Material Considerations

Radiation Processing

The Global Leader In Contract Sterilization Services

Sterigenics

RADIATION'S EFFECTS

Radiation interacts with polymers in two ways: chain scission, which results in reduced tensile strength and elongation; and crosslinking, which increases tensile strength but reduces elongation. Both reactions occur simultaneously, but one is usually dominant, depending upon the specific polymer and additives involved.

Chain scission classically affects stressed polymers (containing residual molding stress) to a greater extent than non-stressed polymers. The combined impact of solvent-induced stress, residual molding stress and applied load acts to intensify radiation damage.

Generally, polymers containing aromatic ring structures (e.g. polystyrene) are resistant to radiation effects. Aliphatic polymers exhibit degrees of resistance depending upon their levels of unsaturation and substitution.

Some effects of radiation–such as reduced elongation due to chain scission, may detract from the device's performance. Others can be beneficial. For example, crosslinking of poly- ethylene and silicones increases tensile strength.

Manufacturers should be cognizant of the possible impact of radiation on mechanical properties such as tensile strength, elastic modulus, impact strength and elongation. Outcomes may influence performance and should be evaluated in advance by functional testing.

STABILIZERS AND ADDITIVES

Additives and stabilizers are commonly included in small amounts (less than 1%) in commercial polymer products to aid in processing, stabilize the material and impart particular properties to the product.

Tint-based, multi-function stabilizers, for example, are added to PVCs to counteract the color change that is typical when this material is irradiated– an important consideration in situations where color plays a strong role in customer reaction to the product. Other additives known as "antirads" function as antioxidants and help prevent radiation damage.

These additives perform either as reactants, which readily combine with radiation-generated free radicals within the polymer, or as primary energy absorbers, preventing the interaction of the radiation energy with the polymer itself.

MATERIAL EVALUATION

When weighing the radiation stability of a polymer and the ultimate success of a component or medical device, the following factors should be taken into consideration:

- ❑ Stabilizers and antioxidants added to a polymer can reduce the effects of irradiation on the product's mechanical properties and/or physical appearance
- ❑ Thin part sections, thin films and fibers present in a component or product can allow for excessive oxygen exposure during the irradiation process, thus causing degradation of the polymer material
- ❑ Residual mold stress present after molding and assembly of a component or product can promote molecular scissioning during irradiation
- ❑ Highly oriented moldings, which are strong in the axis of orientation but are already very weak in the cross-flow axis, will become weaker after irradiation
- ❑ High molecular weight polymers having low melt flow will survive radiation better by providing longer molecules and stronger parts before and after irradiation.

MATERIAL COMPATIBILITY AND VALIDATION

Each polymer reacts differently to ionizing radiation. Thus, it is important to verify that the maximum administered dose will not have a detrimental effect on the product's function or the patient's safety over the product's intended shelf life.

Experimental samples of the product should be irradiated to at least the highest dose to be encountered during routine processing. For example, a product which is to receive a sterilizing dosage of 25 to 40 kiloGray (kGy) should be tested by dosing samples to at least 40 kGy. A conservative approach is to irradiate samples at doses up to twice the anticipated maximum dose.

Since various product applications call for certain performance properties or functional characteristics, it is important to test each component or product in an appropriate manner, using both new and aged material.

Table 2 (over) reviews typical tests of physical properties. Other tests, which more closely

MATERIAL COMPATIBILITY AND VALIDATION *(CONTINUED)*

approximate the actual mechanical application, may also be employed by the engineering or research staff.

Results of the evaluation should be retained in the product's device history file, serving as physical confirmation that all product claims and specifics have been met. If product testing indicates a potentially adverse effect from high levels of radiation, a maximum permissible dose should be established by the manufacturer and emphasized in the specific processing instructions to the contract sterilizer.

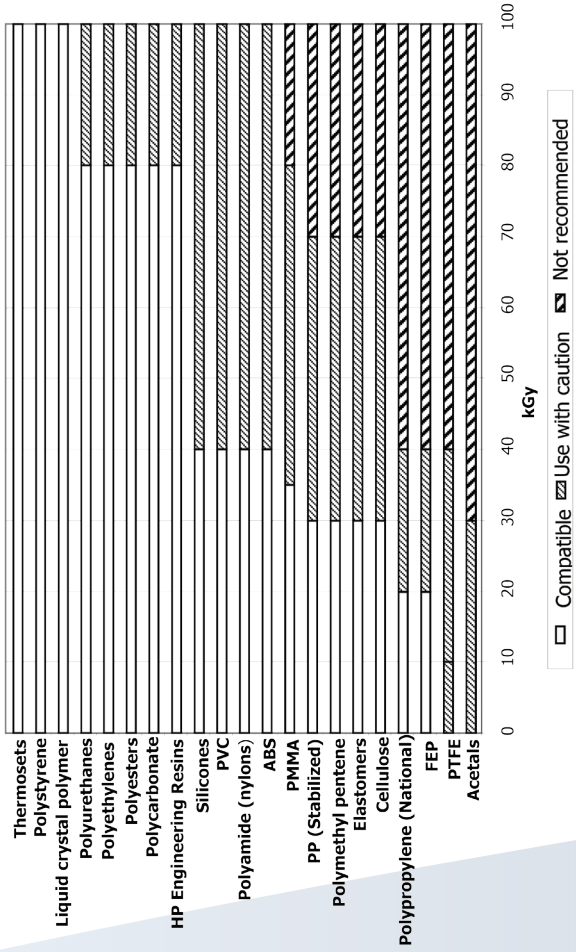
TABLE 2.
PHYSICAL AND FUNCTIONAL TEST METHODS FOR PLASTICS MATERIAL EVALUATION

Test Method	Test References
Test For Embrittleent	
1. Tensile properties	
a) Tensile strength	ISO 527 series
b) Ultimate elongation	ISO 527 series
c) Modulus of elasticity	ISO 527 series
d) Work	ISO 527 series
2. Flexural properties	
a) Flange bending test	Stability of Irradiated Polypropylene 1. Mechanical Properties, Williams, Dunn, Sugg, Stannet, Advances in Chemistry Series, No. 169, Stabilization and Degradation of Polymers, Eds. Allara, Hawkins, pp. 142-150, 1978.
b) Flexbar test	ISO 178
3. Impact resistance	ASTM D-1822
4. Hardness	
a) Shore	ISO 868
b) Rockwell	ASTM D-785
5. Compressive strength	ISO 604
6. Burst strength	ASTM F-2054
7.Tear strength	ASTM D-1004 and ISO 6383-1
Test For Discoloration	
1. Yellowness index	ASTM E-313
2. Optical spectrometry	ASTM D-1746

NOTE Source: International Atomic Energy Agency. Guidelines for industrial radiation sterilization of disposable medical products. Co-60 gamma irradiation. TEC DOC-539. Vienna IAEA, 1990.

FIGURE A.1
RELATIVE RADIATION STABILITY OF MEDICAL POLYMER "FAMILIES"

Figure A.1 graphically displays the dose ranges at which a number of common thermoplastics and thermosets show significant change in properties (i.e., a 25% loss in elongation). Loss of elongation is a commonly used measure of the effect of irradiation because it equates to a brittleness failure. Figure A.1 provides a visual means of making an initial estimate of a polymer's ability to withstand a particular radiation sterilization process.



NOTE—HP = high performance; PVC = polyvinylchloride; ABS = acrylonitrile butadiene styrene; PMMA = polymethylmethacrylate; PP = polypropylene; FEP = Fluorinated ethylene propylene; PTFE = polytetrafluoroethylene.

TABLE A.1
GENERAL GUIDE TO RADIATION STABILITY OF MATERIALS

Table A.1 shows typical radiation resistances of medical polymers in stress-free parts measured at the point where 25% of the polymer's elongation is lost because of radiation. This circumstance might well be the "best case." If the part being considered has a significant degree of residual stress as a result of manufacture, the dose at which the 25% loss of elongation occurs can be considerably lower.

	(•) = poor (••) = fair (•••) = good (••••) = excellent		(NL) = not likely (L) = likely	
Material	Single use (<50 kGy)	Comments	Resterilization (< 100 kGy)	Comments
Thermoplastics				
Acrylonitrile butadiene styrene (ABS)	•••	High-impact grades are not as radiation resistant as standard impact grades because of the higher butadiene content.	L	
Fluoropolymers				
Polytetrafluoroethylene (PTFE)	•	When irradiated, PTFE and PFA are significantly damaged. The other fluoropolymers show significantly greater stability. Some (for example, PVDF) are excellent.	NL	
Perfluoro alkoxy (PFA)	•		NL	
Perchlorotrifluoroethylene (PCTFE)	••• to ••••		L	
Polyvinyl fluoride (PVF)	•••		L	
Polyvinylidene fluoride(PVDF)	••• to ••••		L	
Ethylenetetrafluoroethylene (ETFE)	••• to ••••		L	
Fluorinated ethylene propylene (FEP)	••		NL	
Polyacetals (e.g., polyoxymethylene)	•	Irradiation causes significant chain scission (i.e., embrittlement). Color changes have been noted (yellow to green).	NL	
Polyacrylates (e.g., polymethylmethacrylate)	•• to •••		NL	
Polyamides (e.g., nylon)	•• to •••	Nylon 10, 11, 12, and 6-6 are more stable than 6. Nylon film and fiber are less resistant.	L	Very dependent on design and use requirements.
Polycarbonate (PC)	••• to ••••	Yellows—mechanical properties are not greatly affected; colorcorrected radiation formulations are available.	L	
Polyesters, saturated	•• to •••	Polybutylene terephthalate is not as radiation stable as polyethylene terephthalate resins.	L	
Polyethylene (PE), various densities	••• to ••••	High-density polyethylene is not as stable as mediumdensity polyethylene and low-density polyethylene, linear lowdensity polyethylene.	L	
Polyimides (e.g., polyetherimide)	••••		L	
Polyketones (e.g., polyetheretherketone)	••••		L	

TABLE A.1 *(CONTINUED)* GENERAL GUIDE TO RADIATION STABILITY OF MATERIALS

	(•) = poor (••) = fair (•••) = good (••••) = excellent		(NL) = not likely (L) = likely	
Material	Single use (<50 kGy)	Comments	Resterilization (< 100 kGy)	Comments
Polypropylene (PP)				
Natural	• to ••	Physical properties are greatly reduced when irradiated (for example, chain scissioning). Radiation-stabilized grades, using high molecular weight, copolymerized and alloyed with polyethylene, with additional stabilizers should be used in most radiation applications. Use of electron beam at high dose rate may reduce oxidative degradation.	NL	
Stabilized	•• to •••		NL	
Polystyrene (PS)	••••	Will begin to yellow at >50 kGy.	L	
Polysulfones	••••	Natural material is yellowish.	L	
Polyurethane (PU)	•• to ••••	Aromatic discolors; polyesters are more stable than esters. Retains physical properties.	L	
Polyvinylacetates (PVA)	•••		NL	
Polyvinylchloride (PVC)	•••	Cross-linking dominates and significant yellow color development occurs at doses > 30 kGy). Addition of antioxidants and heat stabilizers to formulations will retard color development. High-molecular-weight organotin stabilizers improve radiation stability: color-corrected radiation formulations are available.	NL	Significant discoloration likely.
PVC, plasticized	•••	Cross-linking (stiffening) dominates.	L	Discoloration likely.
Styrene acrylonitrile (SAN)	••• to ••••		L	
Thermosets				
Epoxy	••••		L	
Phenolics	••••	Includes the addition of mineral fillers.	L	
Polyester, unsaturated	••••	Includes the addition of mineral or glass fibers.	L	
Polyimides	••••		L	
Polyurethanes				
Aliphatic	••••		L	
Aromatic	••• to ••••	Darkening can occur. Possible breakdown products could be derived.	L	
Adhesives				
Acrylic	•• to •••		L	Embrittlement possible.
Epoxy	••••		L	
Fluoroepoxy	••••		L	
Silicone	•• to •••		L	
Elastomers				
Butyl	•	Friable, sheds particulate, chain scission.	NL	
Ethylene propylene diene monomer (EPDM)	••• to ••••		L	
Natural rubber	••• to ••••		L	

TABLE A.1 *(CONTINUED)* GENERAL GUIDE TO RADIATION STABILITY OF MATERIALS

	(•) = poor (••) = fair (•••) = good (••••) = excellent		(NL) = not likely (L) = likely	
Material	Single use (<50 kGy)	Comments	Resterilization (< 100 kGy)	Comments
Nitrile	••• to ••••	Discolors.	L	
Polyacrylic	•• to •••		NL	
Polychloroprene	•••	Discolors; the addition of aromatic plasticizers renders the material more stable to irradiation.	L	
Silicone	•• to •••	Cross-linking dominates. Platinum-cured silicones are superior to peroxidecured silicones because their preirradiation cross-link density is greater. Full cure during manufacture can reduce postirradiation cross-link effects. Phenyl-methyl silicones are more stable than are methyl silicones.	L	Stiffening due to cross-linking likely.
Styrenic block copolymers (e.g., styrene-butadienestyrene, styrene-ethylenebutylene-styrene)	•• to •••	Butadiene scissions.	L	
Urethane	••• to ••••		L	
Metals				
Aluminum	••••		L	
Brass	••••		L	
Copper	••••		L	
Gold	••••		L	
Magnesium	••••		L	
Nickel	••••		L	
Silver	••••		L	
Stainless steel	••••		L	
Titanium	••••		L	
Ceramics/glasses				
Aluminum oxides	••••		L	
Silica	••••		L	
Zirconium oxides	••••		L	
Other materials				
Bioabsorbables				
Polyglycolides	• to ••••		NL	
Polylactides	• to ••••		NL	
Cellulosics				
Cellulose ester	••	Esters degrade less than other cellulosics.	NL	
Cellulose acetate propionate	•• to ••••		L	
Cellulose acetate butyrate	•• to ••••		L	
Cellulose, paper, cardboard	•• to ••••		L	
Liquid crystal polymer (LCP)	• to ••••	Commercial LCPs; natural LCPs are not stable.	L	

REFERENCES

Primary sources: International Atomic Energy Agency; NASA/Jet Propulsion Laboratory; and polymer manufacturers' literature.

AAMI TIR 17, Compatibility of materials subject to sterilization (for Table A.1 and Figure A.1).

1 AAMI TIR29, Guide for process characterization and control in radiation sterilization of medical devices

2 ANSI/AAMI/ISO 11137-1, Sterilization of health care products—Radiation—Part 1: Requirements for development, validation, and routine control of a sterilization process for medical devices.

3 Genova, Hollis, Crowell and Schady, "A Procedure for Validating the Sterility of an Individual Gamma Radiation Sterilized Production Batch," Journal of Parenteral Science and Technology, Volume 41, No.1, pp. 33-36, Jan 1987.

4 Gaughran and Morrissey, "Sterilization of Medical Products," Volume 2, ISBN-0-919868-14-2, pp. 35-39, 1980.

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