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The influence of sterilization processes on the micromechanical properties of carbon fiber-reinforced PEEK composites for bone implant applications

A. Godara [a], D. Raabe [a,*], S. Green [b]

[a] *Max-Planck-Institut für Eisenforschung, Max-Planck-Str. 1, 40237 Düsseldorf, Germany*
[b] *Invibio Ltd., Hillhouse International Thornton, Cleveleys, Lancashire FY5 4QD, UK*

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Abstract

The effect of sterilization on the structural integrity of the thermoplastic matrix composite polyetheretherketone (PEEK) reinforced with carbon fibers (CF) is investigated by nanoindentation and nanoscratch tests. The use of the material as a medical implant grade requires a detailed understanding of the micromechanical properties which primarily define its *in vivo* behavior. Sterilization is a mandatory process for such materials used in medical applications like bone implants. The steam and gamma radiation sterilization processes employed in this study are at sufficient levels to affect the micromechanical properties of some polymer materials, particularly in the interphase region between the polymer matrix and the reinforcing fibers. Nanoindentation and nanoscratch tests are used in this work to reveal local gradients in the hardness and the elastic properties of the interphase regions. Both methods help to explore microscopic changes in the hardness, reduced stiffness and scratch resistance in the interphase region and in the bulk polymer matrix due to the different sterilization processes employed. The results reveal that neither steam nor gamma radiation sterilization entails significant changes of the reduced elastic modulus, hardness or coefficient of friction in the bulk polymer matrix. However, minor material changes of the PEEK matrix were observed in the interphase region. Of the two sterilization methods used, the steam treatment has a more significant influence on these small changes in this region and appears to increase slightly the thickness of the interphase zone.

Keywords: Biomaterial; Composite; PEEK; Carbon fibers; Bone implant

1. Introduction

The macroscopic behavior of composites depends not only on the properties of their individual constituents but also on the elastic–plastic interaction between the different phases, such as fiber and matrix. During processing of a polymer matrix composite material, the interaction between the surfaces of the fibers and the polymer matrix may create various chemical and morphological inhomogeneities. These are typically discussed in terms of two distinct regions, namely, the interface and the interphase zones. The inter*face* is defined at the atomic scale as the layer of the immediate chemical bond between the fiber and the polymer matrix. The inter*phase* region is much larger. It is formed by local changes of the polymer matrix in the vicinity of a fiber. In this region local properties like morphology, thermomechanical behavior and chemical composition can differ from the corresponding values observed in the bulk polymer matrix [1–3]. It is obvious that the overall mechanical properties of fiber-reinforced polymer composite materials are influenced by the micromechanical behavior of both the interface and the interphase regions.

Sterilization is a mandatory process for materials used in medical applications like bone implants. Sterilization procedures commonly employed are steam sterilization

* Corresponding author. Tel.: +49 (0)211 6792340; fax: +49 (0)211 6792333.
E-mail addresses: a.godara@mpie.de (A. Godara), d.raabe@mpie.de (D. Raabe), sgreen@invibio.com (S. Green).

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and sterilization by radiation, such as gamma radiation. These two methods are employed in the present study at a level sufficient to affect the micromechanical properties of some polymer materials, particularly in the interphase region between the polymer matrix and the reinforcing fibers. The influence of the steam or radiation treatment, respectively, is known to affect the amount of moisture that can be absorbed by the polymer.

The structural integrity and overall performance of fiber-reinforced polymer composites are strongly influenced by the stability of the fiber/polymer interfacial region. The absorption of moisture causes dilatational expansion and induces stresses which are associated with the moisture-induced expansion entailing degradation of the structural stability [4]. The mechanism of moisture absorption in the polymer matrix or at the interface region is by diffusion or capillary processes [5–7]. This may induce plastic deformation by plasticization or differential strains due to swelling while stretching the polymeric chains [8]. These effects may strongly alter the physical, chemical and mechanical characteristics of the material at different scales [9]. This results in a significant mismatch in moisture-induced volumetric expansion between the matrix and the fibers, and thus leads to the evolution of localized stress and strain fields in fibrous composites [10,11]. Mensitieri et al. [12] studied the diffusion kinetics of water from vapors with different activity and from liquid state into amorphous and semicrystalline PEEK sheets at different temperatures, respectively. At higher activity levels, the amorphous material showed the occurrence of a relaxation process. However, the water uptake values obtained for both amorphous and semicrystalline PEEK confirmed the good moisture and liquid water resistance of this kind of high-performance thermoplastic polymer. However, the water absorption behavior can be very different under external stress conditions in terms of both the rate of penetration and the solubility (swelling) processes [13]. In these cases the authors reported an increase in the kinetics associated with both processes.

The effects of radiation are also of considerable scientific and commercial importance to the material investigated. Previous studies [14,15] on ultra-high molecular weight polyethylene (UHMWPE) have shown an influence of gamma radiation at low doses. The authors concluded that irradiation at low doses produces simultaneous cross-linking and chain scission events that occurred preferentially in the amorphous phase and at the crystal fold surfaces. At high doses, they concluded that chain scission may become a significant competitive process to cross-linking [16]. Such chain scission phenomena may lead to an increased crystallinity by cutting molecules that may then join the crystalline regions, thereby increasing crystallinity and T_g. If irradiated specimens are melted and recrystallized, the cross-linking may inhibit crystallization associated with reduced crystallinity, and therefore modify the mechanical properties [15]. Similar low-energy gamma irradiation at low temperature studies on PEEK have shown excellent mechanical properties [17]. The mechanical properties at high temperature were improved by the formation of cross-links and by an increase in the glass transition temperature of the PEEK matrix [17–19].

A main feature of the mechanical behavior of such complex microstructures is the formation of heterogeneous plastic-flow patterns when stressed. When complex composite materials are subjected to external mechanical loads, the lateral distribution of the accumulated residual deformation is heterogeneous, entailing strain localization. Such strain localization phenomena in general may lead to crack initiation via fiber breakage, microvoid formation, or debonding between matrix and fibers. The resistance of the interphase to transverse crack propagation is important in preventing surrounding fibers from experiencing the effects of the stress concentration that could ultimately lead to additional fiber failure.

The mechanical properties of many composites for biomedical applications depend to a large extent on the processing and loading history to which they are exposed before their actual use in the body. One of the most important factors in that context is the influence of the cooling and loading rates on the fiber–matrix interface adhesion [20–23]. The interface adhesion between PEEK and carbon fibers was correlated to the degree of crystallinity and the crystalline morphology, as well as to the bulk mechanical properties of neat PEEK resin, all of which were in turn controlled by the cooling rate [20,21]. It was shown that the interface bond strength, the tensile strength and the elastic modulus of PEEK resin decreased while the ductility became better with increasing cooling rate due to its positive effect on crystallinity and spherulite size. The improvement of crystalline perfection and flattened lamella chains with high crystallinity in the interphase regions were mainly responsible for the strong interface bond in carbon fiber-reinforced PEEK composites processed at a low cooling rate. The interphase failure was characterized by brittle debonding in slow-cooled composites, whereas the amorphous PEEK-rich interphase introduced in fast-cooled specimens failed in a ductile manner with extensive plastic yielding [22,23].

The width of the interphase regions between either phenolic or polyester matrices and the glass fibers embedded in them showed the cumulative influence of the processing history and of the type of experiment [24–26]. It was also observed that the shape of the indenter is important and that scratch tests proved in part to be more reliable for the integral micromechanical characterization of the interphase region then nanoindentation. Gregory et al. [26] made comparative studies between different *in situ* neat polymer matrix materials such as epoxy resin and PEEK. The results revealed that for both types of matrix materials the modulus and the hardness were affected in the same fashion by the manufacturing process. In another work along these lines it was reported that the influence of environmental exposure can alter the micromechanical response of some polymers and induce aging phenomena.