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Impact of the heating/quenching process on the mechanical, optical and thermodynamic properties of polyetheretherketone (PEEK) films

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ABSTRACT

Objective. The aim of this study was to investigate the impact of a heating/quenching process on the optical, mechanical and thermodynamic properties of filled (20%_4000) and unfilled PEEK films (0%_2000 and 0%_4000). Heating/quenching was performed to simulate thermoforming as possible method to process thermoplastic polymers for dental application.

Methods. For the investigation, films of different PEEK qualities (0%_2000, 0%_4000, 20%_4000) were produced using isostatic pressing (n = 10/quality). From each PEEK film, round specimens (n = 20/PEEK film) with a diameter of 34 mm were cut and following parameters were determined: translucency (T%), Martens-Hardness (HM), indentation modulus (E_{IT}), glass transition temperature (T_G), melting temperature (T_M) and enthalpy of fusion (ΔH_f). Same specimens were exposed to heating/quenching using defined parameters. Afterwards, T%, HM, E_{IT}, TG, TM and ΔH_f were determined again. Data were analysed using Kolmogorov–Smirnov test, univariate ANOVA followed by post-hoc Scheffé test with partial eta squared ($\eta_p{}^2$), Kruskal–Wallis and Mann Whitney U test. Level of significance was defined to 95%.

Results. Materials showed significant differences for all investigated parameters in the initial state, except of T_G (p = 0.249). The heating/quenching process showed a significant increase on T% for the unfilled materials 0%_2000 and 0%_4000. HM and E_{IT} decreased significantly through heating/quenching for all materials. Moreover, heating/quenching showed a reduction of T_G for 0%_2000 and 20%_4000, while T_M decreased for 0%_2000 and 0%_4000. ΔH_f confirms different crystallinities of tested materials.

Significance. The heating/quenching process showed a significant impact on all investigated parameters. The highest impact was found for mechanical properties resulting in decreased values of HM and E_{IT}.

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1. Introduction

Recently, the high performance thermoplastic polymer polyetheretherketone (PEEK) gains increasing attention for dental applications. It is characterized by high mechanical strength, high heat resistance as well as high resistance towards external influences and has a maximum degree of crystallinity of 48% [1–4]. Moreover, it shows good biocompatibility, a low density and provides a certain ductility as well as dampening properties [8]. The latter fact makes PEEK even more interesting for specific applications in dentistry. So far, PEEK is used for implants, abutments, healing caps and furthermore it has been proven to be suitable as material for fixed dental prostheses (FDPs) and removable dental prostheses (RDPs) [1,5–10].

For these manifold applications, PEEK is available in different qualities and dosage forms. It is either available as pure material with a greyish colour or modified with organic filler particles like titanium dioxide (TiO_2) or bariumsulfate ($BaSO_4$) [11]. Here, the filler content is up to 30 wt%. By adding TiO_2, the unfavourable colour of PEEK can be improved which results in white coloured materials. Moreover, an increase of the flexural strength and flexural modulus of PEEK materials with increasing proportion of TiO_2 powder was found [5,12,13]. This observation was attributed to the provision of a coherent degree of crystallinity but was not present for the addition of $BaSO_4$ particles. PEEK materials are either available as milling blanks for the Computer Aided Design/Computer Aiding Manufacturing (CAD/CAM) technology or as granulate or pellet for the pressing technology. However, in dentistry, PEEK is not available in the dosage form of films yet, that can be processed using the well-established thermoforming technology.

In general, PEEK shows good milling and grinding properties [14] and is known to be well workable using the CAD/CAM technology. In comparison of three-unit FDPs that were either milled from milling blanks or pressed from pellets or granulate, higher fracture loads were observed for CAD/CAM milled FDPs than for FDPs pressed from granulates [1,2].

This fact is important regarding to the implementation of processing PEEK films by thermoforming. This implementation might be interesting to manufacture crowns, implant abutment or even dental veneers for example. These indications made of PEEK might be interesting because of the possibility to provide dampening properties which conserves the antagonist teeth as well as the mandibular joint [15]. From this point of view, PEEK veneers represent advantageous properties in comparison to ceramic veneers. Another fact that encounters the vision of implementing PEEK veneers is that the wear of PEEK is significantly lower than for composite resin-based materials when lateral forces were applied by investigating the two-body wear rate [16].

To thermoform PEEK films, the material must be heated up in the range of the melting temperature of 360 °C [17,18]. In general, literature investigating the impact of the fabrication of PEEK on the material properties is scarce, but it was found to affect the mechanical properties as well as optical properties [2,19].

For this reason, the present investigation simulates the thermoforming process using a heating/quenching process with defined parameters and analyses the impact on optical, mechanical and thermodynamic properties of different qualities of PEEK films. The null hypothesis stated in this study was that the heating/quenching process neither affects the translucency, the Martens-Hardness and indentation modulus nor the glass transition temperature, melting temperature and enthalpy of fusion of the tested PEEK films.

2. Materials and methods

2.1. *Specimen preparation*

A total number of 30 PEEK films with a thickness of 1 mm were manufactured of three different PEEK granulates, namely unfilled Vestakeep 2000 (0%_2000, Batch 400900/B, Evonik Industries, Essen, Germany), unfilled Vestakeep 4000 (0%_4000, Batch 410239, Evonik Industries) and filled Vestakeep 4000 CC20 (20%_4000, Batch 410061, Evonik Industries) by isostatic pressing (P300, Dr. Collin, Ebersberg, Germany). The number of 2000 or 4000 represented different viscosities of the materials while Vestkeep 4000 CC20 additionally contained 20 wt% of ceramic filler particles. Before pressing, the PEEK granulates were dried for 3 h at 160 °C (HELIOmat Turbo, Helios, Rosenheim, Germany). For pressing the PEEK films, defined parameters were used (Table 1).

From each PEEK film, 12 specimens with a diameter of 34 mm were cut. The specimens followed a random principle to balance potentially inhomogeneities in the PEEK films. From these 12 specimens per PEEK film, 2 specimens (n = 20/PEEK material) were randomly picked and put aside for main measurements. All remaining specimens were used for pilot tests, to determine the temperature (T) and the duration (t) for each PEEK material individually to define parameters for the heating/quenching process. For this, the specimen was put between a specimen mounting consisting of two metal sheets with a window in the centre and placed in the centre of the preheated oven (P6/B, MIHM-VOGT, Stutensee-Blankenloch, Germany). The preheated temperature was based on the melting temperature of PEEK (T_M = 334 °C) [17,20] that served as reference point. Therefrom, the temperature was increased and the duration consequently adapted until the material was deformable but not completely melted. Heating parameters were defined as follows: T = 360 °C for all PEEK materials, $t_{0\%\_2000}$ = 12:45 min, $t_{0\%\_4000}$ = 11:00 min, $t_{20\%\_4000}$ = 12:00 min. After the respective heating duration t, the specimen was taken out of the oven and quenched between two metallic plates, which were stored in iced water. This procedure served as quenching and straightening process to guarantee a plane specimen surface.

For 20 specimens per PEEK material, following parameters were determined initially: translucency (T%), Martens-Hardness (HM), indentation modulus (E_{IT}), glass transition temperature (T_G), melting temperature (T_M) and enthalpy of fusion (ΔH_f). Then, specimens were successively heated and quenched. Here only 10 specimens per material achieved a sufficient plane surface, which was necessary for further measurements. The investigated parameters T%, HM, E_{IT}, T_G, T_M and ΔH_f were conducted for 10 heated/quenched specimens per PEEK material.

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