Defense Systems Information Analysis Center

DSIAC TECHNICAL INQUIRY (TI) RESPONSE REPORT

Sterilization Techniques for 3-D-Printed Materials and Medical Items

Report Number:

DSIAC-BCO-2023-455

Completed August 2023

DSIAC is a U.S. Department of Defense Information Analysis Center

MAIN OFFICE
4695 Millennium Drive
Belcamp, MD 21017-1505
Office: 443-360-4600

REPORT PREPARED BY:
SPARC Research

DSIAC is sponsored by the Defense Technical Information Center, with policy oversight provided by the Office of the Under Secretary of Defense for Research and Engineering. DSIAC is operated by the SURVICE Engineering Company.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE	**2. REPORT TYPE**	**3. DATES COVERED** *(From – To)*
17-08-2023	Technical Research Report	

4. TITLE AND SUBTITLE
Sterilization Techniques for 3-D-Printed Materials and Medical Items

5a. CONTRACT NUMBER
FA8075-21-D-0001

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

SPARC Research

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Defense Systems Information Analysis Center (DSIAC)
4695 Millennium Drive
Belcamp, MD 21017-1505

SPARC Research
5310 Edmore Court
Warrenton, VA 20187

8. PERFORMING ORGANIZATION REPORT NUMBER

DSIAC-BCO-2023-455

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Defense Technical Information Center (DTIC)
8725 John J. Kingman Road
Fort Belvoir, VA 22060-6218

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

DISTRIBUTION A: Approved for public release: distribution unlimited.

13. SUPPLEMENTARY NOTES
Materials and Manufacturing Processes: Materials/Processes for Survivability and Life Extension; Advanced Materials, Medical, RMQSI

14. ABSTRACT
The use of polymer additive manufacturing (AM) for single-use and reusable medical devices in austere environments is of interest to the U.S. Department of Defense. The ability to field a deployable AM resource with enough filament to sustain 60–90 days helps create a more independent and well-rounded medical team and closes air gaps on supply chain reliance. This report includes a literature survey to gather insights into the available medical sterilization technologies and align them with the properties of AM polymers and their susceptibility to degradation. Suitability is assessed using a material compatibility matrix, evaluating each method while considering parameters such as glass transition temperature and reactivity. Only thermoplastic polymers used in fused deposition modeling (FDM) printing were considered; geometric challenges were not evaluated. Ethylene oxide and hydrogen peroxide gas plasma sterilization methods were found to be most effective for FDM materials. Conversely, the autoclave and dry-heat methods commonly used for surgical instruments performed poorly. The findings offer stakeholders an early framework for decision-making, enhanced patient safety, and the progressive advancement of AM within the realm of medical applications.

15. SUBJECT TERMS
sterilization techniques, 3-D printed, medical devices, printed polymers, ethylene oxide, hydrogen peroxide gas plasma, polymer degradation

16. SECURITY CLASSIFICATION OF: U			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			Ted Welsh, DSIAC Director
U	U	U	UU	21	**19b. TELEPHONE NUMBER** *(include area code)* 443-360-4600

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

DISTRIBUTION A. Approved for public release: distribution unlimited.

About

DTIC and DSIAC

The Defense Technical Information Center (DTIC) preserves, curates, and shares knowledge from the U.S. Department of Defense's (DoD's) annual multibillion-dollar investment in science and technology, multiplying the value and accelerating capability to the Warfighter. DTIC amplifies this investment by collecting information and enhancing the digital search, analysis, and collaboration tools that make information widely available to decision-makers, researchers, engineers, and scientists across the Department.

DTIC sponsors the DoD Information Analysis Centers (DoDIAC), which provide critical, flexible, and cutting-edge research and analysis to produce relevant and reusable scientific and technical information for acquisition program managers, DoD laboratories, Program Executive Offices, and Combatant Commands. The IACs are staffed by, or have access to, hundreds of scientists, engineers, and information specialists who provide research and analysis to customers with diverse, complex, and challenging requirements.

The Defense Systems Information Analysis Center (DSIAC) is a DoDIAC sponsored by DTIC to provide expertise in 10 technical focus areas: weapons systems; survivability and vulnerability; reliability, maintainability, quality, supportability, and interoperability (RMQSI); advanced materials; military sensing; autonomous systems; energetics; directed energy; non-lethal weapons; and command, control, communications, computers, intelligence, surveillance, and reconnaissance (C4ISR). DSIAC is operated by SURVICE Engineering Company under contract FA8075-21-D-0001.

TI Research

A chief service of the U.S. Department of Defense's Information Analysis Centers is free technical inquiry (TI) research limited to four research hours per inquiry. This TI response report summarizes the research findings of one such inquiry. Given the limited duration of the research effort, this report is not intended to be a deep, comprehensive analysis but rather a curated compilation of relevant information to give the reader/inquirer a "head start" or direction for continued research.

Abstract

The use of polymer additive manufacturing (AM) for single-use and reusable medical devices in austere environments is of interest to the U.S. Department of Defense. The ability to field a deployable AM resource with enough filament to sustain 60–90 days helps create a more independent and well-rounded medical team and closes air gaps on supply chain reliance. This report includes a literature survey to gather insights into the available medical sterilization technologies and align them with the properties of AM polymers and their susceptibility to degradation. Suitability is assessed using a material compatibility matrix, evaluating each method while considering parameters such as glass transition temperature and reactivity. Only thermoplastic polymers used in fused deposition modeling (FDM) printing were considered; geometric challenges were not evaluated. Ethylene oxide and hydrogen peroxide gas plasma sterilization methods were found to be most effective for FDM materials. Conversely, the autoclave and dry-heat methods commonly used for surgical instruments performed poorly. The findings offer stakeholders an early framework for decision-making, enhanced patient safety, and the progressive advancement of AM within the realm of medical applications.

Contents

List of Figures

List of Tables

1.0 TI Request

1.1 Inquiry

What kind of additive manufacturing (AM) material can be reused, while maintaining integrity, under the standards of military central sterile processing?

1.2 Description

This question is driven by austere environments and medical survivability. The more independent and well rounded a medical team is, the better the outcome in regard to patient care. Testing/fielding a deployable AM resource with enough filament to sustain 60–90 days seems logistically feasible and closes air gaps on supply chain reliance.

2.0 TI Response

2.1 Introduction

The manufacture of medical equipment has recently undergone a significant transformation due to the integration of AM technology, colloquially known as three-dimensional printing (3DP). Although acceptance of printed medical components was already underway, their widespread adoption was fueled by the special exigency surrounding the COVID-19 pandemic. A common anecdote was hobbyists using their three-dimensional (3-D) printers to manufacture personal protective equipment for use by hospital staff within their communities. While demand has tampered, the postpandemic era has witnessed a substantial deployment of 3DP to address supply chain disruptions, facilitate the creation of customized medical implements, and enhance surgical procedures.

However, this amalgamation of 3DP and healthcare mandates a meticulous adherence to rigorous safety and effectiveness metrics. This includes the need to establish robust sterilization protocols, where the new 3-D-printed medical artifacts, implants, and anatomical models must still maintain pristine hygienic conditions to prevent infection or the introduction of other contaminants into the body that would trigger an immune response. As such, there is an evident imperative to develop comprehensive sterilization frameworks.

The medical community has generally gravitated toward time-tested sterilization equipment and procedures. Within the U.S. Department of Defense (DoD) community, for example, the more

common methods are the use of the autoclave and dry heat. In the former method, the autoclave uses steam heated to 121 °C or 134 °C—depending on the model—to deactivate enzyme and protein activity within the microbes, killing them. Dry heat abstains from the use of steam and rather ratchets the heat further to 160–180 °C to achieve metabolic disruption in microbe colonies. Both are extremely effective at achieving a sterility assurance level of 10-6 (i.e., 1 microbe in 106 cleaned instruments) for metals, oils, and powders [1].

Many polymeric materials, however, have limited suitability to these processes. Those in fused deposition modeling (FDM)—the most common version of polymer 3DP—have relatively lower glass transition temperatures (Tgs) and melting points, which can lead to deformation, degradation, or changes in mechanical properties. This consequently makes them unsuitable for their intended applications or for their reuse. As a result, alternative sterilization methods that operate at lower temperatures or do not rely on heat are often preferred to maintain the integrity of the polymers.

During the course of this survey of the literature, it quickly became apparent that evaluating the suitability of a sterilization process for each of the FDM filament feedstocks on the market would be inordinately time consuming. Each filament has unique values of molecular weight (MW) and Tg. It would be more beneficial, however, to generate a broader, approximate evaluation framework that uses key properties and generally accepted values thereof. The other inherent advantage is that, in addition to FDM feedstocks that are already on the market, this analytical framework is also applicable to any other polymer that debuts on the market after the publication of this report.

This report is divided into three distinct parts. First, it provides an overview of common sterilization processes for polymeric tools, devices, and equipment. This includes outlining the most important advantages and disadvantages of each process. Next is the discussion of key material properties that must be considered in the evaluation of a sterilization process's suitability for use. This section also includes general heuristic and delineating criteria. The last part of this report employs property data and the heuristic methods to determine the suitability of each FDM polymer feedstock to individual sterilization processes.

2.2 Description of Sterilization Processes

It is instructive to first begin with brief descriptions of the sterilization processes and discuss impacts on polymeric materials. For quick reference, a summary of these is presented in Table 1.

Table 1. Overview of Sterilization Methods for Medical Equipment

Method	Advantages	Disadvantages
Autoclave	Cost-effective, nontoxic, environmentally friendly/sustainable	Use of heat can induce warping within polymers having low Tgs or extreme moisture sensitivities
Dry Heat	Cost effective, nontoxic, environmentally friendly	Heat more extreme than that of the autoclave, only high-temperature polymers are usable in the process
Ethylene Oxide (EtO)	Suitable for heat-sensitive materials	Extremely long sterilization time (>14 hr), EtO is toxic and a known carcinogen, high equipment costs and availability of chemicals is challenging in some forward-deployed regions
Hydrogen Peroxide Gas Plasma (HPGP)	Suitable for heat-sensitive materials, affordable	Hydrogen peroxide concentration is difficult to measure in operando, high equipment costs
Gamma Radiation	High penetration of the component, no toxic residues	Highest equipment costs, radiation safety hazards, requires dedicated facility for operation
Electron Beam (E-Beam)	Very fast cycle time, low-temperature process	Only surface penetration due to attenuation of electrons, very high equipment costs, typically requires dedicated facility

2.2.1 Autoclave Sterilization

The autoclave process is a crucial method of sterilization widely employed in laboratories, medical facilities, and various industries to eliminate microbial life and ensure the safety of equipment and materials. This process involves subjecting the items to high-temperature steam under controlled pressure, effectively neutralizing bacteria, viruses, and other pathogens. The autoclave consists of a sealed chamber where items to be sterilized are placed and the chamber is then heated to 121 °C. At this temperature, the steam can permeate the entire chamber, penetrating even hard-to-reach areas and effectively deactivating microorganisms by denaturing their proteins and enzymes.

The advantages of using the autoclave process include its efficiency, reliability, and wide applicability. It achieves thorough sterilization, ensuring that most microorganisms are eliminated and, thus, significantly reducing the risk of contamination. The process is also relatively quick, with sterilization cycles typically lasting around 15–20 min, depending on the load and chamber size. Moreover, autoclaves are versatile, capable of sterilizing a variety of materials from glassware and metal instruments to certain heat-resistant polymeric materials. Also being cognizant of costs, it is noted that the autoclave process is relatively cheap due to

economies of scale making the equipment affordable. A brief search showed that small-scale autoclaves with ~20-liter capacity were on the order of $5,000. Autoclaves also have a logistical advantage for the DoD, requiring only water and electrical power for operation.

However, certain disadvantages must be acknowledged. Many polymeric materials have lower heat resistance and may undergo deformation or structural changes when exposed to the high temperatures and moisture levels used in autoclaves. This can lead to alterations in the material's physical properties, potentially affecting its performance or integrity. An excellent example of this is shown in Figure 1, where a polylactic acid (PLA) part deformed under an autoclave cycle. Additionally, some FDM polymers may release harmful chemicals or breakdown products when subjected to high temperatures and steam.

Figure 1. Warping of PLA After Autoclave Process [2].

2.2.2 Dry-Heat Sterilization

Dry-heat sterilization is a widely used method for effectively eliminating microbial life and ensuring the safety of equipment and materials by subjecting them to elevated temperatures without the presence of moisture. In this process, items to be sterilized are placed in an oven-like chamber, where heat is evenly distributed to achieve a desired temperature, typically ranging from 160–180 °C. The absence of moisture prevents the formation of steam, and, instead, microorganisms are deactivated through processes such as oxidation, protein denaturation, and disruption of cell membranes.

The advantages of dry-heat sterilization include its ability to sterilize items that may be sensitive to moisture, such as powders, oils, and certain types of glassware. The method is particularly effective for heat-resistant materials, and it does not cause corrosion or dulling of sharp instruments. Dry-heat sterilization is also suitable for items that may be damaged by steam or that cannot withstand the moisture present in other sterilization methods. Moreover, like the autoclave process, dry-heat sterilization chambers are also economical, with vendor searches showing~20–30-liter machines costing between $6,000 and $10,000.

However, there are some limitations and disadvantages associated with dry-heat sterilization. It generally requires longer exposure times and higher temperatures compared to moist-heat methods like autoclaving. This extended exposure time or multiple sterilization cycles can potentially lead to further degradation of heat-sensitive materials such as polymers [3]. Additionally, the uniform distribution of heat within the chamber is crucial to ensure effective sterilization and inadequate temperature control or uneven heating can result in incomplete sterilization.

2.2.3 Gamma Radiation Sterilization

Gamma radiation sterilization is a widely recognized method for achieving effective and thorough sterilization of various materials and products by utilizing high-energy gamma rays emitted from a radioactive source, typically cobalt-60 or caesium-137. This process disrupts the DNA and cellular structures of microorganisms, rendering them unable to reproduce or cause infections. Items to be sterilized are placed in a specially designed chamber or facility, known as an irradiator, where they are exposed to controlled doses of gamma radiation.

The advantages of gamma radiation sterilization are numerous. It offers a reliable and efficient means of achieving sterility. Due to the mass attenuation coefficients for polymers being low with respect to gamma radiation, the photons go completely through the devices, ensuring that any internal passages containing pathogens receive the same dose as that on the outside. Gamma radiation sterilization is also a cold process, making it suitable for items that are heat sensitive or moisture-sensitive, and it can be applied to both prepackaged and bulk products. However, when considering the use of gamma radiation sterilization with polymeric materials, it is important to recognize that some polymers may experience radiation-induced changes.

Overexposure to gamma radiation can lead to chain scission, lowering the MW of the polymer chains [4]. This will consequently affect the material's mechanical properties, color, and stability. However, the rate at which these changes will occur or become critical is dependent on

a number of factors, such as initial chain MW and if there are additives present as countermeasures such as free radical scavengers (e.g., sterically hindered phenols or quinones) [5].

More substantial are the logistical considerations and limitations associated with gamma radiation sterilization. A major disadvantage to this process is its cost. Due to the use of radioactive agents, the necessary safety measures, and associated compliance costs with material handling regulations, the initial cost of this equipment is typically over $1M. For this reason, gamma radiation sterilization is usually handled through third-party contracting outside the medical facility. Accordingly, gamma irradiation capabilities may not be available in forward-deployed locations.

2.2.4 E-Beam Sterilization

E-beam sterilization is a cutting-edge method used to achieve high-level sterilization of various products and materials by utilizing accelerated electrons. In this process, items to be sterilized are exposed to a controlled stream of high-energy electrons generated by an electron accelerator. These electrons penetrate the materials, effectively disrupting the genetic material of microorganisms and preventing their ability to reproduce [6].

The advantages of E-beam sterilization are compelling. It offers rapid and efficient sterilization, often completing cycles within minutes, making it a viable option for high-throughput production environments. E-beam technology does not require the use of chemicals, water, or high temperatures, minimizing the risk of altering the physical or chemical properties of sensitive materials. Moreover, E-beam sterilization can uniformly treat complex and dense products, such as medical devices, pharmaceuticals, packaging, and cosmetics, ensuring consistent results.

However, like other sterilization methods, E-beam sterilization has certain considerations and limitations. The main challenge is logistical. Establishing an E-beam facility involves significant initial capital investment in the electron accelerator and necessary shielding systems. This can significantly hamper its use for forward-deployed environments unless there is a good hub location in theatre. Regulatory compliance and safety measures are additionally paramount due to the ionizing radiation involved. Operators must adhere to strict guidelines and ensure proper safety protocols to protect personnel and the environment. The second challenge is penetration depth. Electrons at these acceleration voltages are easily attenuated within the samples. Thus,

E-beam sterilization is only able to penetrate 10s of microns below the surface. At present, there are limited studies on use of E-beam sterilization on printed medical equipment [7].

2.2.5 HPGP Sterilization

HPGP sterilization is an innovative and highly effective method used for the sterilization of medical instruments and equipment. In this process, a low-temperature plasma is generated from hydrogen peroxide vapor and oxygen gas at approximately 60 °C. The plasma contains free radicals that react with and destroy microorganisms, rendering them nonviable [8].

The advantages of HPGP sterilization are significant. It operates at low temperatures, which makes it suitable for heat-sensitive and delicate medical devices, such as endoscopes and electronics, that may be damaged by traditional high-heat sterilization methods. The process is relatively quick, with sterilization cycles typically lasting around an hour, making it well suited for busy healthcare settings. Additionally, HPGP sterilization does not leave toxic residues, eliminating the need for aeration and reducing the potential for harm to patients or staff.

However, there are considerations to bear in mind. The method requires specialized equipment equipped with plasma chambers and controls, and the initial investment can be substantial. Additionally, peroxides are strong oxidizers and can alter the surfaces of the polymers in which they come in contact. Examples may include nucleophilic attack of carbonyls to produce carboxylic acids or conversion of alkenes to epoxides. However, due to steric effects, the result on polymers for short-exposure times are relatively small compared to a low-MW species in a reactor. Oxidation from excessive sterilization cycles may appear as discoloration or a loss in properties [9]. Since any heterogeneous (gas/solid) oxidation reaction is inherently a surface phenomenon, major changes would be more noticeable on equipment that has large surface-to-volume ratios. The additional consideration must be cost. While the inputs are relatively inexpensive, a typical HPGP system with equivalent volumes to the dry-heat and autoclave systems are on the order of $40,000 per unit, representing nearly an order of magnitude increase in initial capital expenditures.

2.2.6 EtO Sterilization

EtO sterilization is a widely adopted method for achieving high-level sterilization of medical devices, pharmaceuticals, and other heat-sensitive products. This technique employs EtO gas to infiltrate materials and disrupt microorganisms' genetic material, rendering them inactive through alkylation reactions [10]. One notable advantage of EtO sterilization is its operation at

low temperatures (37–63 °C), rendering it ideal for heat-sensitive materials like polymers and plastics that might deform or degrade under higher heat. Furthermore, its capability to deeply penetrate porous and intricate materials ensures comprehensive sterilization throughout the entire product. EtO sterilization is compatible with a wide range of materials, including diverse polymers, metals, and electronics, making it a versatile choice for various applications. It typically leaves minimal residues, and post-sterilization aeration can further reduce any remaining gas levels. Additionally, the gentle nature of the EtO process is particularly beneficial for sterilizing delicate medical devices and electronics.

However, there are certain disadvantages of employing EtO sterilization, particularly when considering its application to polymers. Despite its minimal residual effects, certain polymers might retain traces of EtO, which could raise concerns for specific sensitive applications or patients. Like HPGP, there is additionally a potential for polymer degradation over time due to EtO exposure, where groups such as amines can conduct nucleophilic attack on the epoxide's electrophilic carbons, leading to alterations in mechanical properties, color, or surface characteristics. Adequate aeration time is required post-sterilization to eliminate any lingering EtO gas, which can extend the overall processing duration. Additionally, safety concerns are associated with EtO, as it is flammable and explosive and is classified as a carcinogen. Proper handling, specialized equipment, and stringent safety measures are crucial to prevent exposure risks to personnel.

2.3 Key Parameters for Evaluating Sterilization Methods

When considering the suitability of a sterilization process for polymer materials, several key material properties play a crucial role. These properties help determine how a polymer will respond to sterilization methods and whether it can maintain its structural integrity and desired functionality after the process. The following lists some key polymer material properties that are relevant in assessing the suitability of sterilization processes.

- Tg: The Tg is the temperature at which an amorphous polymer transitions from a brittle, glassy state to a more flexible, rubbery state. Sterilization processes that involve high temperatures, such as autoclaving, may impact polymers near or above their Tg, potentially leading to softening, distortion, or even melting. This includes the potential for deformation under the material's own weight. In some cases such as silicone or butadiene rubbers, flexibility is the desired property with a Tg less than room temperature. In such cases, Tg is not a good measure for evaluating the suitability of a

high-temperature process. Instead, other thermal properties can be considered, such as melting temperature (Tm). In general, if a process's operating temperature is above Tg, then it is recommended to not use that process out of caution against warping the part.

- Tm: For semicrystalline polymers, the Tm is the temperature at which they transition from a solid to a molten state. Sterilization methods involving elevated temperatures can cause melting or degradation of these polymers if the sterilization temperature approaches or exceeds their Tm. As with Tg, it is not recommended to use a process if the result would be the melting of the polymer. For example, polycaprolactone (PCL) is nearly precluded from all processes, including EtO and HPGP, as the operating temperature of those processes is approximately 50 °C and the melting point is approximately 60 °C.

- Chemical Resistance: The resistance of a polymer to chemical degradation during the sterilization process is critical. Some sterilization methods involve exposure to harsh chemicals, such as HPGP or EtO. Polymers that are chemically incompatible with these agents can experience degradation, leading to changes in mechanical properties, color, or other characteristics. Resistance is dependent on the polymer being attacked and the attacking species. For example, peroxides can successfully attack alkenes to form epoxides but alkenes cannot be alkylated with EtO. Furthermore, the polymer structure may also hinder access of the attacking chemical species to candidate reaction sites. In this case, the chemical resistance will be high, despite having functional groups susceptible to attack.

- Radiation Resistance: Ionizing radiation (gamma rays, E-beams) is another common sterilization method. Polymers exposed to ionizing radiation may undergo chain scission, cross-linking, or other structural changes that can affect their mechanical properties. Radiation-resistant polymers are preferred for such sterilization processes. For example, the formation of radicals by irradiation of polyethylene would merely lead to cross-links instead of permanent degradation. Fluorinated polymers are especially susceptible to gamma radiation due to generation of fluorine radicals. On the other hand, polymers having a high number of phenyl rings are highly stable, as the pi bonding delocalizes any effect on any one of the atoms in the ring.

- Moisture Sensitivity: Some sterilization methods, like autoclaving or steam sterilization, expose materials to high levels of moisture or steam. Polymers may be hydrophilic or hydrophobic. As the words suggest, hydrophilic polymers have a "liking" for moisture and are prone to swelling; hydrophobic polymers, on the other hand, have a strong resistance to moisture. The extent of sensitivity depends on the chemical structure of the polymer, and effects include swelling, warping, or degradation. A polymer having moisture sensitivity is automatically precluded from the autoclave due to risk of dimensional changes during the process.

2.4 Properties of Common 3-D-Printable Polymers for Medical Equipment

Based on the literature available, as well as property tables for engineering polymers, the following answers for the key properties mentioned were able to be aggregated. Properties of common 3-D-printable polymers for medical equipment are presented in Table 2. A few things should be noted. First, determinations for specific polymers are noted where references exist. However, since the literature on sterilization of 3-D-printed polymers is in its infancy, this is supplemented by professional analysis. For instance, a heat-driven process such as that of an autoclave is a poor choice for a polymer if the steam temperature is within 5 °C of a polymer's Tg or Tm. Another example is if there are functional groups on a polymer that are prone to alkylation from an epoxide. Additionally, there is some uncertainty in the values of Tg and Tm given by vendors, as the values for the filaments vary based on the average MW of the polymer chains. As such, the values quoted should instead be taken as good prevailing estimates, with uncertainties up to ±5 °C. Lastly, based on preliminary questions to the Defense Systems Information Analysis Center, the polymers have been limited to thermoplastics printable by FDM. These were said to be of most interest by the inquiring entity.

2.5 Conclusions Regarding Applicability of Sterilization Techniques For 3-D-Printable Polymers

Using the values in Table 2, a set of conservative recommendations can be made for the applicability of the discussed sterilization methods previously presented. These are given in Table 3. Out of an abundance of caution, the process is not recommended unless the resistance to radiation or chemical attack is good or better; fair and poor resistance leads to a negative recommendation for a process involving the respective polymer.

Table 2. Properties of Common FDM Polymers

Polymer	Thermal		Radiation Resistance		Chemical Resistance		
	T_g (°C)	T_m (°C)	Gamma Radiation	E-Beam	EtO	H_2O_2	Moisture Sensitivity
Biopolymers							
PCL	–60	60	Good	Good	Good [11]	Good [11]	No
PLA	60	170	Poor [4]	Poor [1, 4]	Good [1, 2]	Good [1, 2, 9]	No
PHB	120	170	Poor [12]	Poor [12]	Good	Good	No
PLLA	58	180	Poor [1]	Poor [1]	Good [1]	Good [1]	Yes
PLGA	40	240	Good [13]	Good [13]	Good [13]	Good [13]	Yes
Elastomers							
TPE	–60	150	Good	Good	Good	Good	No
TPU	–50	185	Fair [14, 15]	Fair	Good	Good	No
Silicone	–30	180	Poor [16]	Poor [16]	Good	Good	No
Polyamides							
Nylon 6	50	240	Fair [4, 16]	Poor [4, 16]	Good	Good	Yes
Nylon 11	43	190	Fair [4, 16]	Fair [4, 16]	Good	Good	Yes
Fluoropolymers							
PTFE	115	327	Poor [16]	Poor [16]	Good	Good	No
Styrenics							
ABS	105	200	Fair [4]	Fair [4]	Good	Good	No
ASA	100	220	Fair [4]	Fair [4]	Good	Good	No
Other Engineering Thermoplastics							
PEEK	143	335	Good	Good	Good	Good	No
PEI	217	300	Good	Good	Good	Good	No
PC	140	220	Good [4]	Good [4]	Good	Good	No
PETG	76	260	Good [16]	Good [16]	Good	Good [9]	No

Note: PHB = polyhydroxybutyrate, PLLA = poly(l-lactic acid), PLGA = poly(lactic-co-glycolic acid), TPE = thermoplastic elastomer, TPU = thermoplastic polyurethane, PTFE = polytetrafluoroethylene, ABS = acrylonitrile butadiene styrene, ASA = acrylonitrile styrene acrylate, PEEK = polyether ether ketone, PEI = polyethylenimine, PC = polycarbonate, and PETG = polyethylene terephthalate glycol.

Table 3. Recommendations for Sterilization of Selected FDM-Printable Polymers

Polymer	Autoclave	Dry Heat	Gamma Radiation	E-Beam	EtO	HPGP
Biopolymers						
PCL	No	No	Yes	Yes	No	No
PLA	No	No	No	No	Yes	Yes
PHB	No	No	Yes	No	Yes	Yes
PLLA	No	No	No	Yes	Yes	Yes
PLGA	No	No	No	No	Yes	Yes
Elastomers						
TPE	Yes	No	Yes	Yes	Yes	Yes
TPU	No	No	No	No	Yes	Yes
Silicone	Yes	Yes	No	No	Yes	Yes
Polyamides						
Nylon 6	No	No	No	No	Yes	Yes
Nylon 11	No	No	No	No	Yes	Yes
Fluoropolymers						
PTFE	No	No	No	No	Yes	Yes
Styrenics						
ABS	No	No	No	No	Yes	Yes
ASA	No	No	No	No	Yes	Yes
Other Engineering Thermoplastics						
PEEK	Yes	No	Yes	Yes	Yes	Yes
PEI	Yes	No	Yes	Yes	Yes	Yes
PC	No	No	Yes	Yes	Yes	Yes
PETG	No	No	Yes	Yes	Yes	Yes

References

[1] Davila, S. P., L. G. Rodriguez, S. Chiussi, J. Serra, and P. Gonzalez. "How to Sterilize Polylactic Acid Based Medical Devices." *Polymers,* vol. 13, no. 2115, 2021.

[2] Wiseman, J., T. Rawther, M. Langbart, M. Kernohan, and Q. Ngo. "Sterilization of Bedside 3D-Printed Devices for Use in the Operating Room." *Annals of 3D Printed Medicine* , vol. 5, no. 100045, 2022.

[3] Fuentes, J. M., M. P. Arrieta, T. Boronat, and S. Ferrandiz. "Effects of Steam Heat and Dry Heat Sterilization Processes on 3D Printed Commercial Polymers Printed by Fused Deposition Modeling." *Polymers,* vol. 14, no. 855, 2022.

[4] Wady, P., A. Wasilewski, L. Brock, R. Edge, A. Baidak, C. McBride, L. Leay, A. Griffiths, and C. Valles. "Effect of Ionising Radiation on the Mechanical and Structural Properties of 3D Printed Plastics." *Additive Manufacturing,* vol. 31, no. 100907, 2020.

[5] Kirschweng, B., D. Tatraaljai, E. Foldes, and B. Pukanszky. "Natural Antioxidants as Stabilizers for Polymers." *Polymer Degradation and Stability,* vol. 145, pp. 25–40, 2017.

[6] Huang, M., M. K. Hasan, S. D. Pillai, M. Pharr, and D. Staack. "Electron Beam Technology for Re-Processing of Personal Protective Equipment." *Radiation Physics and Chemistry*, vol. 202, no. 110557, 2023.

[7] Chen, Y., M. Neff, B. McEvoy, Z. Cao, R. Pezzoli, A. Murphy, N. Gately, M. Hopkins, N. J. Rowan, and D. M. Devine. "3D Printed Polymers Are Less Stable Than Injection Moulded Counterparts When Exposed to Terminal Sterilization Processes Using Novel Vaporized Hydrogen Peroxide and Electron Beam Processes." *Polymer*, vol. 183, no. 121870, 2019.

[8] Kyi, M. S., J. Holton, and G. L. Ridgeway. "Assessment of the Efficacy of a Low Temperature Hydrogen Peroxide Gas Plasma Sterilization System." *Journal of Hospital Infection,* vol. 31, pp. 275–284, 1995.

[9] Oth, O., C. Dauchot, M. Orellana, and R. Glineur. "How to Sterilize 3D Printed Objects for Surgical Use: An Evaluation of the Volumetric Deformation of 3D-Printed Genioplasty Guide in PLA and PETG After Sterilization of Low-Temperature Hydrogen Peroxide Gas Plasma." *The Open Dentistry Journal,* vol. 13, pp. 410–417, 2019.

[10] Shintani, H. "Ethylene Oxide Gas Sterilization of Medical Devices." *Biocontrol Science,* vol. 22, pp. 1–16, 2017.

[11] Oliveira, L. M., E. S. Araujo, and S. M. L. Guedes. "Gamma Irradiation Effects on Poly(hydroxybutyrate)." *Polymer Degradation and Stability,* vol. 91, pp. 2157–2162, 2006.

[12] Sosnowski, E. P., and J. Morrison. "Sterilization of Medical 3D Printed Plastics: Is H_2O_2 Vapour Suitable" *Proceedings of the 2017 CMBEC40 Conference,* pp. 23–26, Winnipeg, Manitoba, May 2017.

[13] Turker, N. S., A. Y. Ozer, B. Kutlu, R. Nohutcu, A. Sungur, H. Bilgili, M. Ekizoglu, and M. Ozalp. "The Effect of Gamma Radiation Sterilization on Dental Biomaterials." *Tissue Engineering and Regenerative Medicine,* vol. 11, pp. 341–349, 2014.

[14] M'Bengue, M. S., T. Mesnard, F. Chai, M. Maton, V. Gaucher, N. Tabary, M. J. Garcia-Fernandez, J. Sobocinski, B. Martel, and N. Blanchemain. "Evaluation of a Medical Grade Thermoplastic Polyurethane for the Manufacture of an Implantable Medical Device: The Impact of FDM 3D-Printing and Gamma Sterilization." *Pharmaceutics,* vol. 15, no. 456, 2023.

[15] Shintani, H., H. Kikuchi, and A. Nakamura. "Effects of Gamma-Ray Irradiation on the Change of Characteristics of Polyurethane." *Polymer Degradation and Stability,* vol. 32, pp. 17–30, 1991.

[16] Nordion, Inc. "Gamma Compatible Materials: Reference Guide." *Nordion: A Sortera Health Company,* https://www.nordion.com/wp-content/uploads/2014/10/GT_Gamma_Compatible_Materials.pdf, August 2021.