommended RH value for storage is between 40–45%, in polyethylene boxes.<sup>57</sup> High pH values cause faster hydrolysis of keratin, causing weakening and brittleness.<sup>58</sup>

## Horn

Horn is a keratinous tissue, tough, flexible, moldable, and fusible. It can be considered biocomposite material, mainly consisting of keratin with a small content of calcium mineral.<sup>59</sup> Like tortoiseshell, it is a natural thermoplastic polymer<sup>60</sup> and can undergo flattening, splitting and joining when soaked in hot water.<sup>61</sup> Compared to other biocomposites, toughness and work of fracture, values are higher and can be compared to polycarbonate (bulletproof “glass”).<sup>62</sup> Archaeological keratinous tissues, including horn, if found survived in burials, are fragile, matt, opaque and dark brown to black or metal corrosion.<sup>63</sup> Very often keratinous tissues, including horn, survive in unfavorable burial conditions as mineral preserved the organic (MPO) remains, due to close contact with corroding metals: organic material is coated or colored and/or invaded by corrosion products.<sup>64</sup> A PhD thesis on degradation of archaeological horn, antler and ivory provides information on deterioration processes and analysis of deterioration of material in different burial environments with research to relate degradation processes to specific environment.<sup>65</sup> Horn can decay by physical-, chemical- and biodegradation. Water loss causes horn to split and warp.<sup>66</sup> Regarding preventive conservation, archaeological horn is not a suitable material as it generally continues to deteriorate if it is not adequately conserved.<sup>67</sup> A study on conservation of ivory and related material reports on specific consolidants and

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57 V. Millona, “Conservation of the Lyre from Grave 48 in the Area between the So-Called ‘Eriai’ Gates and the Dipylon (470–50 BC)”, *Greek and Roman musical studies*, Vol. 8, 2020, 49–50.

58 J. M. Cronyn, *Elements of Archaeological Conservation*, London, 1990, 282.

59 S. O’Connor, C. Solazzo et M. Collins, “Advances in identifying archaeological traces of horn and other keratinous hard tissues”, *Studies in Conservation*, 60 (6), 2014, 393.

60 P. Craddock, *Scientific Investigation of Copies, Fakes and Forgeries*, Amsterdam, 2009, 449.

61 J. M. Cronyn, *op. cit.*, 283.

62 L. Tombolato et al., “Microstructure, elastic properties and deformation mechanisms of horn keratin”, *Acta Biomaterialia*, Vol. 6, 2010, 320.

63 S. O’Connor, “Conservation of Bone, Horn, and Ivory”, in: *The Encyclopedia of Archaeological Sciences*, ed. S. L. López Varela, JohnWiley & Sons, Inc., 2018, 2.

64 S. O’Connor, C. Solazzo et M. Collin, *op. cit.*, 395.

65 P. Simpson, *Studies of the Degradation of Horn, Antler and Ivory at Archaeological Site* (PhD thesis), University of Portsmouth, 2011.

66 *ibid.*, 37–43.

67 *ibid.*, 233.

adhesives used.<sup>68</sup> Recommended storage conditions are: temperature not greater than 25 °C, RH in the range 45–55%, illumination should be kept below 150 lux, for colored objects up to 50 lux, UV light below 75 µW/lm.<sup>69</sup>

### Natural and synthetic rubber

Natural rubber is sticky, easily deformable material when heated and brittle when cold, with a low level of elasticity. Products based on natural rubber include pneumatics, protection gloves, toys etc. Properties of natural rubber are improved by a vulcanization process. Vulcanized rubber possesses high elasticity, tensile strength, wearing resistance and insolubility in organic solvents.<sup>70</sup> It can be dissolved in oxidizing acids, while concentrated bases and acids etch the surface. Natural, unvulcanized, rubber, is soluble in most solvents but is insoluble in water, diluted acids and bases, alcohol, and acetone.<sup>71</sup> Depending on the sulfur content, vulcanized rubber can be “soft” or “hard” (ebonite).<sup>72</sup> Synthetic rubber comprises various types (butadiene, polyurethane rubber, silicone rubber, etc.) and has properties similar to natural rubber.<sup>73</sup> Vulcanized natural rubber artifacts show blooming, cracking, hardening and brittleness and also softening and tackiness.<sup>74</sup> Degradation of synthetic rubber occurs due to the influence of oxygen, ozone, heat, and light. Oxygen activity causes depolymerization which manifests in rubber stickiness or dryness and elasticity loss. UV radiation and heat catalyze degradation.<sup>75</sup> The influence of ozone on natural vulcanized rubber objects in stressed condition causes linear cracking, while on unstressed objects a hard surface is formed.<sup>76</sup> Hard rubber can suffer from sulfur migration to surface which then reacts with water to form sulfuric acid. Removal of acid is also problematic, causing streaking, as it was shown in a study on an ebonite-bodied prototype of a daylight film developing tank.<sup>77</sup> The description of surface effects found on rubber artifacts is reported in literature.<sup>78</sup> Rubber can suffer from biodegradation.<sup>79</sup> In general, natural, and synthetic rubbers show similar

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68 C. E. Snow et T. D. Weisser, “The examination and treatment of ivory and related materials”, *Studies in Conservation*, Vol. 29: sup1, 1984, 141–145.

69 Canadian Conservation Institute, “Care of Ivory, Bone, Horn and Antler”, *CCI Notes* 6–1. <https://www.canada.ca/en/conservation-institute/services/conservation-preservation-publications/canadian-conservation-institute-notes/care-ivory-bone-horn-antler.html>

70 I. Živković et R. Aleksić, *POZNAVANJE I IZBOR MATERIJALA za studente primenjene umetnosti*, Univerzitet umetnosti u Beogradu, Beograd, 2013, 252–253.

71 F. Waentig, *op. cit.*, 183.

72 *ibid.*, 175.

73 I. Živković et R. Aleksić 2013, *op. cit.*, 254.

74 S. A. Connors, *Chemical and physical characterization of the degradation of vulcanized natural rubber in the museum environment* (master thesis), Queen’s University, Ontario, Canada, 1998, 1.

75 M. Manfredi et al., “An analytical approach for the non-invasive selection of consolidants in rubber artworks”, *Analytical and Bioanalytical Chemistry*, Vol. 48, 2016, 5712.

76 F. Waentig, *op. cit.*, 188.

77 R. D. Stevenson, “A. W. McCurdy’s Developing Tank: Degradation of an Early Plastic”, in: *Saving the twentieth century: the conservation of modern materials*, ed. D.W. Grat-tan, Ottawa, 1993, 183.

78 M. J. R. Loadman, “Rubber: Its History, Composition and Prospects for Conservations”, in: *Saving the twentieth century: the conservation of modern materials*, ed. D.W. Grat-tan, Ottawa, 1993, 65–66.

79 A. Ali Shah et al., “Biodegradation of natural and synthetic rubbers: A review”, *International Biodeterioration & Biodegradation*, Vol. 83, 2013, 145–147.

aging reactions.<sup>80</sup> Both natural and modern rubber artifacts can suffer from crystal formation, as could be seen on Mexican ethnographic artifacts, as well as on a NASA spacesuit. Chemical composition and morphology investigations of both led to the conclusion that technological knowledge of modern rubber can be used in studying old rubber.<sup>81</sup> The results of the study focused on the investigation of the best consolidation treatment for rubber works of art, applying accelerated photo-degradation tests and resulting in recovery of original materials, were used for treatment of the work of art *Presagi di Birnam* by Carol Rama.<sup>82</sup> Replacing degraded material for Richard Serra's assemblage *Untitled* (1967) was done by adding a new rubber material, in agreement with the author.<sup>83</sup> Degraded Paul Thek's latex *Fishman* was shown at the conservation exhibition of the Hirshhorn Museum, representing an example of a modern artwork that was challenging for treatment. Polyester fabric, Stabiltex, was used for connecting gaps in the material, on which paper-pulp fill or wax is placed. Small tears were filled with pigmented wax. As for the missing parts, oven dried molded Sculpey Clay was used to which tinted wax was added in order to adjust original dimensions.<sup>84</sup> General recommended storage conditions are the following: temperature between 9–18 °C, RH ± 50%, exclusion of UV and light radiation, if possible, the absence of oxygen, or absorbent usage (e.g., Ageless).<sup>85,86</sup>

### Cellulose-nitrate

Cellulose-nitrate (CN) is the first man-made plastic material.<sup>87</sup> It is a thermoplastic polymer that has good stability, hardness and stiffness, high surface shine and is very flammable. When camphor is used as a plasticizer to cellulose-nitrate, the name of the compound is Celluloid.<sup>88</sup> CN is used for ivory and tortoiseshell imitation,<sup>89</sup> table-tennis balls, knife handles, and was used for photographic film, shadow puppets, dolls, spectacle frames, etc.<sup>90</sup> If not damaged, CN shows resistance to water, diluted acids, weak bases, salt solutions and petrol; it is not resistant to concentrated acids, strong bases and various organic solvents like weak alcohols and ketones.<sup>91</sup> Cellulose-nitrate is one of the four polymer types that works of art and museum artifacts are made from, most prone to deterioration, the other being cellulose-acetate, plasticized poly(vinyl chloride) and polyurethane foam.<sup>92</sup> CN is subjected to thermal,

80 F. Waentig, *op. cit.*, 190.

81 M. T. Baker, "Ancient Mexican Rubber Artifacts and Modern American Spacesuits: Studies in Crystallization and Oxidation", *MRS Proceedings*, 352, 1995, 223–231.

82 M. Manfredi et al., *op. cit.*, 5711–5722.

83 S. Weerdenburg et al., "The conservation of an early assemblage by Richard Serra: a rubber issue", in: *ICOM-CC 17th Triennial Conference Preprints*, Melbourne, Australia, 15–19 September, 2014.

84 T. Ausema, T. S. Lake et W. Hopwood, "WEIGHING THE OPTIONS: ANALYSIS AND TREATMENT OF PAUL TREK'S FISHMAN AS A VEHICLE FOR PUBLIC EDUCATION", *Studies in Conservation*, Vol. 49 (2), 2014, 96–99.

85 F. Waentig, *op. cit.*, 201.

86 Y. Shashoua et S. Thomsen, "A field trial for the use of Ageless in the preservation of rubber in museum collections", in: *Saving the twentieth century: the conservation of modern materials*, ed. D.W. Grattan, Ottawa, 1993, 363–372.

87 Y. Shashoua, 2008, *op. cit.*, 3.

88 F. Waentig, *op. cit.*, 206.

89 *ibid.*, 16a0.

90 Y. Shashoua, 2008, *op. cit.*, 237.

91 F. Waentig, *op. cit.*, 206.

92 Y. Shashoua, 2008, *op. cit.*, 177.

photochemical, and hydrolytic degradation. CN breakdown is autocatalytic since breakdown products, if not removed, act as catalysts for further reactions. As for physical factors, loss of plasticizer leads to shrinkage and disintegration.<sup>93</sup> A study based on accelerated aging tests showed that degradation is connected to levels of sulfate content in CN and that inorganic fillers can reduce degradation.<sup>94</sup> Degraded celluloid museum objects, comprising toothbrushes, were in focus of investigation during which they were subjected to interventive conservation treatment. It included cleaning, consolidation and reinforcement, and also neutralization of acid celluloid decay products.<sup>95</sup> A group of authors investigated the relationship between the mechanical properties of CN and the modification of the weight-average molar mass ( $M_w$ ) during aging, suggesting a threshold value that could indicate degradation of CN.<sup>96</sup> Another group of authors proposed a swab test for detection of oxalates, which indicates CN chain-scission.<sup>97</sup> Storage recommendation is the following: temperature between 4–20 °C, light level below 50 lux, RH below 50%, exclusion of UV light, open storage containers with activated charcoal and air exchange.<sup>98</sup>

### Cellulose-acetate

Cellulose-acetate (CA) is a thermoplastic polymer with good stability, impact resistance and high surface elasticity.<sup>99</sup> It found usage in fabrication of photographic film, packaging films, graphic tracing films, display boxes, spectacle frames, hairbrushes, combs.<sup>100</sup> CA shows resistance to water, ether, benzene, xylene, turpentine, petrol, petroleum; but not resistant to alcohol, ethyl acetate, chlorinated hydrocarbons, inorganic acids, and bases.<sup>101</sup> CA degrades by physical and chemical factors.<sup>102</sup> Physical factors refer to migration and loss of plasticizer causing hardening and shrinking. An important chemical degradation reaction is acid hydrolysis, by which acetyl groups are removed from CA forming acetic acid with water. Due to specific smell, this deterioration is known as ‘vinegar syndrome’.<sup>103</sup> If  $TiO_2$  pigment is present in CA, it acts as a photo-oxidation catalyst.<sup>104</sup> A doctoral thesis was focused on degradation of cel-

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93 Y. Shashoua, “Inhibiting the inevitable: current approaches to slowing the deterioration of plastics”, *Macromolecular Symposia*, 238(1), 2006a, 68–69.

94 R. Stewart, “The Use of Accelerated Ageing Tests for Studying the Degradation of Cellulose Nitrate”, in: *Triennial meeting (11th), Edinburgh, 1–6 September 1996: preprints*, London, 1996, 967–970.

95 A. B. Strzelczyk et H.E. Rosa, “Chemical and Microbiological Causes of Deterioration of Toothbrushes that used to belong to Prisoners of Auschwitz-Birkenau Concentration Camp: Research and Methods of Their Conservation”, in: *Art, Biology, and Conservation: Biodeterioration of Works of Art*, eds. R. Koestler et al., The Metropolitan Museum of Art, 2003, 60–71.

96 A. Lattuati-Derieux, et al., “The use of  $M_w$  value to characterize the conservation condition of cellulose nitrate based objects”, in: *ICOM Committee for Conservation 17th Triennial Conference*, ed. J. Bridgland, The International Council of Museums, Paris, 2014.

97 A. Quye et al., “Investigation of inherent degradation in cellulose nitrate museum artefacts”, *Polymer Degradation and Stability*, Vol. 96, 2011, 1369–1376.

98 F. Waentig, *op. cit.*, 215.

99 *ibid.*, 218.

100 Y. Shashoua, 2008, *op. cit.*, 236.

101 F. Waentig, *op. cit.*, 218.

102 Y. Shashoua, 2008, *op. cit.*, 180.

103 F. Waentig, *op. cit.*, 219.

104 J. Puls, S. A. Wilson et D. Hölter, “Degradation of Cellulose Acetate-Based Materials: A Review”, *Journal of Polymers and the Environment*, 2011, 160.

lulose-based plastics (CN and CA) and their stabilization procedure.<sup>105</sup> A well known problematic issue when it comes to the conservation and restoration of cellulose esters, i.e., CN and CA works of art are sculptures of Naum Gabo, Antoine Pevsner, László Moholy-Nagy and Marcel Duchamp, for which detailed investigation analysis of compositions and degradation products were performed.<sup>106,107,108</sup> Another study was focused on testing treatments for slowing down the CA degradation.<sup>109</sup> Two artist's books *Ombres transparentes* made from CA by Lourdes Castro were analyzed for degradation in order to find adequate conservation treatment. With regards to that, artificial aging experiment of CA sheets has started and treatment methodology using temperature and pressure is being developed for the recovery of warped CA sheets.<sup>110</sup> The results of cleaning tests on CA plastics performed within POPART project were used on some CA works of Lourdes Castro, and the tested cleaning agents were chosen after performing additional trials for specific parts of these works.<sup>111</sup> The following conditions are recommended for storage: temperature below 20 °C, RH 50–55% constant, light of 50 lux, total exclusion of UV radiation. Also, the object should be surrounded by activated charcoal cloth and buffered paper.<sup>112</sup>

### Casein-formaldehyde

Casein-formaldehyde, CF, is a protein-based plastic material obtained by hardening casein with formaldehyde, and is also known as Galalith.<sup>113</sup> It is a thermosetting polymer. CF was used for small decorative boxes, combs,<sup>114</sup> as a decorative inlay on furniture, and is still used for buttons. Damage examples on historic casein plastics are: distortion, discoloration, pitting and fracture.<sup>115</sup> CF shows resistance to majority of organic solvents but is not resistant to bases and acids (except for weak inorganic acids). Also, CF is not resistant to water and moisture, as it can suffer from

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105 A. Hamrang, *Degradation and Stabilisation of Cellulose-based Plastics & Artifacts* (PhD thesis), The Manchester Metropolitan University, 1994.

106 M. Derrick, D. Stulik et E. Ordonez, "Deterioration of Cellulose Nitrate Sculptures Made by Gabo and Pevsner", in: *Saving the twentieth century: the conservation of modern materials*, ed. D.W. Grattan, Ottawa, 1993, 169–182.

107 J. Mazurek et al., "Investigation of cellulose nitrate and cellulose acetate plastics in museum collections using ion chromatography and size exclusion chromatography", *Journal of Cultural Heritage* Vol. 35, 2019, 263–270.

108 B. A. Price, "Naum Gabo's Construction in Space: Two cones: History and Materials", in: *PLASTICS Looking at the Future Learning from the Past*, eds. B. Keneghan et L. Egan, London, 2008, 81–88.

109 S. Mossman et M. L. Abel, "Testing treatments to slow down the degradation of cellulose acetate", in: *PLASTICS Looking at the Future Learning from the Past*, eds. B. Keneghan et L. Egan, 2008, 106–115.

110 A. Cudell et al., "Strategies for the conservation of cellulose acetate works – case study of two plastic books", *ICOM-CC Lisbon 2011 : preprints : 16th triennial conference*, Lisbon, 19–23 September 2011, paper 1003.

111 POPART: Preservation Of Plastics ARTefacts research project, "Studies in cleaning plastics", 258–260. [https://popart-highlights.mnhn.fr/wp-content/uploads/5\\_Active\\_conservation/2\\_Studies\\_in\\_cleaning\\_plastics/5\\_2\\_StudiesInCleaningPlastics.pdf](https://popart-highlights.mnhn.fr/wp-content/uploads/5_Active_conservation/2_Studies_in_cleaning_plastics/5_2_StudiesInCleaningPlastics.pdf)

112 F. Waentig, *op. cit.*, 221.

113 *ibid.*, 225–226.

114 S. Lang, "Milk and Modernism: Conservation of a Smoker's Cabinet designed by Charles Rennie Mackintosh", *V&A Conservation Journal*, Issue 21, 1996. <http://www.vam.ac.uk/content/journals/conservation-journal/issue-21/milk-and-modernism-conservation-of-a-smokers-cabinet-designed-by-charles-rennie-mackintosh/>

115 J. Kaner, F. Ioras et J. Ratnasingam, "Performance and Stability of Historic Casein Formaldehyde", *e-Plastory*, No. 2, 2017, 9–10.

changes in dimensional stability.<sup>116</sup> The found available literature provides report on conservation-restoration treatment of CF inlay on furniture.<sup>117</sup> There was also research conducted on investigating possibility of reversing aged and distorted CF, which was present in the Mackintosh furniture inlay. Effects of plasticization were tested using three-point bend test. In addition, tests were performed to investigate effects of different RH on CF samples, providing a suggestion for optimal RH range for storage.<sup>118</sup> Recommended storage conditions are: temperature 18–21° C, RH 50–55%; individual storing of objects in polyethylene bags/boxes, objects on exhibition should be protected by wax polish.<sup>119</sup>

### Poly(vinyl chloride)

Poly(vinyl chloride), PVC, a thermoplastic polymer, in pure state is rigid and brittle. For improving properties and performance, additives are added to it or it is combined with other polymers. Hard PVC is tough; it does not contain plasticizers, while for soft PVC they are added even above 30%. Hard PVC has better mechanical properties than the soft one, with higher resistance to heat, atmospheric influence, and chemicals, while soft PVC is more flexible, has better stretching ability and easier workability. Due to chlorine presence, PVC does not burn.<sup>120</sup> PVC is insoluble in majority of common solvents; it is soluble in acetone and carbon disulfide mixtures, tetrahydrofuran, cyclohexanone. Swelling can be caused by ketones and chlorinated hydrocarbons, while water can cause whitening.<sup>121</sup> PVC is used for window frames, water pipes (hard) and for toys, hoses, flooring, waterproof clothing, cable insulation (plasticized) etc. Vinyl LP records are made from copolymers of vinyl chloride and vinyl acetate.<sup>122,123</sup> Majority of PVC museum artifacts are made from plasticized PVC.<sup>124</sup> For PVC objects stored indoors at room temperature, thermal elimination of HCl and migration of plasticizer are considered the main degradation pathways.<sup>125</sup> Physical loss of plasticizers causes stickiness of surface. Due to hydrolysis of some plasticizers, white crystals can appear on surface.<sup>126</sup> UV radiation and light cause discoloration.<sup>127</sup> The found literature on conservation of PVC objects provides various articles on a range of sub-topics: the necessary step of characterization of degraded PVC artifacts – connected to studying the plasticized PVC components that are present in Apollo spacesuits,<sup>128</sup> investigations of the deterioration extent and rate with relation to plasticizer loss, by

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116 F. Waentig, *op. cit.*, 226.

117 S. Lang, *op. cit.*

118 J. Kaner, F. Ioras et J. Ratnasingam, *op. cit.*, 1–18.

119 F. Waentig, *op. cit.*, 228.

120 I. Živković et R. Aleksić, 2013, *op. cit.*, 210.

121 F. Waentig, *op. cit.*, 246.

122 Y. Shashoua, 2008, *op. cit.*, 252.

123 Patrick, S. G., *Practical Guide to Polyvinyl Chloride*, 1st ed., Shawbury, UK, 2005, 4.

124 T. Rijavec, M. Strlič et I. Kralj Cigić, "Plastics in Heritage Collections: Poly(vinyl chloride) Degradation and Characterization", *Acta Chimica Slovenica*, Vol 67, 2020, 994.

125 *ibid.*, 1002.

126 *ibid.*, 995.

127 Y. Shashoua, 2008, *op. cit.*, 163.

128 Y. Shashoua, U. Schnell et L. Young, "Deterioration of plasticized PVC components in Apollo spacesuits", in: *Plastics in Art – History, Technology, Preservation*, eds. T. van Oosten, Y. Shashoua et F. Waentig, Munich, 2002, 69–79.

performing artificial aging tests,<sup>129</sup> development of passive conservation methodology, by assessing different inhibitors activity.<sup>130</sup> The research studies on the impact of enclosure, surface cleaning<sup>131</sup> and wrapping<sup>132</sup> on PVC degradation are helpful for planning the strategy of preservation of PVC artifacts. Tests for developing effective cleaning methodology for plasticized PVC objects included the use of Hildebrand solubility parameters and formulation of a Plasticizer Index.<sup>133</sup> The practical treatment was performed on the degraded balloon *Aeromodeller OO-PL*, consisting of cleaning and reattachment. Adhesives were tested by light aging and peel strength test, and repair materials by heat aging and creep test.<sup>134</sup> General recommendations for storage are: temperatures not above 20 °C, RH values up to 50%, dark environment, exclusion of UV radiation. It is advised that hard PVC objects should be stored with zeolites (adsorbers for HCl), while for soft PVC air ventilation should be avoided and no adsorbers present.<sup>135</sup> PVC should not be used for packaging purposes for museum artifacts, since it emits volatile acids that can cause degradation of artifacts.<sup>136</sup>

### Polyurethane

Polyurethane, PU, polymers are a versatile group that includes flexible and rigid foams, cross-linked and linear thermoplastic elastomers, coatings, adhesives, and fibers.<sup>137</sup> PU foams have been popular among modern artists.<sup>138</sup> In general, they are used for toys, fake leather, sports gear, packaging, textiles, and cushioning.<sup>139</sup> PU foams are resistant to chemical cleaning agents, but not to hot water or aggressive chemicals.<sup>140</sup> PU foams are one of the least stable synthetic polymers. They undergo photo-oxidation and hydrolysis. Depending on the polyol base used, there are ester-type and ether-type foams, the former being more prone to hydrolysis and the latter to photo-oxidation. Besides light, moisture and temperature are important degradation factors.<sup>141</sup> When it comes to biological factors, PU is one of the polymer

129 Y. Shashoua, "Deterioration and conservation of plasticized poly(vinyl chloride) objects", in: *International Council of Museums 13th Triennial Meeting*, ed. J. Bridgland, London, 2002, 927–934.

130 Y. Shashoua, "A passive approach to the conservation of polyvinyl chloride", *ICOM committee for conservation, 11th triennial meeting in Edinburgh, Scotland, 1–6 September 1996: Preprints*, London, 1996.

131 A. Royaux, "Aging of plasticized polyvinyl chloride in heritage collections: The impact of conditioning and cleaning treatments", *Polymer Degradation and Stability*, Vol. 137, 2017, 109–121.

132 A. Royaux et al., "Conservation of plasticized PVC artifacts in museums: Influence of wrapping materials", *Journal of Cultural Heritage*, Vol. 46, 2020, 131–139.

133 C. Morales Muñoz et al., "A model approach for finding cleaning solutions for plasticized poly(vinyl chloride) surfaces of collections objects", *Journal of the American Institute for Conservation*, Vol. 53 (4), 2014, 236–251.

134 F. Huys et T. B. van Oosten, "The *Aeromodeller OO-PL*: the conservation of a PVC balloon", in: *ICOM 14th Triennial Meeting Preprints*, London, 2005, 335–342.

135 F. Waentig, *op. cit.*, 252–254.

136 M. Shelley, ed., *The Care and Handling of Art Objects: Practices in The Metropolitan Museum*, New York, 2019, 213.

137 I. Živković et R. Aleksić, 2013, *op. cit.*, 233.

138 T. Van Oosten, *PUR Facts: Conservation of Polyurethane Foam in Art and Design*, Amsterdam, 2011, 47–54.

139 F. Coles, "Challenge of materials? A new approach to collecting modern materials at the Science Museum London", in: *PLASTICS Looking at the Future Learning from the Past*, eds. B. Keneghan et L. Egan, London, 2008, 128.

140 F. Waentig, *op. cit.*, 304.

141 T. Van Oosten, *op. cit.*, 43–44.

types with the smallest resistance to microorganisms, which negatively affects mechanical properties.<sup>142</sup> An overview of PU foam conservation history can be found in the literature.<sup>143</sup> Poly(ether urethane) elastomer *Stage Evidence* by Loris Cecchini was analyzed in a study with the purpose of evaluating the degradability of material.<sup>144</sup> PU foams, as a constitutive material of works of art, were a subject of various studies about aging and reports on preventive and interventive conservation treatments. Some of the topics include storage condition investigation using aging tests<sup>145</sup> and research on consolidants testing.<sup>146,147,148</sup> Regarding practical conservation-restoration treatments on works of art, with prior application of scientific-based testing of conservation materials to be used, a very nice example of an interdisciplinary approach is the paper on the conservation-restoration of Piero Gilardi's work that includes both the preventive and interventive conservation issue. Interventive conservation included cleaning, consolidation, adhesion of layers, detached and broken fragments, integration of missing parts, retouch, and re-assembly. For the selection of proper consolidants, elastic properties of PUR foam were assessed by determining the compression set values. Accelerated photo-oxidation testing was performed in order to test light – and air-stability of consolidated foam.<sup>149</sup> For Gilardi's work *Still life of watermelons*, the consolidation treatment and lining of the torn parts were performed.<sup>150</sup> The work *Funburn* by John Chamberlain was also subjected to cleaning, consolidation and restoration treatments.<sup>151</sup> General storage recommendations are the following: temperature below 20°C, RH between 50–55%, as little light as possible (up to 50 lux at exhibitions), exclusion of UV light, ventilation, separate storing of objects.<sup>152</sup>

### Polystyrene

Polystyrene, PS, is a linear amorphous thermoplastic polymer. When unmodified, PS is hard and brittle, has high tensile strength, excellent thermal and electrical

142 F. Waentig, *op. cit.*, 305.

143 T. van Oosten, *op. cit.*, 47–56.

144 M. Lazzari, et al., “Plastic matters: An analytical procedure to evaluate the degradability of contemporary works of art”, *Analytical and Bioanalytical Chemistry* 399 (9), 2011, 2939–2948.

145 S. F. De Sá et al., “A new insight into polyurethane foam deterioration – the use of Raman microscopy for the evaluation of long-term storage conditions”, *Journal of Raman Spectroscopy*, Vol. 47 (12), 2016, 1494–1504.

146 E. Pellizzi et al., “Flexible Polyurethane Ester Foam Consolidation: Preliminary Study of Aminopropylmethyldiethoxysilane Reinforcement Treatment”, in: *Proceedings of Symposium 2011: Adhesives and Consolidants for Conservation: Research and Applications*, Ottawa, 2011.

147 E. Pellizzi, et al., “Consolidation of artificially degraded polyurethane ester foam with aminoalkylalkoxysilanes article”, *Polymer Degradation and Stability*, Vol. 129, 2016, 106–113.

148 T. van Oosten et A. Lorne, “Research into the influence of impregnating agents on the ageing of PUR foams using FTIR spectroscopy”, in: *The Sixth Infrared and Raman Users Group Conference (IRUG 6)*, ed. M. Picollo, Florence, 2004, 155–161.

149 A. Rava et al., “The restoration of a group of works of art by Piero Gilardi”, *Studies in Conservation*, Vol. 49, 2014, 160–164.

150 A. Lorne, “Experiments in the conservation of a foam object” in: *Modern Art: Who cares?*, eds. I. Hummelen et D. Sille, Amsterdam, 1999a, 143–148.

151 I. Winkelmeyer, “Contemporary Art made of Polyurethane soft foam”: Production – Ageing – Conservation – Storage, in: Gerhard Banik (Hrsg.): *Wege zur Konservierungswissenschaft. Projekte am Studiengang Restaurierung und Konservierung von Graphik, Archiv – und Bibliotheksgut*, Stuttgart, 2010, 85–86.

152 F. Waentig, *op. cit.*, 311.

insulating properties, dimensional stability, and does not absorb water. Change of PS properties can be achieved by copolymerization with other monomers or blending with other polymers,<sup>153</sup> It is used for disposable cold drink cups, food containers, CD cases, hair combs, and, as foam, for disposable hot drink cups, insulated food containers and thermal insulation.<sup>154</sup> Widely known is expanded polystyrene (Styrofoam), which was primarily used as an insulating material.<sup>155</sup> It is rigid, has low ability of water absorption, good thermal and sound isolation properties.<sup>156</sup> PS shows resistance to alkalis, non-oxidative acids, salt solutions and alcohols; it can be dissolved in esters, ketones, aromatic, and chlorinated hydrocarbons. When unstabilized, PS is one of the least durable plastics. It degrades under the influence of radiation, oxygen, and atmospheric pollutants.<sup>157</sup> Being linear polymer, PS is susceptible to cross-linking, which can be detected through increase in stiffness and brittleness.<sup>158</sup> The found available literature provides information on the investigation of the cleaning treatment effects on PS, reporting existence of scratches not visible to the naked eye.<sup>159</sup> In a study on adhesive testing for rigid polystyrene (General purpose polystyrene, GPPS), besides the examination of working properties, appearance, and color measurement, aging tests before and after joining were performed, with tensile and hardness testing; SEM imaging and stereomicroscopy were used for the visual examination of break types.<sup>160</sup> Another study evaluated the possible effects of heat modeling of GPPS used for sculptures *Pequenas Esculturas* by Ângelo de Sousa on the acceleration of the photo-oxidation process.<sup>161</sup> General recommendation for storing is the following: temperature  $18\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ , RH  $55\% \pm 3\%$ , light up to 50 lux for colored objects and up to 150 lux for transparent, UV radiation below  $75\text{ }\mu\text{W}/\text{lm}$ , adequate ventilation.<sup>162</sup>

### Poly(methyl methacrylate)

Poly(methyl methacrylate), PMMA, is transparent, amorphous thermoplastic material that is hard, brittle and easily polished, but is highly sensitive to stress concentration. PMMA possesses good mechanical strength, optical properties weathering resistance.<sup>163</sup> It is used for lenses for spectacles and optical equipment, safety spectacles, windows, food containers, lighting etc.<sup>164</sup> PMMA shows resistance to water, non-polar solvents, weak acids and bases, salt solutions, aliphatic hydrocarbons, and detergents at room temperature, but no resistance to polar solvents, strong acids and bases, benzene, ketones, esters, and aromatic and chlorinated hydrocarbons.

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153 I. Živković et R. Aleksić, 2013, *op. cit.*, 201–202.

154 Y. Shashoua, 2008, *op. cit.*, 248.

155 F. Waentig, *op. cit.*, 278.

156 I. Živković et R. Aleksić, 2013, *op. cit.*, 205.

157 F. Waentig, *op. cit.*, 282.

158 Y. Shashoua, 2008, *op. cit.*, 165.

159 A. L. Fricker, et al., “Investigating the impact of cleaning treatments on polystyrene using SEM, AFM and ToF-SIMS”, *Heritage Science*, Volume 5, 2017, 28–36.

160 T. Winther et al., “Adhesives for adhering polystyrene plastic and their long-term effect”, *Studies in Conservation*, Vol. 60 (2), 2015, 107–120.

161 R. Milton et J. L. Ferreira, “Preservation of General Purpose Polystyrene (GPPS) sculptures – heat modeling in “Pequenas Esculturas” (1975) by Ângelo de Sousa”, 2016. <https://www.iiconservation.org/node/6614>

162 F. Waentig, *op. cit.*, 285–286.

163 I. Živković et R. Aleksić, 2013, *op. cit.*, 218–219.

164 Y. Shashoua, 2008, *op. cit.*, 245.

During degradation, chain-splitting occurs. PMMA is susceptible to microorganism attack when it contains plasticizer.<sup>165</sup> A consequence of using solvents for cleaning rigid plastics, such as PMMA (PS and PC as well) is the occurrence of cracking, the so-called environmental stress cracking (ESC), which causes the development of white crystalline structures or connected cracks in a material.<sup>166</sup> One study identified a common occurrence of bonding defects in transparent PMMA objects, which are the following: bubbles, haziness, crazing, and joint separation.<sup>167</sup> PMMA objects from a museum collection were examined for damages, followed by cleaning and repair treatments, with the observation that larger fragility of objects made by artists compared to industrial ones is due to the application of an inadequate precision technique.<sup>168</sup> A paper on the examination of the effects of cleaning transparent PMMA suggested using optical microscopy and contact angle measurements for the of scratches and cleaning agents residues.<sup>169</sup> With regard to PMMA adhesion, various research studies investigated the following issues: adhesives having minimal craze- and crack-promotion testing, including a simulation of the bonding operation on 3D replicas of the damaged area, resulting in the practical application on Naum Gabo's *Construction in Space: Crystal*;<sup>170</sup> adhesive crazing of PMMA stressed at specific loads, tensile testing of butt-joined PMMA samples, and the effect of degreasers on the tensile properties of adhesives.<sup>171</sup> General recommendation for storage is the following: temperature  $18\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ , RH  $55\% \pm 3\%$ , light up to 150 lux for colorless and up to 50 lux for colored objects, UV radiation below  $75\text{ }\mu\text{W}/\text{lm}$ .<sup>172</sup>

### Polyethylene

Polyethylene, PE, is a thermoplastic polymer that possesses good mechanical strength and flexibility, low water vapor permeability, easy workability, and great chemical resistance (consequence of hydrocarbon character and high crystallinity). Aging of PE can be decreased by addition of carbon black, antioxidants, and UV light absorbers. PE shows resistance to water, diluted acids, bases and salt solutions, and is not soluble in organic solvents at room temperature.<sup>173</sup> On the other hand, it is not resistant to oxidizing acids, ketones, aromatic and chlorinated hydrocarbons.

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165 F. Waentig, *op. cit.*, 274.

166 Y. Shashoua, 2008, *op. cit.*, 209.

167 A. Laganá et al., "Reproducing reality. Recreating bonding defects observed in transparent poly(methyl methacrylate) museum objects and assessing defect formation", *Journal of Cultural Heritage*, Vol. 48, 2021, 254–268.

168 A. Lorne, "The poly(methyl methacrylate) objects in the collection of The Netherlands Institute for Cultural Heritage", in: *12th Triennial Meeting, Lyon, France, 29 August-3 September 1999: Preprints Volume 21*, London, 1999b, 871–875.

169 Y. Shashoua, A. L. Petersen et E. Rapoport, "The Price of Pristine PMMA", in: *FUTURE TALKS 2009: The Conservation Of Modern Materials in Applied Arts and Design; papers from the conference held at the Pinakothek der Moderne. Munich 22–23 October 2009*, ed. T. Bechthold, Munich, 2011, 51–60.

170 A. Comiotto et M. Egger, "Naum Gabo's Sculpture Construction in Space Crystal (1937): Evaluating a Suitable Bonding Strategy for Stress loaded Poly (methyl methacrylate)", in: *FUTURE TALKS 2009: The Conservation Of Modern Materials in Applied Arts and Design; papers from the conference held at the Pinakothek der Moderne. Munich 22–23 October 2009*, ed. T. Bechthold, Munich, 2011, 61–70.

171 D. Sale, "An Evaluation of Eleven Adhesives for Repairing Poly (methyl methacrylate) Objects & Sculpture", in: *Saving the twentieth century: the conservation of modern materials*, ed. D.W. Grattan, Ottawa, 1993, 325–336.

172 F. Waentig, *op. cit.*, 278.

173 I. Živković et R. Aleksić, 2013, *op. cit.*, 192.

During aging, both low density polyethylene (LDPE) and high-density polyethylene (HDPE) show crack formation and dimensional change.<sup>174</sup> PE is used for zip-lock and carrier bags, food packaging films, Tupperware® containers, bread and beer crates, electrical cable insulation, water pipes etc.<sup>175</sup> When in museum environment, the primary degradation process of PE is due to photo-oxidation. The level of UV stability of a specific polyethylene will depend on its crystallinity, added stabilizers and the fabrication process.<sup>176</sup> With the aim of improving adhesion properties of non-polar polymers, research was conducted applying plasma-pretreatment of surfaces to be joined and the results pointed to significant improvement of adhesive qualities.<sup>177</sup> Polyethylene bags in the series *Bicycles* by Andreas Slominski degraded due to constant load, daylight, and UV radiation. Before conservation treatment, artificial aging tests were performed for studying the degradation process; tensile strength testing of bonds for adhesive selection was performed.<sup>178</sup> A study was conducted for assessing the stability of Tupperware objects in a museum collection. The artificial aging results showed that Tupperware objects should survive 150 years without serious conservation treatment if kept in lighting under 100 lux.<sup>179</sup> General storage recommendations are the following: temperature 18 °C ± 2 °C, RH 55% ± 3%, light up to 50–100 lux for colored translucent and up to 150 lux for colored opaque objects, UV radiation below 75 µW/lm. Adequate ventilation is needed for the removal of pollutants.<sup>180</sup> Apart from being constituent material of works of art and artifacts, PE is also used as packaging material for other museum objects. Storage containers made from it were a subject of testing for volatile organic compounds, VOCs, as well as Oddy tests, resulting in the recommendation that containers should be kept uncovered with their lids for some time between purchase and utilization so that there is enough time for off-gassing.<sup>181</sup>

### Phenol-formaldehyde

Phenol-formaldehyde resins are oligomers and polymers that can exhibit both thermoplastic ('novolac' resins) and thermosetting behavior ('resol' resins).<sup>182</sup> By addition of other components novolac resins cross-link when heated and become thermosetting polymers. Phenol-formaldehyde materials for molding are mostly novolac-based. Fillers and reinforcements are added to phenol-formaldehyde resins

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174 F. Waentig, *op. cit.*, 296–297.

175 Y. Shashoua, 2008, *op. cit.*, 243.

176 T. van Oosten et A. Aten, "Life Long Guaranteed: The Effect of Accelerated Ageing on Tupperware Objects Made of Polyethylene", in: *ICOM Committee for Conservation, ICOM-CC : 11th Triennial Meeting, Edinburgh, Scotland 1996 : preprints*, London, 1996, 971.

177 A. Comiotto, "Miniaturized cold atmospheric plasma for improving the adhesion properties of plastics in modern and contemporary art", *Objects Specialty Group Post-prints*, Volume Sixteen, 2009, American Institute for Conservation, 2009, 25–35.

178 K. Haider et T. Van Oosten, "Plastic bags – Research into polyethylene bags of the series "Bicycles" by Andreas Slominski?", in *FUTURE TALKS 2009: The Conservation Of Modern Materials in Applied Arts and Design; papers from the conference held at the Pinakothek der Moderne. Munich 22–23 October 2009*, ed. T. Bechthold, Munich, 2011, 41–50.

179 T. van Oosten et A. Aten, *op. cit.*, 971–977.

180 F. Waentig, *op. cit.*, 300.

181 N. Larkin, N. Blades et E. Makridou, "Investigation of volatile organic compounds associated with polyethylene and polypropylene containers used for conservation storage", *The Conservator*, No. 24, London, 2000, 41–51.

182 I. Živković et R. Aleksić, 2013, *op. cit.*, 241.

with the aim of improving their properties. The combination of reinforcements with high cross-linking degree results in high stability, rigidity, and hardness.<sup>183</sup> Phenol-formaldehyde Bakelite was the first fully synthetic polymer. It was resistant to acids and organic liquids.<sup>184</sup> Bakelite was used for household and consumer goods and costume jewelry.<sup>185</sup> Phenol-formaldehyde resins have good resistance to thermal and thermo-oxidative decay as well to microorganisms.<sup>186</sup> Storage condition recommendations are the following: temperature 18–21 °C, RH 50% ± 2%, lighting 150 lux, UV radiation up to 75 μW/lm.<sup>187</sup> Having in mind that phenol-formaldehyde is a very stable synthetic polymer, it does not surprise that it is not easy to find reports on conservation-restoration treatments.

### Epoxies

Epoxy resins have a range of good properties like good chemical resistance and excellent adhesive properties, hardness, flexibility, toughness. They have excellent water resistance,<sup>188</sup> Also, they show resistance to dilute acids and alkalis, alcohol, benzene, petrol, and most solvents, but are not resistant to concentrated acids and alkalis, ammonia, acetone.<sup>189</sup> They are used in production of adhesives and coatings. Epoxy resins are also used as a matrix for fiber reinforced composites that show excellent mechanical properties.<sup>190</sup> The main aging reaction is bond-splitting.<sup>191</sup> Prediction of durability for epoxy materials used for works of art (*Nemea's Lion* by Francisco Leiro and *3D Bodyscans 1:9* by Karin Sander) using the simulation of natural aging test showed agreement with the monitored aging process in the original works of art.<sup>192</sup> General storage recommendations are the following: temperature 18 °C ± 2 °C, RH 55% ± 3%, UV radiation below 75 μW/lm.<sup>193</sup> As epoxies are characterized by very good stability it is understandable why case studies and papers about conservation-restoration treatments cannot be found in literature.

### Polyester

Polyester, PES, polymers comprise a large group of materials that consists of thermoplastic PES, alkyd and saturated PES, unsaturated polyesters (UP) and PES for polyurethanes. When cross-linked, without fillers, UPs are hard, brittle, and transparent; properties can be changed by changing starting components. UPs are resistant to strong acids, weak bases, salt solutions, various solvents, but are not resistant to strong bases, warmed acids, and chlorinated hydrocarbons. They are mainly used as matrix materials for composite materials and are most often reinforced with

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183 F. Waentig, *op. cit.*, 235–236.

184 Y. Shashoua, 2008, *op. cit.*, 26.

185 F. Waentig, *op. cit.*, 232.

186 *ibid.*, 238.

187 *ibid.*, 240.

188 I. Živković et R. Aleksić, 2013, *op. cit.*, 245.

189 F. Waentig, *op. cit.*, 314.

190 I. Živković et R. Aleksić, 2013, *op. cit.*, 246.

191 F. Waentig, *op. cit.*, 315.

192 M. Lazzari, M. Nieto-Suárez et T. López Morán, "Epoxy resins: From industrial material to contemporary art medium", in: *Science, Technology and Cultural Heritage*, ed. M. A. Rogerio-Candelera, London, 2014, 171–176.

193 F. Waentig, *op. cit.*, 316.

glass fibers.<sup>194</sup> They are used for boat shells,<sup>195</sup> auto-repair kits, in building construction, for manufacture of artificial stone, sculptures, facades etc.<sup>196</sup> In recent years, harmful styrene emissions during production of polyester matrix composites have prompted the uptake of green resins with low styrene content and emissions<sup>197</sup> and thermoplastic polymers as well.<sup>198,199</sup> Besides being used as an artistic medium,<sup>200</sup> as casting resins, they are also used as a pinning material for restoration of large sculptures, as glass fiber reinforced polyester, GFRP.<sup>201</sup> GFRPs are water and weathering resistant. In general, they show good aging properties.<sup>202</sup> Osmosis, photo-oxidation, and hydrolysis cause UP deterioration, particularly if objects are kept outdoors.<sup>203</sup> A study conducted in order to provide useful information on preventive conservation of UP artifacts (specifically *The Last Milk Platform* by Jan Erik Andersson and *Cocotte with two dogs* by Kari Tykkylainen) showed that there are significant differences in the stability and the aging properties of different commercial UP products. It was concluded that water, humidity, UV light and temperature fluctuations damage objects made from low quality UP composites.<sup>204</sup> Interesting is an example of *Mobile Home for Kröller-Müller* by Joep van Lieshout, a large-scale GFRP outdoor sculpture, which needed conservation treatment due to the exposure to external degradation factors. Artificial aging testing was performed in order to select the material for crack filling.<sup>205</sup> Regarding fiberglass reinforced polyester outdoor sculptures, they should be maintained by regular surface cleaning.<sup>206</sup> When it comes to transparent objects, it is very difficult to obtain invisible repair. In order to avoid invasive treatments, less invasive alternatives were investigated for different types of damages (breaks, abrasions and losses).<sup>207</sup> Adhesives were tested for applicability and appear-

194 I. Živković et R. Aleksić, 2013, *op. cit.*, 237.

195 I. Živković et al. "Influence of moisture absorption on the impact properties of flax, basalt and hybrid flax/basalt fiber reinforced green composites", *Composites Part B: Engineering*, Vol. 111, 2017, 148–164.

196 I. Živković et R. Aleksić, 2013, *op. cit.*, 237.

197 I. Živković et al., *op. cit.*, 148–164.

198 I. Živković et al. "Indentation damage detection in thermoplastic composite laminates by using embedded optical fibers", *Journal of Advanced Materials*, Vol. 37 (1), 2005, 33–37.

199 I. Živković, Pavlović, Ana et Fragassa, Cristiano, "Improvements in wood thermoplastic matrix composite materials properties by physical properties and chemical treatments", *International Journal for Quality Research*, Vol. 10 (1), 2016, 205–218.

200 G. Stamatakis et al., "Analysis and aging of unsaturated polyester resins in contemporary art installations by NMR spectroscopy", *Analytical and Bioanalytical Chemistry*, Vol. 398, 2010, 3203.

201 C. Riccardelli et al., "The Treatment of Tullio Lombardo's Adam A New Approach to the Conservation of Monumental Marble Sculpture", *Metropolitan Museum Journal*, Vol. 49, 2014, 49–116.

202 F. Waentig, *op. cit.*, 261–262.

203 S. Stigter, et al., "Joep van Lieshout's Mobile Home for Kröller-Müller: outdoor polyester sculpture in transit", *ICOM-CC 15th Triennial Conference, New Delhi, Vol. 1*, Allied Publishers Pvt Ltd, New Delhi, 2008, 492.

204 U. Knuutinen et P. Kyllonen, "Two case studies of unsaturated polyester composite art objects", *E-Preservation Science*, Issue 3, 2006, 11–19.

205 Stigter, Sanneke et al., *op. cit.*, 489–496.

206 L. Beerkens et F. Breder, TEMPORARY ART? The Production and Conservation of Outdoor Sculptures in Fiberglass-Reinforced Polyester, *Conservation Perspectives*, Fall 2012, 2012. [https://www.getty.edu/conservation/publications\\_resources/newsletters/27\\_2/temporary\\_art.html#3](https://www.getty.edu/conservation/publications_resources/newsletters/27_2/temporary_art.html#3)

207 A. Lagana et al., "Looking through plastics: Investigating options for the treatment of scratches, abrasions, and losses in cast unsaturated polyester work of art", in: *ICOM-CC 17th Triennial Conference Preprints, Melbourne, 15–19 September 2014*, J. Bridgland (ed.), 2014, art. 1005.

ance for treatments on two untitled works of art of Mathilde ter Heijne; research included artificial light aging and joints tensile testing.<sup>208</sup> *Nuredduna*, made from UP resin-based composite, by Aligi Sassu, was studied for the chemical characterization, manufacturing technique and state of conservation.<sup>209</sup> An example of degradation due to human factors, i.e., vandalizing act, is the work *Chair*, by Allen Jones, made from GFRP, which was subjected to a conservation-restoration treatment since paint stripper was thrown over it, causing painted layer damage.<sup>210</sup> General recommendation for storage is: temperature  $18\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ , RH  $55\% \pm 3\%$ , light up to 150 lux for colorless and up to 50 lux for colored objects, UV radiation below  $75\text{ }\mu\text{W}/\text{lm}$ .<sup>211</sup>

## CONCLUSION

An overview of the found available literature on conservation-restoration treatments of works of art and museum artifacts made from polymer materials shows that, apart from treatments of natural polymers, it has only started to develop formally since the last decade of the 20<sup>th</sup> century. This field is still in expansion, especially when it comes to interventive conservation since there are polymer materials for which definite conservation-restoration methodologies have not been developed yet. In general, a necessary step prior to any treatment is material identification, i.e., identification of both polymers and their degradation products. In addition to this, for the prediction of degradation behavior artificial aging tests are required, and also mechanical characterization of aged materials, as well as monitoring of the natural aging of polymer materials. All these scientific techniques, along with identification of the effects of degradation due to various factors, are very important for planning future conservation-restoration methodologies and protocols.

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211 F. Waentig, *op. cit.*, 271.

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## LIST OF ABBREVIATIONS

UV light – Ultraviolet light  
 RH – Relative humidity  
 CN – Cellulose-nitrate  
 CA – Cellulose-acetate  
 CF – Casein-formaldehyde  
 PVC – Poly(vinyl chloride)  
 PU – Polyurethane  
 PS – Polystyrene  
 PMMA – Poly(methyl methacrylate)  
 PE – Polyethylene  
 PES – Polyester  
 UP – Unsaturated polyester  
 PVAc – Poly(vinyl acetate)

Радмила Б. ДАМЈАНОВИЋ, Мина Љ. ЈОВИЋ, Радмила М. ЈАНЧИЋ-HEINMANN,  
 Ирена Д. ЖИВКОВИЋ

## КОНЗЕРВАЦИЈА И РЕСТАУРАЦИЈА УМЕТНИЧКИХ ДЕЛА И АРТЕФАКАТА ОД ПОЛИМЕРНИХ МАТЕРИЈАЛА – ПОЉЕ УСКЕ САРАДЊЕ НАУКЕ И УМЕТНОСТИ: ПРЕГЛЕД ДОСАДАШЊЕ ПРАКСЕ

Природни полимери, а од краја 19. века и синтетички полимери, користе се за израду декоративних и функционалних предмета као и као средство за уметничко изражавање. Због органске природе, њихово пропадање је брже у поређењу са другим групама материјала. Деградација полимерних материјала је узрокована физичким, хемијским и биолошким факторима и доводи до структурних промена, погоршања својстава, промене њиховог изгледа и губитка функције. Идеја анализе у овом раду била је да се на једном месту, на основу пронађене доступне литературе, прикупе основни подаци о типовима полимера који се обично користе за израду уметничких дела и музејских артефаката укључујући ћилибар, корњачевину, рог, природну и синтетичку гуму, нитрат и ацетат целулозе, казеин-формалдехид, поли(винил хлорид), полиуретан, полистирен, поли(метил метакрилат), полиетилен, фенол-формалдехид, епоксид и полиестар. Анализа се фокусира само на 3Д уметничка дела и употребне артефакте. У раду је дат преглед класификације фактора деградације, као и општи подаци о конзервацији уметничких дела и музејских артефаката од полимерних материјала. Према наведеним основним типовима полимерних материјала, овај рад садржи опште информације о карактеристичним својствима, факторима и процесима деградације, а затим даје примере конзерваторско-рестаураторских интервенција уз примену научних техника. На основу доступних података, може се закључити да међу полимерним материјалима постоје разлике у брзинама деградације. Естри целулозе, поли(винилхлорид) и полиуретанска пена су најсклонији распадању, док су фенол-формалдехид и епоксиди најстабилнији. Методологија конзервације и рестаурације уметничких дела и музејских артефаката од полимерних материјала, још увек није прецизно дефинисана за све врсте полимера. Генерално, успостављени су превентивни конзерваторски протоколи, док је, када је у питању интервентна конзервација, ова област још увек у развоју, уз снажну подршку научних метода и технолошких сазнања. За планирање одговарајућих протокола конзервације-рестаурације потребно је обезбедити идентификацију материјала, тестове вештачког старења и разумевање производних процеса и својстава синтетичких полимера, услед чега су интердисциплинарни и мултидисциплинарни приступ неопходни.

**Кључне речи:** полимери, пластика, конзервација, рестаурација, деградација