Journal of Thermal Analysis and Calorimetry, Vol. 93 (2008) 2, 535–539

SELECTING POLYMERS FOR MEDICAL DEVICES BASED ON THERMAL ANALYTICAL METHODS

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This biomaterials overview for selecting polymers for medical devices focuses on polymer materials, properties and performance. An improved understanding of thermoplastics and thermoset properties is accomplished by thermal analysis for device applications. The medical applications and requirements as well as the oxidative and mechanical stability of currently used polymers in devices are discussed. The tools used to aid the ranking of the thermoplastics and thermosets are differential scanning calorimetry (DSC), thermogravimetry (TG), thermal mechanical analysis (TMA) and dynamic mechanical analysis (DMA) as well as a number of key ASTM polymer tests. This paper will spotlight the thermal and mechanical characterization of the bio-compatible polymers e.g., olefins, nylon, polyacetals, polyvinyl chloride and polyesters.

Keywords: *DMA, DSC, nylon, OIT, OOT, PET, polyacetal, polyamide, polycarbonate, polyester, polyether ether ketone, polyethylenes, polyglycolide, polyketal, polylactide, polymethyl methacrylate, polyurethane, polyvinyl chloride, prosthetic devices, PTFE, silicones polypropylene, TG, TMA*

Introduction

Implantable grade synthetic polymers are the focus of this review [1–4]. Synthetic polymers are relatively new to the biomaterial field for implants compared to metals [5]. Polymerization technology and processing have been refined and expanded over the past three decades [6–8]. These advances have placed various polymers in the hands of bio-material engineers working on prosthetics devices. Parts are now easily prepared by injection molding, blow molding and casting (melt processing). Polymer parts are normally transparent to X-rays, unless filled with a chemical that is opaque to X-rays e.g., barium sulfate.

The intrinsic properties of implantable synthetic polymers are that they are bio-stable to oxidative, hydrolytic and enzymatic degradation [9]. They are non-toxic or nontoxic-producing, hypo-allergenic, biocompatible (encourage growth of bone and tissue), are thermally stable to processing conditions during manufacture and have desirable combinations of thermal transitions (glass transition temperature, T_g, melt temperature, T_m, etc.). The synthetic polymers must have a variety of quality physical properties, such as, appropriate hardness, superior wear resistance and good impact strength. They must also have good melt flow properties (for manufacture purposes), high tensile strength, and appropriate flow resistance under stress. Use of specific polymers is based on their flexural strength and good dimensional stability as well as sufficient elastic modulus and finally superior structural integrity of the formed prosthetic parts.

The most useful thermoplastic and thermoset polymers for long-term implants are: Polyethylene (PE), Silicones, Polypropylene (PP), Polyamides ('nylons'), Polyvinyl chloride (PVC), Polyacetal, Polyketal, Acrylics as polymethyl methacrylate (PMMA), Polyether Ether Ketone (PEEK), Polyester (e.g. Dacron®) and Polyurethane (PU). The current uses for the following polymers as prosthetic devices in the human body described in Fig. 1: acrylics, PE, PVC, Silicones, Ultrahigh molecular mass polyethylene (UHMWPE), PU, PP, Polyester (e.g., Dacron®), P-aldehyde, Polyacetal, Nylons, Epoxy, Poly-glycolide and Poly-lactide.

Polymer backbone conformation is a regular helix for the linear UHMWPE. Its crystallinity reflects the ability of the polymer molecules to align with each other in a regular manner, and thus affects their physical properties, e.g. melt and crystallization temperatures and heats (J g^{-1}). The linear low density PE (LDPE) is 50–60% crystalline with a m.p. (melting point) of 100–125°C, linear medium density PE (MDPE) is 60–70% crystalline with a m.p. of 110–115°C, and linear high density PE, 75–80% crystalline with a m.p. of 125–140°C. UHMWPE comprises a linear high density PE conformation with an approximate molecular mass of 10^7.

DSC is an invaluable tool in ranking polymers, e.g. the PEs by their m.p. and heat of fusion and the

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1388–6150/$20.00

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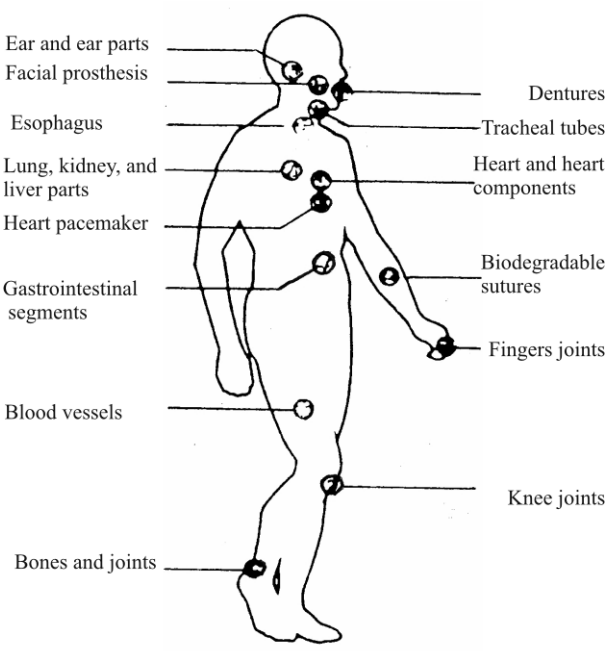

Body Part (Top to Bottom)	Polymer
Ear & Ear Parts	Acrylic, PE, PVC, Silicone
Facial Prosthesis	Acrylic, PE, PVC, Silicone
Dentures	Acrylic, UHMWPE, Epoxy
Esophagus & Tracheal Tubes	Acrylic, PVC, PU
Upper body	PE, PP, PVC
Lung, Kidney & liver parts	Polyester, PVC, P-Aldehyde
Heart Pacemaker	PE, P-Acetal
Heart & Heart Components	Polyester, PVC, Silicones
Gastro-intestinal Segments	Silcone, PVC, Nylons
Biodegradable sutures	Poly-glycolides
Finger Joints	Silicones, UHMWPE
Blood Vessels	Polyester, PVC
Knee joints	PE
Foot Bones and Joints	PE

Fig. 1 Biomaterial overview citing where polymers are being used as medical devices

structure is confirmed by X-ray diffraction (XRD) analysis [10]. The Society of Plastics Engineers Resin Kit® samples of a variety of polyethylene's have been characterized and reported [10]. DMA is a powerful adjunct to DSC in fixing and verifying PE properties in manufacturing or determining property-performance relationships for implants and predicting long term durability. Therefore, the PE selected for use in the body must be tough. Its general properties must be known as to deformation which depends on structure and molecular mass (MW). Deformation is the greatest for low MWPE followed by high MWPE and least deformation with the UHMWPE. Typically the PE is opaque but that depends on the degree of crystallinity determined by DSC. The melt viscosity of UHMWPE is appropriate and can, therefore, be formed by melt processing at 150–200°C. This unique polymer, UHMWPE, can be fabricated with a relatively low friction surface, necessary to minimize wear properties. It is also abrasion resistant but can be shred under pressure.

Prosthesis applications for PE or UHMWPE are bearing surfaces in hip, knee, and fingers and joints (UHMWPE) as well as small bone replacement (UHMWPE). Other uses are catheters, heart pacemakers (parts and coatings), and dental, surgical (bone replacements, supports).

Thermal degradation studies of substituted polyanilines was accomplished by TG and FTIR [11]. This work highlights the need to evaluate polymer degradation by structure (FTIR) and property (TG) tools. The mechanism of degradation of the polymers was based on the determined kinetic parameters.

Menczel and Jaffe focused on determining the rigid amorphous phase content and the glass transition of semicrystalline polymers [12]. For future polymer selection one has to determine also other thermal analytical paramters by DSC. Properties of importance are TG, mobile amorphous phase content, rigid amorphous phase content and crystallinity. Recent studies in our laboratory to determine the percent amorphous and crystalline phase of organic compounds by Dielectric Analysis should also be investigated for candidate polymers.

Experimental

Methods

A TAI 2920 DSC was used with the following method: heating rate 20°C min^{-1}, 10 mg sample size, aluminum pans and lids, nitrogen atmosphere, heat and cool cycle, temperature range from room temperature to 40°C above the melting temperature.

ASTM E1858 and ASTM E2009: A TAI 2920 DSC was used with the following method: heating rate 40°C min^{-1}, 5 mg sample size, aluminum open pan, isothermal oxygen atmosphere at 175°C for Pressure DSC and 200°C isothermal for DSC.

A TAI 2980 DMA was used in the following mode: heating rate 10°C min^{-1}, 10 mg sample tines from the SPE Resin Kit, nitrogen atmosphere, and temperature range from room temperature to 20°C above the melting temperature.

A TAI 2940 TMA was used with the following method: heating rate 10°C min^{-1}, 10 mg sample size, nitrogen atmosphere, temperature range from room temperature to the melting temperature.

A TA 2950 TGA was used with the following method: heating rate 20°C min^{-1}, 5–10 mg sample size, platinum pans, nitrogen and air atmosphere, temperature range from room temperature to 40°C above the decomposition temperature.

Results and discussion

Biomaterial's overview reveals the polymers in use for various body replacements or repair parts, see Fig. 1. Acrylics, polyethylene and silicones are most used currently in the body. Polymers currently used in joint prostheses are UHMWPE in knee and hip joints. Polymers as heart valve patches are Dacron® Polyesters especially for repairing mitral valves or heart valve 'skirts'.

Structure, property and performance relationships must be developed in order to select the appropriate polymer for a medical device in the body. Polymer characterization tools used to rank polymers include: fractography, microscopy, Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance spectroscopy (NMR), gas chromatography/mass spectrometry (GC/MS), X-ray methods and thermal analysis (DSC, TG, TMA, & DMA). DSC properties easily attained are the glass transition temperature (T_g), melt temperature, crystallization temperature, Oxygen Induction Time (OIT) and percent of cure of thermosets, Table 1 and Fig. 2. Thermoset curing can be viewed when comparing the first and second heating runs of a partial cured thermoset shows residual cure and the change in T_g with polymerization.

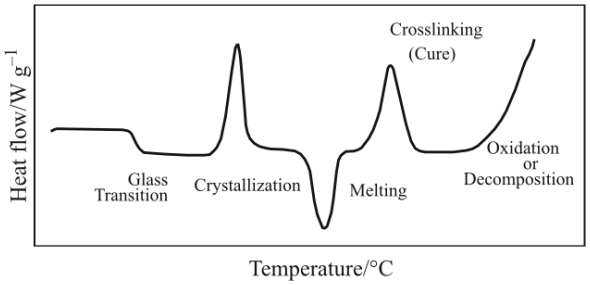

Fig. 2 Typical DSC curve with various transitions and physical changes

Selections of polymers for medical devices based on TMA and DSC is summarized in Fig. 3. The TMA coefficient of thermal expansion (CTE) is compared with the DSC T_m and T_g of nine polymer candidates. When one is looking for structural stability then a low CTE, a high T_g and/or T_m is in order. Polyether ether ketone PEEK, polytetrafluorethylene (PTFE) nylons and olefins appear to stand out.

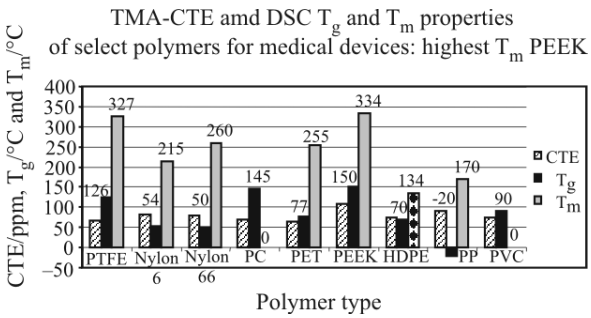

Fig. 3 Selection of polymers for medical devices based on TMA and DSC properties

A complete analysis of the T_g is reviewed in Fig. 4. The T_g at half the height of the change in heat capacity at the T_g, ΔC_p, are worthy properties to consider when T_g is an important criteria in polymer characterization. Likewise, the percent crystallinity plays a significant role in polymer manufacturing and ultimate properties, Fig. 5. The percent crystallinity of the poly-(ethylene terephthalate) PET before the DSC determination is 21%. This value plays an important role in polymer strength and ultimate properties.

Table 1 A review of physical properties measured in the following materials: TP thermoplastics, TS thermoset polymers, EL elastomers, CH chemicals & drugs, PE petroleum, GL glasses, ME metals & bio proteins and starches

	TP	TS	EL	CH	PE	GL	ME	Bio
Glass transition temperature (T_g)	✓	✓	✓	✓	✓	✓	✓	✓
Glass transition size (ΔC_p)	✓		✓	✓		✓	✓	✓
Melting temperature (T_m)	✓		✓	✓	✓	✓	✓	✓
Crystallization temperature (T_c)	✓		✓	✓	✓	✓	✓	
Crystallinity (J g^{-1} not %)	✓		✓	✓		✓	✓	✓
Heat capacity (J g^{-1} °C)	✓					✓		
Oxidative stability (temp. or time)	✓				✓			
Texturing (process) temperature/°C	✓							
Curing/degree of cure/%		✓	✓					
Polymorphic transitions				✓				
Denaturation/gelatinization								✓

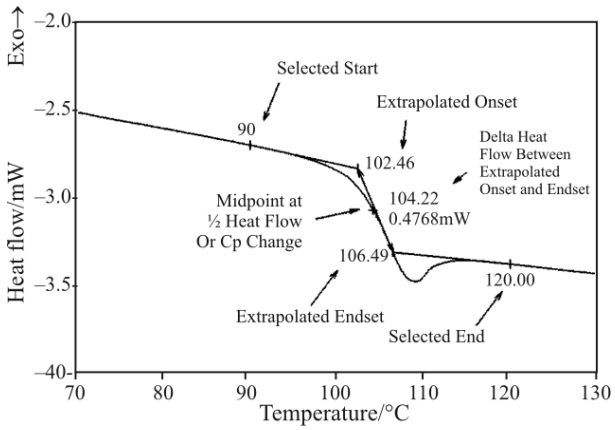

Fig. 4 Glass transition of a polymer by DSC

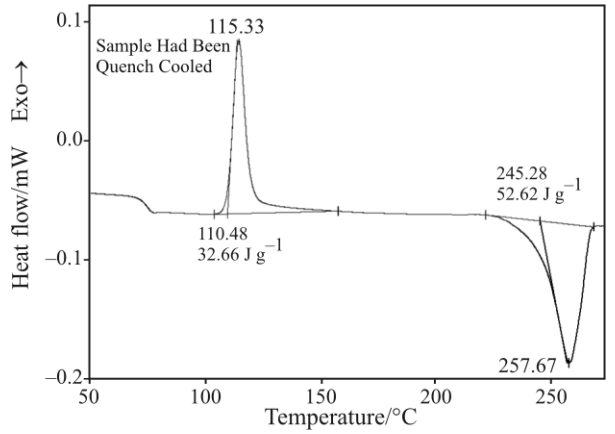

Fig. 5 DSC of PET: % crystallinity by heat of fusion and crystallization

The oxidative properties of polymers can be ascertained by either ASTM E1858 or ASTM E2009, the oxidation induction time OIT or the oxidation onset temperature OOT, respectively. A comparison of the OIT vs. the OOT for 11 polyolefins (PE and PP) yield a linear relationship with a r^2 of 0.94, Fig. 6. Therefore, either of these tests would benefit a candidate search of polyolefins relative to their oxidative stability. TG in air, another oxidation test, ranked six commercial polymers with Kapton® being the most stable and Nomex® being the least stable, Fig. 7.

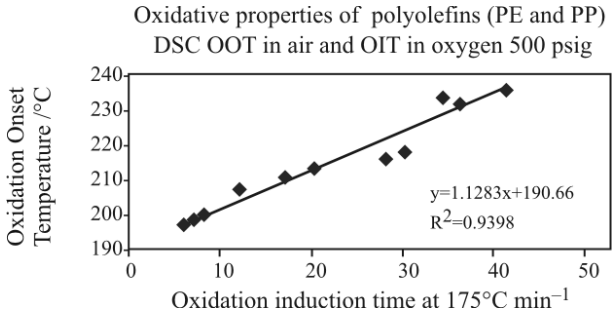

Fig. 6 Oxidative behavior of polyolefins by OIT ASTM E1858 and OOT ASTM E 2009

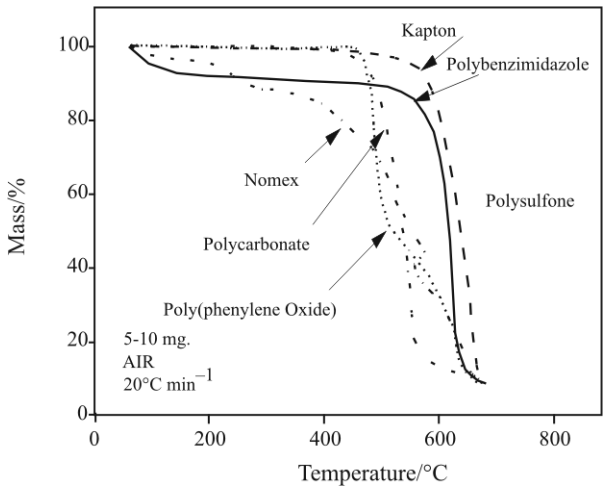

Fig. 7 Oxidative behavior of various polymers by TG in 21% oxygen (air)

Thermal stability measured by TG in nitrogen reports polyimide, PI, the most stable and PVC, polyvinyl chloride as the least stable, Fig. 8. Selection of medical device polymers based on TG in nitrogen is given in Fig. 9. PEEK, PTFE, High Density PE, HDPE, Nylon 6, PET and PP all had decomposition temperatures above 400°C. These polymers in an inert atmosphere would be most stable.

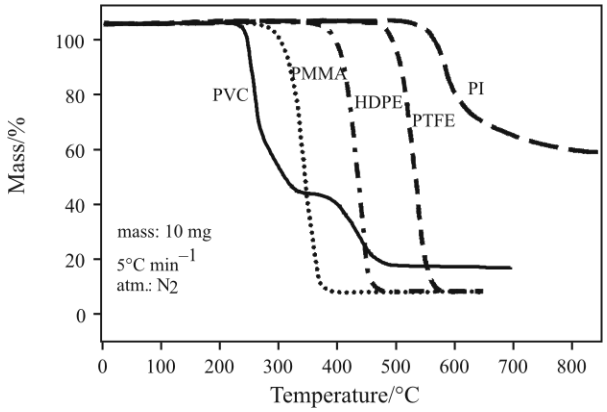

Fig. 8 Thermal behavior of various polymers by TG in 100% nitrogen

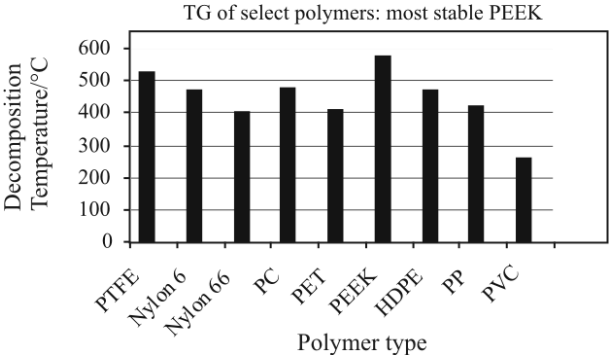

Fig. 9 TG selection of medical device polymers based on relative decomposition

The DMA flexural modulus of selected polymer candidates for medical devices is reported in Fig. 10. PEEK had the highest modulus at 3900 MPa, a good candidate for medical device. Polymer selection based on impact properties is summarized in Fig. 11. HDPE and poly-carbonate, in this set of polymers, succinctly were the most impact stable.

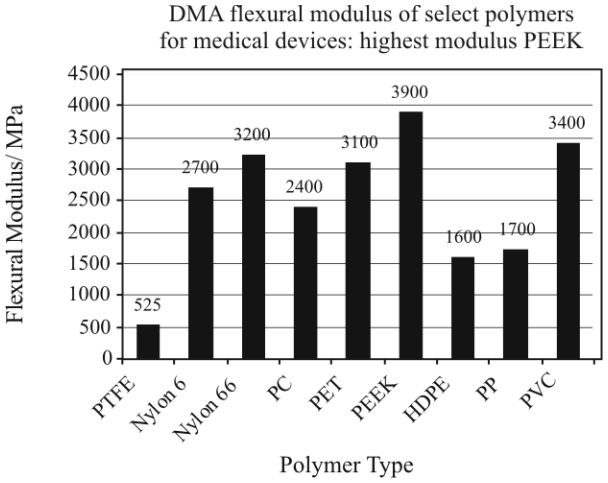

Fig. 10 DMA flexural modulus of polymers for medical devices

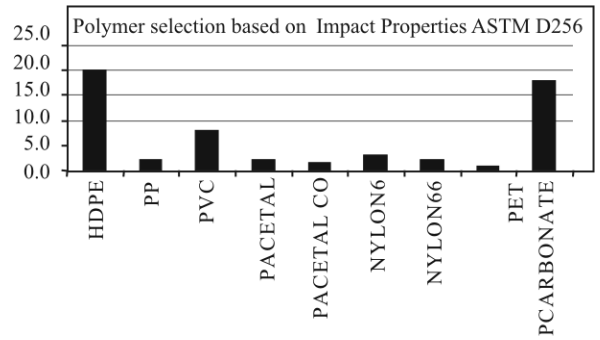

Fig. 11 ASTM Impact Test D256 ranked a variety of candidate polymers: high density polyethylene and polycarbonate had the best impact properties

Conclusions

To achieve improved design and performance one must gain a better understanding of the polymer structure and its related properties. Application of a variety of complimentary analytical techniques, in these studies thermal analytical methods, is essential to effectively evaluate key performance criteria in selecting bio-compatible polymers for medical devices.

References

1 F.W. Billmeyer, Jr., Textbook of Polymer Science, 3rd Edition, J. Wiley, New York 1984.
2 H. Morawetz, Macromolecules in Solution, 2nd Ed., Wiley-Interscience, NY 1975.
3 L.H. Sperling, Introduction to Polymer Science, Wiley, NY 1992.
4 B.D. Ratner, A. Hoffman, F. Schoen and J. Lemons, Biomaterials Science: An Introduction to Materials in Medicine, Academic Press, San Diego 1996.
5 E. Chiellinini, Ed., Biomedical Polymers and Polymer Therapeutics, Academic/Plenum Publishers, NY, 2001.
6 M. Chanda and S. Roy, Eds., Plastics Technology Handbook, 47, 3rd Ed., (2006) 171–214.
7 R. Chartoff, 'Thermoplastic Polymers', in Thermal Characterization of Polymeric Materials, E. Turi, Ed., 2nd Ed, 1, (1997) 518–523.
8 A. Hale and H. Bair, Polymer Blends and Block Copolymers, in Thermal Characterization of Polymeric Materials, E. Turi, Ed., 2nd Ed, 1, (1997) 745–870.
9 V. Reitz, Engineering Success with Implantable Polymers, Medical Design Magazine, 2006.42
10 A. Riga, D. Young, G. Mlachak and P. Kovach, J Thermal Anal., 49 (1997) 425.
11 D. K. Dash, S. K. Sahu and P. L. Nayak, J. Therm. Anal. Cal., 86 (2006) 517.
12 J. D. Menczel and M. Jaffe, J. Therm. Anal. Cal., 89 (2007) 357.

Received: March 3, 2008
Accepted: May 21, 2008

DOI: 10.1007/s10973-008-9086-z