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Research paper

Effects of aging procedures on the molecular, biochemical, morphological, and mechanical properties of vacuum-formed retainers

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ABSTRACT

The influence of intraoral exposure procedures on the physical characteristics of thermoplastic vacuum-formed retainers (VFRs) is still unclear. The effects of thermoforming and intraoral use on the molecular, chemical, morphological, and mechanical properties of thermoplastic VFRs were investigated. VFRs with a 0.8-mm-thick thermoplastic PETG sheet acquired from 48 patients were investigated with two aging procedures, including vacuum forming and intraoral exposure, for 2-week and 6-month. Eight evaluating sites for thermoplastic VFRs were assessed with seven analytical techniques. LM, SEM, and AFM microscopic findings showed that the surface characteristics increased with increasing *in vivo* exposure time (a four-fold increase) and varied depending on the sites evaluated (an occlusal surface). Raman and EDX spectroscopic findings showed that aging procedures led to a significant change in the molecular composition of VFRs, leading to a decrease in the composition rate of carbon (C) and the presence of silicon (Si), phosphorus (P), and calcium (Ca). Compressive strength and tensile tests showed that aging procedures led to a significant increase ($P<0.01$) in ultimate tensile strength, elastic modulus, the stored energy at a 6-mm deflection ($u_{6\ mm}$), and the compressed load at a 3-mm deflection ($\sigma_{3\ mm}$). Thermoforming led to a smoother surface and no crystallization of PETG sheets. Intraoral exposure accelerated changes in surface morphology, tensile strength, and elastic modulus of VFRs. This change was site-specific and enhanced with an increase in intraoral exposure time. Therefore, thermoforming and *in vivo* oral exposure procedures led to the molecular, morphological, and mechanical properties of thermoplastic VFRs.

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1. Introduction

Esthetics is a critical component of dental fields, particularly in orthodontics. Invisible orthodontics has become popular, and the thermoplastic polymer is of major interest to orthodontic retainers due to its excellent esthetic characteristics and formability (Lindauer and Shoff, 1998; Sheridan et al., 1993; Ponitz, 1971). The vacuum-formed retainer (VFR) is one of the most common types used in daily orthodontic practice. VFRs are removable, clear, transparent, and thermoplastic retainers that were first developed by Kesling in 1945 (Kesling, 1945; Meade and Millett, 2013). The VFRs were fabricated from elastic polymers and were the first attempt to introduce such material in the field of orthodontics. Thermoplastic polymers of VFRs are considered to be either amorphous or semicrystalline according to the degree of crystallinity (Sawyer et al., 2008). Various materials are currently used and most are polypropylene (PP), polyethylene (PE), or copolyester polymers (Gardner et al., 2003; Ryokawa et al., 2006). Regardless of the type, they show highly viscoelastic characteristics and are sensitive to temperature, humidity, time elapsed after elastic deformation, and manufacturing process (Schuster et al., 2004). Since the forming procedure always includes a heating cycle of either vacuum forming or pressure forming, it might cause distinct changes in their morphologic and mechanical properties. Furthermore, thermoplastic materials under intraoral use eventually undergo thermal, mechanical, and chemical degradation, and these changes can be observed through molecular structure and orientation (Schuster et al., 2004; Shpack et al., 2014).

In clinical situations, thermoplastic VFRs have inevitable limitations due to their material properties. They show poor wear resistance and durability along the incisal and occlusal surfaces after only a few months of use (Lindauer and Shoff, 1998; McNamara and Brudon, 1993; Thickett and Power, 2010). Occlusal wear with subsequent cracks and a decrease in vertical height were observed frequently in thermoplastic VFRs. Some studies (Hichens et al., 2007; Mai et al., 2014; Pascual et al., 2010) reported that a considerably greater number of VFR-equipped patients replaced the new VFRs due to breakage or loss compared to the Hawley retainers. These problems resulted in an increase not only in replacement costs but also in the risk of orthodontic relapse. However information regarding the limitations of VFR materials, including surface alterations, structural conformation, and changes in mechanical properties with temperature and intraoral exposure, is insufficient for solving these problems. Furthermore the experimental conditions for simulating the intraoral environment are very complicated, and there was no correlation between *in vivo* and *in vitro* wear (Lutz et al., 1984; Powers et al., 1983). Therefore, this study examined the effects of aging procedures on the molecular, chemical, morphological, and mechanical properties of thermoplastic VFRs through multiple assessments, including light microscopy (LM), scanning electron microscopy (SEM), atomic force microscopy (AFM), Raman spectroscopy, energy dispersive X-ray (EDX) spectroscopy, compressive strength testing, and tensile testing. Vacuum forming and *in vivo* oral exposure for 2 weeks and 6 months, respectively, were used as aging procedures.

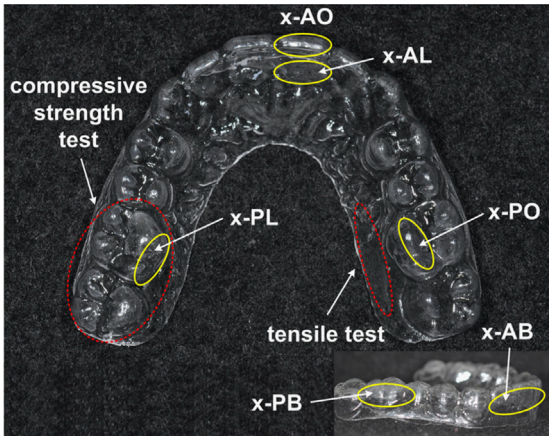

Fig. 1 – VFR preparation evaluating sites. Six sites (yellow) were evaluated by five scope-based assessments. Another two sites (red) were evaluated by tow mechanical testing assessments. The x-AO, x-AB, and x-AL indicate the occlusal, buccal, and lingual surfaces of the central incisors, respectively. The x-PO, x-PB, and x-PL indicate the occlusal, buccal, and lingual surfaces of the first molars, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2. Materials and methods

2.1. *Preparation of VFRs*

A total of 48 thermoplastic VFRs containing polyethylenterephthalat-glycolmodified ethylen-1,4-cycloexylen dimethylenterephthalat copolymer (PETG) were evaluated (Fig. 1). A 0.8-mm-thick thermoplastic polymer sheet (Thermoforming Foil Track A; Forestadent, Pforzheim, Germany) was vacuum-formed and used according to the manufacturer's instructions. The PETG sheet was selected due to its greater impact and wear resistance, more environmentally friendly, exceptional optical property, good thermoformability, and cost-effectiveness, compared to other materials including polyethylene, polycarbonate, and polypropylene. It is available in several thickness, a 0.8-mm thickness is usually preferred for the orthodontic retainers for its ease to fabrication and patients' compliance. Informed consent was obtained from each subject in the Department of Orthodontics, Kyung Hee University Dental Hospital. All procedures involving humans adhered to the Declaration of Helsinki and were approved by the Institutional Review Board (IRB) of Kyung Hee University Dental Hospital (KHDIRB 1503-4).

2.2. *Aging procedure*

According to two aging procedures, including vacuum forming and *in vivo* oral exposure, all thermoplastic VFRs were randomly divided into four groups (Table S1, Supplemental Information): control (CO, intact sheet, $n=6$), thermoformed (T, thermoformed sheet without intraoral use, $n=6$), short-term exposure (S-xx, intraoral use for 2 weeks after thermoforming, $n=18$), and long-term exposure (L-xx, intraoral use