Material Considerations

Irradiation Processing

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 predominant, 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 polyethylene 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.*

Table 1 (inside) provides an overview of the polymers commonly used for medical devices, along with their typical characteristics following irradiation. It is important to remember that not all brand products share the same characteristics.

For some materials and products that are sensitive to oxidative effects, such as low molecular weight polypropylene, polytetrafluorethylene and polyacetals, radiation tolerance levels for electron beam (e-beam) exposure may be slightly higher than for gamma exposure. This is due to the higher dose rates and shorter exposure times of e-beam irradiation which have been shown to reduce the degradative effects of oxygen.

Most materials, however, have good oxidative resistance and retain physical properties equally well regardless of the radiation source, as the references by Ishigaki and Hermanson have demonstrated.

A comparison of radiation's effect of e-beam versus gamma is not easily accomplished unless product-specific characteristics–including part thickness, volume of product, molecular weight, scission to crosslink ratio, oxygen sensitivity, use of antioxidants and aging effects–are known and entered into the evaluation.

Table 1.
Radiation Tolerance Levels of Polymers Used for Medical Applications

Material	Tolerance Level (kGy)	Comments
Elastomers[1]		
Butyl	50	Sheds particulate after irradiation.
Ethylene-Propylene Diene Monomer (EPDM)	100-200	Crosslinks, yellows slightly.
Fluoro Elastomer	50	Avoid multiple sterilization.
Natural Rubber (Isoprene)	100	Very stable with sulfur or resin cure systems. Avoid stressing product by not bending, folding or wrinkling in packaging.
Nitrile	200	Avoid multiple sterilization.
Polyacrylic	50-200	Avoid multiple sterilization.
Polychloroprene (Neoprene)	200	Avoid multiple sterilization.
Silicones (Peroxide & Platinum Catalyst System)	50-100	Crosslink density increases more in peroxide systems than in platinum systems. Silicones retain a slight memory of coiling shape in packaging.
Styrene-Butadiene	100	Avoid multiple sterilization.
Urethanes	100-200	Wide variations in urethane chemistry applied to medical devices. Requires testing of part process and geometry to validate.
Thermosets		All thermosets as a class are highly resistant.
Allyl Digylcol Carbonate (Polyester)	5,000-10,000	Retains clarity.
Epoxies	1,000	Many good formulations available. Test the formulation selected for use. Frequently substituted for toxic solvents in assembly. Success depends on joint design and application process.
Phenolics	50,000	
Polyesters	10-1,000	Use of glass and other fillers improves physicals.
Polyurethanes	100-1,000	Wide formulation variations for urethanes. Dose tolerance depends on monomers used in formulation. Minimum 100-1,000 kGy are tolerated for thermosets.
Thermoplastics		
Acrylonitrile/Butadiene/Styrene (ABS)	1,000	Protected by Benzene ring structure. Butadiene impact modifier degrades above 100 kGy. Avoid high dose on high impact grades.
Aromatic Polyesters (PET, PETG)	1,000	Very stable, retains excellent clarity. Drying is essential. Good in luer connectors.
Cellulosics		
Esters and Ethers	50	Thin films and fibers embrittle above 50 kGy.
Paper, Card, Corrugated Fibers	100-200	Papers discolor and embrittle, but are acceptable for single use.
Cellulose, Acetate, Propionate, and Butyrate	50	Plasticized versions slowly embrittle above 50 kGy.
Fluoropolymers		
Tetrafluoroethylene (PTFE)	5	Liberates fluorine gas, disintegrates to powder. Avoid use.
Polychlorotrifluoroethylene (PCTFE)	200	
Polyvinyl Fluoride	1,000	
Polyvinylidene Fluoride (PVDF)	1,000	
Ethylene-Tetrafluoroethylene (ETFE)	1,000	
Fluorinated Ethylene Propylene (FEP)	50	

[1] *Elastomers:*
1. Radiation tolerance is affected by the base polymer and the curing system used. Sulfur and resin cures are more durable.
2. All elastomers are subject to crosslinking in the shape packaged during sterilization and can be expected to take on a memory of that shape. Avoid folds, coils, curves.

Where a range of dose is listed the lower number is the threshold of damage where the first change in physical properties can be detected (all radiation is cumulative). Where conflicting data is presented in the literature, the lower, more conservative dose has been selected.

Table 1. (continued) Radiation Tolerance Levels of Polymers Used for Medical Applications

Material	Tolerance Level (kGy)	Comments
Thermoplastics (continued)		
High Performance Engineering Resins	1,000-10,000	Substitutes for metal, these resins have high strength and good elongation that tolerate radiation well. Resins include nylon, polycarbonate, ABS, polysulfone, polyester, polyether ketone, liquid crystal polymer, polyetherimide, polyimide, and others.
Polyacetals (Delrin, Celcon)	15	Avoid use due to embrittlement.
Polyacrylics		
Polymethylmethacrylate	100	Yellows at 20-40 kGy; clarity recovers partially on aging.
Polyacrylonitrile	100	Yellows at 20-40 kGy.
Polyacrylate	100	Yellows at 20-40 kGy.
Polycyanoacrylate	200	Many good formulations. Adhesives function at 100 kGy with less than 30% degradation.
Polyamides (Nylons)		
Aliphatic & Amorphous Grades	50	Discolors, no resterilization. Avoid thin films and fibers. Nylon 11 and 12 perform better. Dry before molding.
Aromatic Polyamide-imide	10,000	High heat/strength grade. Stabilized by Benzene ring structure.
Polycarbonate	1,000	Discolors, clarity recovers after aging. Dry before molding.
Polyethylene (LDPE, LLDPE, HDPE, UHMWPE)	1,000	Crosslinks to gain strength, loses some elongation. All polyethylenes tolerate radiation well. Low density is most resistant. HDPE packaging film including spin-bonded porous packaging may lose 40-50% elongation at doses of 50 kGy. Implants of UHMWPE have reports of early wear at 50 kGy.
Polyamides	10,000	
Polymethylpentene	20	Subject to oxidation degradation. Avoid use.
Polyphenylene Sulfide	1,000	
Polypropylene, Radiation Stabilized		Higher tolerance levels reported using e-beam.
Homopolymer	20-50	Used with marginal success in syringes. Subject to orientation and oxidation embrittlement. Degrades over time. Validate with real time aging. Avoid use of non-stabilized Polypropylene.
Copolymers of Propylene-Ethylene	25-60	More stable than Homopolymer. Successful in syringe applications using suitable stabilizer package.
Polystyrene	10,000	All styrenes are stabilized by Benzene ring structure.
Polysulfone	10,000	Amber color before irradiation.
Polyurethane, Polyether and Polyester	100-200	Excellent physicals and chemical resistance to stress-cracking.
Rigid and flexible		Drying is essential to success. Good in luer connectors. All types show irreversible yellowing.
Polyvinylbutyral	100	Yellows.
Polyvinylchloride (PVC)	100	Yellows, can be tinted for color correction. Success depends on quality of material, formulation and processing. Tubing crosslinks becoming slightly stiffened.
Polyvinylidene Chloride (PVDC)	100	Yellows, releases HCL.
Styrene/Acrylonitrile (SAN)	1,000	Yellows at 40 kGy.

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 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/R 527:1966
b) Ultimate elongation	ISO/R 527:1966
c) Modulus of elasticity	ISO/R 527:1966
d) Work	ISO/R 527:1966
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 178:1975
3. Impact resistance	1985 ASTM Standards, Vol. 08.01-Plastics, D-1822-84
4. Hardness	
a) Shore	ISO 868:1985
b) Rockwell	1985 ASTM Standards, Vol. 08.01-Plastics, D-785-65
5. Compressive strength	ISO 604:1973
6. Burst strength	1985 ASTM Standards, Vol. 08.01-Plastics (Tubing), D-1180-57
7.Tear strength	1985 ASTM Standards, Vol. 08.01-Plastics, D-1004-66, and ISO 6383/1-1983
Test For Discoloration	
1. Yellowness index	1985 ASTM Standards, Vol. 08.02-Plastics, D-1925-70
2. Optical spectrometry	1985 ASTM Standards, Vol. 08.02-Plastics, D-1746-70

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.

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