

10 Polymers used as biomaterials

10.1 Please summarize the most important properties of PEEK implants necessary for the selected medical application. Describe the use of the selected implant including advantages and potential problems.

Properties in general:

- excellent mechanical properties: Young's modulus 3.6 GPa, tensile strength 80 to 170 MPa
- glass transition temperature 143°C (well above body temperature), melting temperature 334°C
- excellent chemical resistance against solvents, bases and acids (except highly concentrated acids)
- radiolucent (facilitates radiographical analysis in contrast to metal implants)
- bioinert (no cell adhesion, no osseointegration)
- easily shapable (milling, injection molding)

Table 1: Advantages and disadvantages of implants.

Implant	Advantage	Problem
Pacemaker housings	Bioinert (exchange); Insulating properties; Mechanical properties	Slipping (no cell adhesion)
hip stem	Mechanical properties; tunable with composite materials to match bone (isoleastic): less stress shielding	Bioinert (coating such as Ti or HA needed for osseointegration); Production costs of coated composite PEEK implants
Spine implants	MR compatible; radiolucent (to investigate bone fusion); Isoelastic mechanical properties	

10.2 Based on the binding mechanisms in polymers on the molecular scale, it should be explained, why PEEK is mechanically much more stable than PE.

PEEK is mechanically much more stable than PE because of 3 carbon rings within its monomer unit, as the figure below shows.

The interaction of the rings in different layers result in relatively strong intermolecular bonds, which explain the stability.

In PEEK, the aryl rings are interconnected via ketone and ether groups located at opposite ends of the ring (referred to in chemistry as the "para" position). The resonance stabilized chemical structure of PEEK results in delocalization of higher orbital electrons along the entire macromolecule, making it extremely unreactive and inherently resistant to chemical, thermal, and post-irradiation degradation. In contrast, polyethylene only consists of carbon-carbon bonds and therefore only weak intermolecular van der Waals interactions occur.

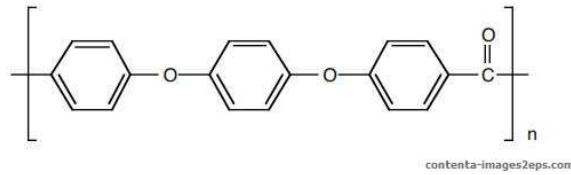


Figure 1: PEEK Structure

10.3 One should define the term glass transition temperature. How the glass transition temperature of a polymer is measured? What are the differences in the mechanical properties of a selected polymer below and above the glass transition temperature?

Amorphous or partially crystalline solids can undergo a change of their bonding state, which is not a phase transition in the conventional way. The properties of the material change from brittle (glassy) to soft (rubbery) during heating or rubbery to brittle during cooling. The transition is related to local bond breaking forming stable clusters in soft environment. Finally, above the glass transition temperature the material can be plastically deformed without fracture. For PE the glass transition temperature is well below 0 °. Often this property is related to heat capacity changes, as shown in the thermograms.

Identification and quantification of thermal phase transitions of a well-defined amount of pure polymer by Differential Scanning Calorimetry (DSC):

1-Glass transition temperature T_g

2-Crystallization temperature T_c

Melting temperature T_m

Also, temperature of a polymer is measured by "Differential scanning calorimetry" or DSC technique which belongs to the thermal analysis methods, in which sample and related reference are individually heated at the selected rate by separately controlled heaters. The thermal processes (enthalpic: heat-generating or heat-absorbing) are recorded as the difference in heat energy supplied to sample and reference material to maintain the heating rate.

The temperature regime for DSC analysis is designed such that the specimen temperature increases linearly as a function of time. The reference

should have a well-defined heat capacity over the range of temperatures to be scanned. As the solid specimen melts it will require more heat.

10.4 For a selected material the differences in mechanical properties between crystalline, amorphous and cross-linked state should be qualitatively compared.

The properties of polymers are dependent on many factors including inter- and intra-chain bonding, the nature of the backbone, processing events, presence/absence of additives including other polymers, chain size and geometry, and molecular weight distribution.

While most materials have melting/freezing and vaporization/condensing points, polymers do not boil because the energy necessary to put a polymer into the vapor state is greater than the bond energies of the atoms that hold the polymer together, thus they degrade prior to evaporation. In order for a polymer to be flexible, its various units or segments must be able to move. The **glass transition temperature** T_g is the temperature where polymer units or segments can move but the entire chain cannot. Most vinyl polymers have T_g values below room temperature so that they appear to be flexible and act as rubber and plastic materials. Most condensed polymers have T_g values above room temperature and are used as hard plastics and fibers. The temperature where entire chain movement occurs is called the **melting point** T_m and is greater than the T_g .

Many polymers are themselves brittle at room temperature. For these polymers to become more pliable, additives called plasticizers that allow segmental mobility, and consequently segmental flexibility, are added for synthetic polymers such as poly(vinyl chloride) (PVC).

The inflexible regions of a polymer, such as crystalline regions, are often referred to as "hard" regions. Conversely, the flexible regions of a polymer, where segmental mobility occurs, are referred to as "soft" regions. This combination of hard and soft can be illustrated with so-called segmented PVC. The urethane portion of such polymers is involved in hydrogen bonding and is considered "hard," while the polyether portion, flexible at room temperature, is considered "soft." These segmented polyurethanes are sold under a number of trade names including Spandex.

10.5 Please explain in some detail the procedure a medical doctor carries out applying PMMA as bone cement.

Polymethylmethacrylate (PMMA), commonly known as bone cement, is a widely used method of implant fixation; this technique has largely contributed to the success of modern joint replacement. As will be discussed, cement is a misnomer because, in general, the word cement is used to describe a substance that bonds two things together. Thus the term cement implies that the material sticks the implant into the bone; in reality, however, PMMA should be called bone grout, because it acts as a space-filler that creates a tight space which holds the implant against the bone. Bone cement is the only implant that is manufactured in the operating room (OR). Nevertheless, it must meet the same high standards that are demanded of any other implant supplied by the industry. In addition, due to its composition, PMMA has unique safety considerations that are related to its preparation and its use in the OR. Accurate bone cement mixing and precise application techniques are the basis of successful patient outcomes, as they both increase the stability and the longevity of the prosthesis. Also, safe handling of PMMA bone cement is critical in ensuring that the potential health risks to both patients and healthcare professionals are minimized.

It is important that the personnel involved in the preparation and mixing of PMMA bone cement understand the handling characteristics and the setting times of the various types of cement. These factors directly impact surgery time and surgical outcomes. Once the liquid and powder components are mixed during the routine application of acrylic bone cement in a surgical procedure, the polymerization process is divided into four phases: mixing, waiting, working, and hardening.

Mixing Phase. The mixing phase starts with the addition of the liquid to the powder and ends when the dough is homogenous and stirring becomes effortless. When the liquid and powder components of the cement are mixed together, the liquid wets the surface of the prepolymerized powder. Because PMMA is a polymer that dissolves in its monomer (which is not the case for all polymers), the prepolymerized beads swell and some of them dissolve completely during mixing. This dissolution results in a substantial increase in the viscosity of the mixture; however, at this stage the viscosity is still relatively low, compared with the later phases of polymerization. At the end of the mixing phase, the mixture is a homogenous mass and the cement is

sticky and has a consistency similar to toothpaste.

Waiting Phase. The mixing phase is followed by a waiting period to allow further swelling of the beads and to permit polymerization to proceed. This leads to an increase in the viscosity of the mixture. During this phase, the cement turns into sticky dough. This dough is subsequently tested with gloved fingers every 5 seconds, using a different part of the glove on another part of the cement surface on each testing occasion. This process provides an indication of the end of the waiting phase when the cement is neither sticky nor hairy.

Working Phase. The beginning of the working phase occurs when the cement is no longer sticky, but is of sufficiently low viscosity to enable the surgeon to apply the cement. During this period, polymerization continues and the viscosity continues to increase; in addition, the reaction exotherm associated with polymerization leads to the generation of heat in the cement. In turn, this heat causes thermal expansion of the cement, while there is a competing volumetric shrinkage of the cement as the monomer converts to the denser polymer. During the working phase, the viscosity of the cement must be closely monitored because with a very low viscosity, the cement would not be able to withstand bleeding pressure. This would result in blood lamination in the cement, which causes the cement to weaken. This phase is completed when the cement does not join without folds during continuous kneading by hand; at this point, an implant can no longer be inserted. Therefore, the prosthesis must be implanted before the end of the working phase.