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Developing an ivory-like material for stereolithography-based additive manufacturing

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ABSTRACT

Through history, numerous art, religious and every-day objects were carved from ivory because of its aesthetic appearance, convenient workability and its durability. Since the ivory trading ban was passed in 1989, many natural and synthetic materials were introduced as a replacement, but these are typically only available in bulk. To restore sometimes very complex and delicate artefacts, it is economically reasonable to develop a substitute that can be built by additive manufacturing to reduce carving time and material waste. Such a substitute material should especially mimic the aesthetic characteristics of ivory by means of the colour, translucency and surface gloss. All merchantable 3D printable substitute materials have evidential limitations in exactly those important characteristics. The newly developed substitute material called "Digory" is processible with an additive manufacturing technique that derived from stereolithography. Layer by layer, a photosensitive slurry that consists mainly of a dimethacrylic resin filled with calcium phosphate particles is polymerized with a UV laser. The solids loading, which was adjusted to fit the translucency of ivory, was around 30 vol.%. At this content, the density of about 1.79 g cm^{-3} and the hardness of 35.7 HV0.2 are equivalent to the values for ivory found in the literature. Small quantities of yellow and red colour pigments were used to modify the basic colour. With further post-processing using traditional handcraft techniques, such as staining and polishing of the surface, an optical imitation of natural ivory was achieved.

1. Introduction

Ivory is the dentine of an elephant or mammoth tusk. Sometimes, it is also referred to the dentine of different species with pronounced canine teeth, such as a warthog, walrus or hippopotamus. Elephant tusk dentine generally consists of Mg enriched hydroxyapatite crystals embedded in a matrix of type I collagen fibres [1]. It is known for its durability and aesthetic appearance, which includes colour, translucency and surface gloss. Another important characteristic are the so-called Schreger lines. They emerge from interlinked rhombic regions that appear slightly darker in colour and spiral clockwise and anti-clockwise around the tusk axis [2–5]. This unique pattern is most distinctive at the transversal cross-section of the tusk.

Due to the enacted ivory trading ban, set in place by the Convention on International Trade in Endangered Species of Wild Fauna and Flora (CITES) in 1989 ivory resources are limited and the use of elephant ivory is ethically unreasonable. Currently, mammoth ivory found in permafrost reservoirs are still available, yet intensely discussed whether or not to include it in the CITES trade regulations [6,7]. To restore or preserve cultural and religious artefacts that were carved originally from ivory, substitute materials are often used. Ivory is sometimes replaced with natural materials, such as bone, shell or so-called vegetable ivory, like nuts of the Tagua palm tree or the Jarina seed [3,8]. Alternatively, there are also a variety of manufactured ivory substitutes available made of a polymer composite with either inorganic particles, casein or sometimes even ivory sawdust [3]. These substitutes are mostly available as bulk and it can take a lot of time and effort to carve the desired shape. Especially delicate structures consume various

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resources. Developing a substitute material that can be processed with additive manufacturing (AM) technologies provides, therefore, a resource-friendly alternative. Additionally, by using AM, it is possible to recapture the style of the original artist and, hence, preserve the character and appearance of an art piece exactly as intended.

AM technologies present a practical tool for a variety of applications and are of increasing interest in restoring and copying cultural artefacts for preservative purposes [9–11]. The restoration of objects made of ivory requires a high printing resolution. This can be accomplished by stereolithography, which uses the energy of light to polymerize mainly epoxy or (meth)acrylate resins [12]. A dimethacrylate resin was chosen that reacts with the photosensitive initiator as the foundation for the 3D printable material. Tricalcium phosphate (TCP) particles, were added to obtain a translucent material. TCP is chemically close to hydroxyapatite and was used because it had shown promising 3D printing results in previous projects [13,14]. An UV-absorber was used to reduce excess polymerisation caused by light scattering at the TCP particles to ensure high geometric accuracy and enhance the surface quality. Finally, colour pigments were mixed to the white slurry to provide an ivory base colour. Samples were printed for three-point-bending and density measurements and the results were compared to values for ivory found in the literature. As each ivory is unique in appearance and surface gloss, a final post-processing step with traditional handcraft techniques to blend the replaced element into the surrounding original material is advisable. In the following, examples for such applications are presented as well. As materials produced by AM technologies are sometimes referred to as digital materials, this digital ivory is henceforth called "Digory". This material was developed to enable a more efficient and high-quality restoration and preservation of cultural artefacts made of ivory. Yet, its application is not necessarily limited to this purpose, as it can also be used for any object with decorative value.

2. Material and methods

The organic part of the ivory substitute comprises of the commercially available bisphenol-A ethoxylated dimethacrylate (Bis EMA, SR348C) obtained from Arkema. The inorganic part consists of β-TCP particles (21,218) by Sigma-Aldrich with a purity of $\geq$ 96.0% and a mean particle diameter of 7 µm. Liquid ethyl phenyl phosphinate (SpeedCure TPO-L) by Lambson initiates the photochemical reaction. Excess polymerisation, caused by light scattering at the ceramic particles, is absorbed by 2,2′-dihydroxy-4,4′-dimethoxybenzophenone (BP-6, D0575) with a purity of > 90.0%, produced by TCI. Fumed silica powder (S5130) with an average particle size of 0.007 µm by Sigma-Aldrich serves as a rheology additive to hinder the TCP particles from settling. Red and yellow zirconium oxide-based colour particles are added to adjust the base colour. All components were used as received. The parts were weighed with an analytical balance by Sartorius, with an accuracy of 10^{-4} g, and mixed using a speed mixer (DAC 150 FVZ) by Hauschild. The amount of TPO-L, BP-6 and the yellow and the red colour particles were, respectively, 1, 0.1, 0.2 and 0.02 wt.% with respect to the monomer mass. The amount of fumed silica was 0.5 wt.% with respect to the amount of the TCP powder. The solids loading was evaluated according to the translucency of the material.

Samples with simplified compositions of Bis EMA, TPO-L and different amounts TCP were prepared for that purpose. The solids loadings were 0, 15, 30, 45, 50, 55, 60 and 65 wt.%. Each composition was cast in a 2 × 4 × 45 mm^3 silicone mould and cured in a UV chamber (INTELLI RAY 600) by UViTron with a lamp power of 600 W for 120 s at a wavelength of 320-390 nm. The translucency test was conducted in a direct comparison with a flashlight that illuminated both, a 2 mm thick ivory lamella and one sample at a time.

The parts were printed with a Hot Lithography 3D printer of the Caligma 200 series by the company Cubicure GmbH that is heatable up to 120 °C and contains a laser unit with a laser spot size of 18 µm, a wavelength of 375 nm and a power of 70 mW. 50 µm thick layers were polymerised at a temperature of 50 °C and a laser speed of 1400 mm s^{-1}. After printing the parts were cleaned using isopropanol with a purity of 70% and post-cured with the aforementioned UV chamber for 600 s. After 300 s the parts were turned around to gain even curing results.

The material density was measured according to Archimedes' principle. Ten specimens with dimensions of 10 × 10 × 4 mm^3 were weighed with a hydrostatic balance by Sartorius, with an accuracy of 10^{-5} g, both, in air (m_a) and water (m_w). By knowing the density of water (ρ_w) at the testing temperature, which is 0.99791 g cm^{-3} at 21.5 °C, and by applying correction factors defined by the provider to reduce the error caused by the buoyancy of the sample holder in water, the density of the part (ρ_p) can be calculated by:

$$\rho_p = \frac{m_a * (\rho_w - 0.0012)}{(m_a - m_w) * 0.99983} + 0.0012$$

The flexural mechanical properties were determined with a three-point-bending unit of a Zwick/Roell testing machine (Zwick Z050). Two sets of ten specimens each were printed with dimensions of 25 × 4 × 3 mm^3 in XYZ and ZXY orientation, respectively, to compare the results to natural ivory tested by Pfeifer et al. [15]. The surfaces of the specimens were polished with FEPA P2000 abrasive paper by Struers. The sample carrier radii were 2 mm with a distance of 16 mm. The loading speed was 2 mm min^{-1} with a preload of 0.5 MPa. The work of fracture was determined by integrating the area underneath the force-deflection-curve with regard to the initial cross-section of the sample.

A hardness testing machine by EmcoTest (M1C 010) was used to measure the indentation hardness with a Vickers pyramid loaded at 200 g for 10 s. The samples with dimensions of 50 × 10 × 10 mm^3 were polished with 3 µm polishing suspension. Twenty indentation marks were placed at least six times the size of the indents apart and at least ten times that size from the edge.

The chosen examples of application include two pawns and a capital that was copied from a state casket, the so-called shrine of Friedrich III of Austria from the parish church of Mauerbach. The casket is currently located at the Archdiocese Vienna. The surface of one of the pawns was textured by projecting a picture of the Schreger lines onto the surface and extending the brighter parts by 50 µm using the AM software Netfabb by Autodesk. The surface of the pawns was stained with black tea, by tabbing a wet tea bag along the surface, or with Gouache colours. Subsequently, the texture was polished with 4000-grade flour paper to remove the colour from the heights. For hairline fractures, a carefully applied scalpel was used and the depths coloured with black ink. The surface was then sealed with microcrystalline wax. The original ivory capital was scanned with microcomputed tomography (µ-CT) with a scan voltage of 70 kV, a current of 114 µA, an integration time of 0.2 s and an isotropic voxel size of 16.4 µm. Any technical artefact that occurred during the scanning process was removed using the AM software Netfabb. The capital was printed upside-down and required no additional support structure. The part was polished with either 4000-grade flour paper, a ceramic grade polishing compound on a Dremel felt wheel, a gilders agate or a combination of these three methods, depending on the accessibility and the required gloss of the surface.

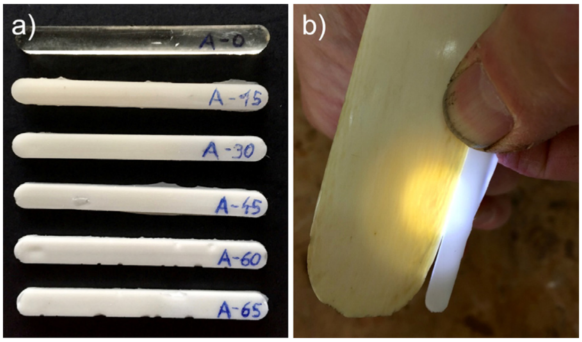

Fig. 1. (a) Polymerised Bis EMA with various TCP content, indicated in wt.% at the right side of each bar and (b) the comparison of the translucency of ivory (left) and Bis EMA with a solids loading of 55 wt.% (right).

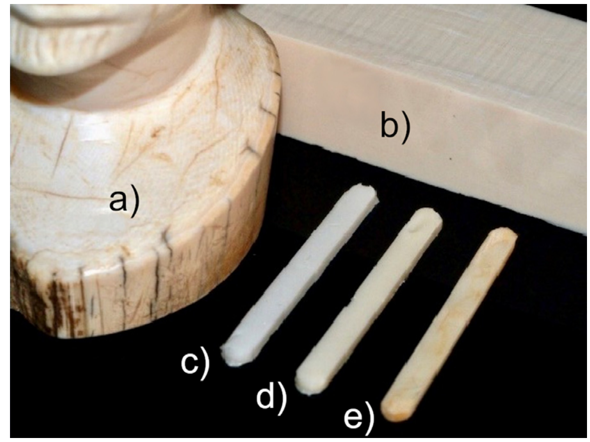

Fig. 2. Comparison of (a) ivory, (b) ivory substitute Elforyn, (c) ivory substitute Digory without colouring, (d) with colour pigments and (e) with colour pigments and superficial tea staining.

3. Results and discussion

Ivory is a translucent material that transmits part of the light particles freely and others are reflected and scattered along their path through the material. This interaction broadens the transmitted light beam and reduces its intensity. By mixing the transparent Bis EMA resin with the opaque TCP powder, this behaviour can be achieved for the substitute material Digory as well. The higher the content of the TCP powder is, the higher is the opacity of the material. Eight samples with solids loadings ranging from 0-65 wt.% were compared to an ivory lamella of equal thickness, to assess the necessary content of TCP powder. As shown in Fig. 1, a flashlight illuminated both, the cured sample and ivory, at the same time. When the transmitted light showed a continuous circle with a uniform radius, the translucency was considered to be equivalent. This was established at 55 wt.% TCP, which is equal to 30 vol.%. Comparing the translucency in this manner is well established amongst restorers and for the final decision, which filler content to use, a professional restorer and expert was consulted as well. Ivory is a natural material with varying translucency and colour, depending on the species, its habitat and even the position the part was taken from the tusk. For that reason, this qualitative method is sufficient to determine the filler content needed for a similar translucency behaviour. If necessary, it is possible to adjust the translucency by varying the TCP content, or by replacing part of the inorganic filling with glass ceramics that are also used in dental applications [14,16,17].

The density of the 3D printed ivory substitute Digory is 1.78 ± 0.02 g cm^{-3}. This value is comparable to the density of ivory found in the literature of 1.7-1.9 g cm^{-3} [8,18,19]. The small standard deviation leads to the expectation that there are no crucial inhomogeneities, such as pores, inside the material. The theoretical density of the suspension is 1.73 g cm^{-3}. The increased density of the printed part could indicate a higher degree of TCP, since the ceramic powder with a density of 3.14 g cm^{-3}, as opposed to 1.12 g cm^{-3} of the Bis EMA, would influence the overall density the most. This is most likely a result of the printing process. When the building platform, and later part of the already printed object, immerses into the liquid suspension coated on the vat, it displaces part of the suspension. The TCP particles, however, are probably being compressed rather than washed away, especially at the centre of the immersing object. This leads to a higher solids loading, which, considering the density difference, can be estimated to about 57–58 wt.%. This degree of filling would be closer to the mineral phase of 59.4 wt.% reported for the ivory specimens used by Pfeifer et al. [15].

The aforementioned composition was used to print specimens for bending tests that were recreated to compare the results to those of natural ivory according to Pfeifer et al. [15]. For this purpose, specimens of $25 \times 4 \times 3$ mm^3 were extracted parallel (longitudinal) and perpendicular (transversal) to the growth direction of the tusk. In the same manner, specimens were 3D printed with an XYZ (longitudinal) and ZXY (transversal) orientation. The flexural modulus, the flexural strength and the work of fracture are material properties that describe the stiffness of a material, as well as the maximal load and maximal energy, that can be applied before the material fails. The results of these parameters, as summarized in Table 1, exhibit for ivory a substantial difference between longitudinal and transversal orientation [15]. The provided substitute material Digory shows a similar trend, however, the difference is not as significant. The flexural strength of ivory is reduced by 74%, while the reduction of Digory from the flexural strength with XYZ to the ZXY orientation is 28%. The flexural modulus of the substitute material Digory remains constant in both test directions. The values for the flexural modulus, flexural strength and the work of fracture of the substitute material are of the same magnitude as those for natural ivory with transversal orientation. Especially, the flexural modulus of the substitute is comparable to ivory with transversal orientation. The anisotropy of ivory is explained by the orientation of the hydroxyapatite particles, which is evolutionarily optimised to favour the bending strength along the tusk axis [20,21]. The anisotropy of Digory results from the layer-wise structure caused by the AM process [22,23]. Given the difference in the morphology of these two materials, it is natural to expect increased mechanical properties for ivory. It consists of a highly structured network of collagen fibres that increase crack resistance. Digory has a uniform morphology, however there are still possibilities to enhance mechanical properties in photopolymers, which could be considered in a future study [12].

Hardness measurements were conducted to analyse the material's resistance to deformation and penetration. The value for indentation hardness of ivory tested at a load of 200 g was around 35 HV [18,20]. The result for Digory measured with the same load were 35.7 ± 1.3 HV and, thus, matches the hardness of ivory. It is favourable if the density and mechanical properties of the substitute material are similar to ivory. A restorer, who is used to working with ivory, will be able to process the substitute with familiar techniques.

Another important property to consider is the colour. The combination of Bis EMA and TCP generates a white material (Fig. 2 c). The addition of yellow and red pigments to the slurry results in a more ivory-like base colour, shown in Fig. 2(d). This colouration is similar to the commercially available ivory substitute Elforyn (Fig. 2 b). However, natural ivory is not typically uni-

Table 1
Results of the three-point-bending test of the 3D printed ivory substitute Digory with XYZ and ZXY orientations in comparison to natural ivory with longitudinal and transversal orientation [15].

	Flexural modulus [GPa]	Flexural strength [MPa]	Work of fracture [kJ m^{-2}]
Digory XYZ	6.3 ± 0.3	106.5 ± 8.8	2.8 ± 0.5
Digory ZXY	6.4 ± 0.8	76.7 ± 5.0	0.9 ± 0.2
Ivory longitudinal	10.7 ± 0.6	369.0 ± 21.8	23.8 ± 6.9
Ivory transversal	5.0 ± 0.5	97.0 ± 6.9	1.1 ± 0.5

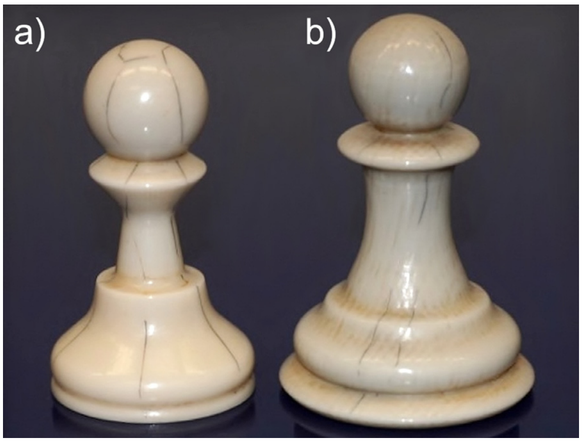

Fig. 3. 3D printed pawns with inked scalpel lines; tea-stained and polished (a) without and (b) with a surface texture to imitate the characteristic Schreger lines.

formly coloured (Fig. 2 a), thus, subsequent staining with black tea enhances a more natural appearance (Fig. 2 e). Tea staining is a common method restorers use to adjust the surface colour to the surrounding material. It needs be noted that ivory absorbs water to some extent, while Digory and most synthetic substitutes, are repellent to water. In order to gain better results, a roughened surface is favourable because it creates a higher surface area and allows the tea to deposit inside the grooves. It is also recommended to additionally apply a coating of wax, which fixates the tea stains and adds a surface gloss, as further displayed below.

The ivory object displayed in Fig. 2(a) shows characteristic fractures that can occur during ageing and typically appear radially along the tusk axis or in-between growth layers [24,25]. They become black when filled with dust. To imitate these hairline fractures also for the substitute Digory, a scalpel was carefully applied and the depths coloured with black ink. The surface was further stained with black tea and sealed with microcrystalline wax. This led to convincing results, which are depicted in Fig. 3. The pawn in Fig. 3(b) shows, additionally to the hairline fracture, a surface texture, which was applied as a first attempt to mimic the so-called Schreger lines. The surface of the texture was stained with a subtly darker Gouache colour than the basic colour of the pawn, and the heights were polished to the same level. The colour does not penetrate the material and vigorous polishing will, hence, remove the colour not only from the heights as intended but also from the depths. Therefore, some difference in height due to the texture remains, disrupting the desired smooth surface that is common in objects made of ivory. This is a challenge yet to overcome.

To show the replication of a more complex artefact, a column capital made of ivory was scanned with μ-CT to create a 3D model, which was then printed. It was disassembled from a state casket, the shrine for Friedrich III of Austria, which is depicted in Fig. 4. Eighteen of the twenty-four columns, including the capitals, are lost and need replacement. The 3D printed element, which is presented in Fig. 5(b), displays a matt surface. Three different ways of polishing that produce varying degrees of surface gloss were applied. A gilders agate, which is rubbed on the surface, provides a burnished, soft gloss. Smoothing the surface with a fine 4000-grade flour paper and subsequent polishing using microcrystalline wax creates a higher degree of shine. Whereas, a white ceramic grade polishing compound on a Dremel felt wheel produces a very shiny surface. A combination of these methods was then applied for the appropriate surface gloss to match the original ivory capital, seen in Fig. 5. The developed substitute consists of a polymer matrix with ceramic particles, which are not necessarily bond together. Thus, when the surface is rapidly polished, sometimes particles are torn out of the matrix and leave a dent. This is not visible to the naked eye, however, it could result in a slightly higher surface roughness, than intended. In order to avoid such defects, a moderate polishing speed is necessary.

Fig. 4. State casket, the shrine for Friedrich III of Austria, from the parish church of Mauerbach, currently located at the Archdiocese Vienna, which was made in the second half of the 17th century (©Stephan_Doleschal).

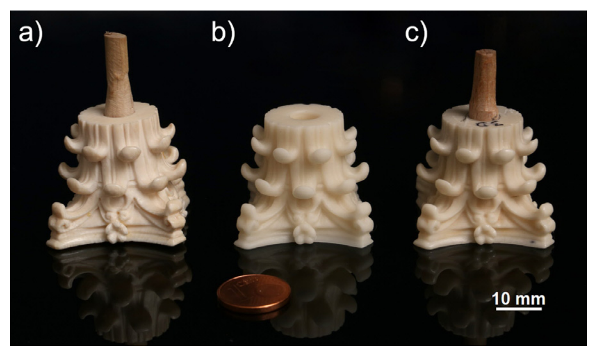

Fig. 5. (a) Original ivory capital removed from the shrine for Friedrich III of Austria and the 3D printed capital (b) after post-curing and (c) after post-processing with handcraft techniques.

When imitating a natural material, especially one with a questionable source of origin, or when complementing or replicating a work of art or an historical object, it is important to keep a distinction between the original and the substitute. Such a defining feature should not disrupt the overall appearance, yet be easy to discover with non-distractive methods. In the case of ivory, the Schreger lines, while being part of the aesthetic incentive, are still the most distinctive identification mark. This pattern is unique in natural materials and most of the synthetic substitute materials are restricted by the manufacturing technique to implement such interlocking features [26,27]. Another method to distinguish natural ivory is the density, which is for most other manufactured substitutes lower than 1.5 g cm^{-3} [18,26]. Also vegetable ivory, such as the Jarina seed is less dense compared to ivory [8]. Bones show a higher density compared to ivory and the polished surface is covered with pits resulting from canals of the supply system [18,26,28]. Depending on the manufacturing technique, synthetic substitute materials might sometimes show production errors such as air pockets or streaks of an inhomogeneous material. The risk of such occurrences is reduced with additive manufacturing because of the decreased volume of each layer. Synthetic substitutes are also identifiable by long wave UV light, which they absorb and thus appear dull blue. Ivory, on the other hand, when illuminated with UV light, appears white or light blue fluorescent [28]. Also, the presented substitute material Digory is best distinguishable via UV light, since the physical criteria are quite similar to ivory. Those identification marks ensure that the demands of *the Charta of Venice*, the international guidelines for preservation and restauration, are redeemed in using Digory for restauration.

4. Summary

Restoring cultural or religious objects made of ivory for preservative purposes requires a lot of resources. Many materials that are used to substitute ivory are only available in bulk form and need to be carved into shape. In many cases, especially for complex parts or when multiple copies of one object are required, restoration is economically not feasible. To reduce the effective working time and material costs, a substitute material called Digory was developed that can be shaped with stereolithography-based AM. With the introduction of a 3D printable substitute material for ivory the applications are, however, not limited to restoring purposes but could also be found in jewellery or interior design. The material based on a dimethacrylic Bis EMA resin and TCP powder exhibits at a filler content of 30 vol.% a translucency and density that is comparable to ivory. Regarding the mechanical properties, ivory is more anisotropic than the substitute Digory. The flexural modulus, the flexural strength and the work of fracture of the specimens made of the substitute with XYZ and ZXY orientation are similar to natural ivory with a transversal orientation. The indentation hardness measured with a Vickers pyramid is equivalent to hardness values of ivory found in the literature. The base colour of Digory was adjusted by adding pigments to the unpolymerized slurry. Additional superficial staining of the printed objects provides an even more natural appearance. Ivory-characteristic features, such as hairline fractures and surface gloss can be achieved as well. This was presented by different examples of application.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Thaddäa Rath: Methodology, Investigation, Writing - original draft, Writing - review & editing. **Otmar Martl:** Investigation. **Bernhard Steyrer:** Conceptualization, Methodology. **Konstanze Seidler:** Writing – original draft. **Richard Addison:** Methodology, Resources. **Elena Holzhausen:** Conceptualization. **Jürgen Stampfl:** Conceptualization, Supervision.

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Data Availablability

The raw and the processed data required to reproduce these findings are available in the Supplementary Information file.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.apmt.2021.101016.

References

[1] F.Z. Cui, H.B. Wen, H.B. Zhang, C.L. Ma, H.D. Li, Nanophase hydroxyapatite-like crystallites in natural ivory, J. Mater. Sci. Lett. 13 (1994) 1042–1044, doi:10.1007/BF00277033.

[2] A.E.W. Miles, J.W. White, Ivory, Proc. R. Soc. Med. 53 (1960) 775–780 https://pubmed.ncbi.nlm.nih.gov/13770634/.

[3] E.O. Espinoza, M.-J. Mann, The history and significance of the Schreger pattern in proboscidean ivory characterization, J. Am. Inst. Conserv. 32 (1993) 241–248, doi:10.2307/3179547.

[4] E.J. Raubenheimer, M.C. Bosman, R. Vorster, C.E. Noffke, Histogenesis of the chequered pattern of ivory of the African elephant (Loxodonta Africana), Arch. Oral Biol. 43 (1998) 969–977, doi:10.1016/S0003-9969(98)00077-6.

[5] M. Albéric, A. Gourrier, W. Wagermaier, P. Fratzl, I. Reiche, The three-dimensional arrangement of the mineralized collagen fibers in elephant ivory and its relation to mechanical and optical properties, Acta Biomater 72 (2018) 342–351, doi:10.1016/j.actbio.2018.02.016.

[6] P.A. Nikolskiy, L.D. Sulerzhitsky, V.V. Pitulko, Last straw versus Blitzkrieg overkill: climate-driven changes in the Arctic Siberian mammoth population and the Late Pleistocene extinction problem, Quat. Sci. Rev. 30 (2011) 2309–2328, doi:10.1016/j.quascirev.2010.10.017.

[7] L.E. Cartier, M.S. Krzemnicki, M. Gysi, B. Lendvay, N.V. Morf, A case study of ivory species identification using a combination of morphological, gemmological and genetic methods, J. Gemmol. 37 (2020) 282–297, doi:10.15506/jog.2020.37.3.282.

[8] Y. Chu, M.A. Meyers, B. Wang, W. Yang, J.Y. Jung, C.F.M. Coimbra, A sustainable substitute for ivory: the jarina seed from the amazon, Sci. Rep. 5 (2015) 1–10, doi:10.1038/srep14387.

[9] Y.H. Jo, S. Hong, Application of three-dimensional scanning, haptic modeling, and printing technologies for restoring damaged artifacts, J. Conserv. Sci. 35 (2019) 71–80, doi:10.12654/jcs.2019.35.1.08.

[10] M. Fantini, F. De Crescenzio, F. Persiani, S. Benazzi, G. Gruppioni, 3D restitution, restoration and prototyping of a medieval damaged skull, Rapid Prototyp. J. 14 (2008) 318–324, doi:10.1108/13552540810907992.

[11] P. Zhou, W. Shui, L. Qu, F. Gao, Z. Wu, Case study: missing data computation and 3D printing application in symmetrical artifact restoration, in: Proc. - VRCAI 2016 15th ACM SIGGRAPH Conf. Virtual-Reality Contin, Its Appl. Ind., 2016, pp. 63–66, doi:10.1145/3014027.3014032.

[12] J. Stampfl, S. Baudis, C. Heller, R. Liska, A. Neumeister, R. Kling, A. Ostendorf, M. Spitzbart, Photopolymers with tunable mechanical properties processed by laser-based high-resolution stereolithography, J. Micromech. Microeng. 18 (2008) 9, doi:10.1088/0960-1317/18/12/125014.

[13] G. Mitteramskogler, Generative Fertigung von Bauteilen aus T.C.P., Diplomarbeit, TU Wien, 2011. https://scholar.google.com/scholar_lookup?title=Generative Fertigung von Bauteilen aus TCP%2C Diplomarbeit&author=G. Mitteramskogler&publication_year=2011.

[14] R. Gmeiner, G. Mitteramskogler, J. Stampfl, A.R. Boccaccini, Stereolithographic ceramic manufacturing of high strength bioactive glass, Int. J. Appl. Ceram. Technol. 12 (2015) 38–45, doi:10.1111/ijac.12325.

[15] S.J. Pfeifer, W.L. Hartramph, R.D. Kahlke, F.A. Müller, Mammoth ivory was the most suitable osseous raw material for the production of Late Pleistocene big game projectile points, Sci. Rep. 9 (2019) 1–10, doi:10.1038/s41598-019-38779-1.

[16] S. Baumgartner, R. Gmeiner, J.A. Schönherr, J. Stampfl, Stereolithography-based additive manufacturing of lithium disilicate glass ceramic for dental applications, Mater. Sci. Eng. C. 116 (2020) 111180, doi:10.1016/j.msec.2020.111180.

[17] R. Felzmann, S. Gruber, G. Mitteramskogler, P. Tesavibul, A.R. Boccaccini, R. Liska, J. Stampfl, Lithography-based additive manufacturing of cellular ceramic structures, Adv. Eng. Mater. 14 (2012) 1052–1058, doi:10.1002/adem.201200010.

[18] F. Vollrath, R. Mi, D.U. Shah, Ivory as an important model bio-composite, Curator Museum J 61 (2018) 95–110, doi:10.1111/cura.12236.

[19] A. Rajaram, Tensile properties and fracture of ivory, J. Mater. Sci. Lett. 5 (1986) 1077–1080, doi:10.1007/BF01730290.

[20] F.Z. Cui, H.B. Wen, H.B. Zhang, H.D. Li, D.C. Liu, Anisotropic indentation morphology and hardness of natural ivory, Mater. Sci. Eng. C. 2 (1994) 87–91, doi:10.1016/0928-4931(94)90035-3.

[21] G. Nothnagel, S.D. Le Roux, W. Grotepass, Correlation Between Texture of Hydroxyapatite and Mechanical Anisotropy in Loxodonta Africana Ivory, Textures Microstruct 26 (1996) 579–583, doi:10.1155/tsm.26-27.579.

[22] K. Puebla, K. Arcaute, R. Quintana, R.B. Wicker, Effects of environmental conditions, aging, and build orientations on the mechanical properties of ASTM type i specimens manufactured via stereolithography, Rapid Prototyp. J. 18 (2012) 374–388, doi:10.1108/13552541211250373.

[23] M. Monzón, Z. Ortega, A. Hernández, R. Paz, F. Ortega, Anisotropy of photopolymer parts made by digital light processing, Materials (Basel) 10 (2017) 1–15, doi:10.3390/ma10010064.

[24] A. Virág, Histogenesis of the unique morphology of proboscidean ivory, J. Morphol. 273 (2012) 1406–1423, doi:10.1002/jmor.20069.

[25] C.E. Heckel, S. Wolf, Ivory debitage by fracture in the Aurignacian: experimental and archaeological examples, J. Archaeol. Sci. 42 (2014) 1–14, doi:10.1016/j.jas.2013.10.021.

[26] S. Fabian, T. Stephan, DGemG-Information : elfenbein – Eigenschaften, Imitationen und Erkennung, Dtsch. Gemmol. Gesellschaft EV (2017) 13.

[27] M. Locke, Structure of ivory, J. Morphol. 269 (2008) 423–450, doi:10.1002/jmor.10585.

[28] E.O. Espinoza, M.-J. Mann, Identification Guide for Ivory and Substitues, 2nd ed., World Wildlife Fund, Baltimore, USA, 1992.