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Differential scanning calorimetry (DSC) and temperature-modulated DSC study of three mouthguard materials☆

Frank H. Meng[a], Scott R. Schricker[b], William A. Brantley[b,*], Deborah A. Mendel[c], Robert G. Rashid[b], Henry W. Fields Jr.[a], Katherine W.L. Vig[a], Satish B. Alapati[b]

[a] Section of Orthodontics, College of Dentistry, The Ohio State University, Columbus, OH 43218, USA
[b] Section of Restorative and Prosthetic Dentistry, College of Dentistry, The Ohio State University, Columbus, OH 43218, USA
[c] Section of Primary Care, College of Dentistry, The Ohio State University, Columbus, OH 43218, USA

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ABSTRACT

Objectives. Employ differential scanning calorimetry (DSC) and temperature-modulated DSC (TMDSC) to investigate thermal transformations in three mouthguard materials and provide insight into their previously investigated energy absorption.

Methods. Samples (13–21 mg) were obtained from (a) conventional ethylene vinyl acetate (EVA), (b) Pro-form™, another EVA polymer, and (c) PolyShok™, an EVA polymer containing polyurethane. Conventional DSC ($n = 5$) was first performed from −80 to 150 °C at a heating rate of 10 °C/min to determine the temperature range for structural transformations. Subsequently, TMDSC ($n = 5$) was performed from −20 to 150 °C at a heating rate of 1 °C/min. Onset and peak temperatures were compared using ANOVA and the Tukey–Kramer HSD test. Other samples were coated with a gold–palladium film and examined with an SEM.

Results. DSC and TMDSC curves were similar for both conventional EVA and Pro-form™, showing two endothermic peaks suggestive of melting processes, with crystallization after the higher-temperature peak. Evidence for crystallization and the second endothermic peak were much less prominent for PolyShok™, which had no peaks associated with the polyurethane constituent. The onset of the lower-temperature endothermic transformation is near body temperature. No glass transitions were observed in the materials. SEM examination revealed different surface morphology and possible cushioning effect for PolyShok™, compared to Pro-form™ and EVA.

Significance. The difference in thermal behavior for PolyShok™ is tentatively attributed to disruption of EVA crystal formation, which may contribute to its superior impact resistance. The lower-temperature endothermic peak suggests that impact testing of these materials should be performed at 37 °C.

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* *Corresponding author at*: Section of Restorative and Prosthetic Dentistry, The Ohio State University, Mailbox 191, PO Box 182357, Columbus, OH 43218-2357, USA. Tel.: +1 614 292 0773; fax: +1 614 292 9422.
E-mail addresses: brantley.1@osu.edu, wbrantle@columbus.rr.com (W.A. Brantley).

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1. Introduction

Mouthguards are used to minimize injuries to the oro-facial complex of participants in sports [1–5]. The primary protective function of mouthguards is to absorb and spread the energy of impact, therefore reducing the possibility of fractured teeth and/or avulsion, and the secondary function is to protect the lips during an impact [6,7].

Stock mouthguards are rigid or resilient shells that are purchased and worn without modification. While their mechanical properties are normally acceptable [8,9], these mouthguards must be held in place by clenching the teeth together, which inhibits breathing and speech. Mouth-formed mouthguards are heat-stable shells lined by a plastic to improve their fit, or thermoplastic shells that are heated and intraorally adapted. The lined shell can be bulky and short-lasting due to deterioration of the lining component [10]. The thermoplastic types are less bulky and show the potential to fit well. Custom-made mouthguards are fabricated on a cast of the dentition by vacuum-molding a thermoplastic sheet or rim. These mouthguards are generally preferred by athletes because of their superior retention and durability, lack of taste, speech facility, and comfort [8,9].

All mouthguards are fabricated from polymers, whose physical properties can be varied by numerous strategies such as changing the molecular weight, use of additive fillers and plasticizers, and copolymerization with another monomer [11,12]. Ethylene vinyl acetate (EVA) is most commonly used to fabricate custom-made mouthguards [9].

Recent studies by Mendel et al using an impact test [13] at 5, 10 and 20 mile/h (mph) at 37 °C showed that the energy absorption of PolyShok™ and a conventional EVA mouthguard material are similar and much greater than that of Pro-form™, another commercial EVA thermoplastic material [14,15]. It was found that PolyShok™ completely withstood puncturing at the impact speed of 20 mph, which did not occur for conventional EVA and Pro-form™.

Thermal analysis techniques are frequently employed to obtain information about the structural transformations in polymers. Such transformations include glass transitions, melting, and crystallization processes. This information can be used to gain insight into their mechanical properties. For example, a higher glass transition temperature, corresponding to the midpoint of the temperature range over which a rigid polymer becomes flexible, is indicative of a stiffer polymer [12]. Polymers are also typically viscoelastic, with substantial loading rate or time dependence in mechanical properties not found for metallic and ceramic materials, and which corresponds to several temperature regimes where structure and elastic modulus change [11].

A highly convenient thermal analysis technique to investigate polymeric transformations is differential scanning calorimetry (DSC), which tracks differences in heat flow to a test specimen and an inert reference material while a specific heating rate is applied [16]. If a test specimen undergoes an endothermic or exothermic transition, the heat flow to the specimen must change relative to that of the reference material, which results in a peak on the DSC curve. With the more recently introduced technique of temperature-modulated DSC (TMDSC) [17,18], a small sinusoidal heating or cooling waveform is superimposed on the principal linear heating or cooling ramp for conventional DSC. This superposition of the linear and sinusoidal temperature-change regimens enables the total heat flow difference between the test sample and reference material that is measured in conventional DSC to be mathematically subdivided for TMDSC into the reversing and nonreversing heat-flow components. TMDSC can thus determine whether a transition is a reversible or nonreversible event. For example, a glass transition is reversible so that it is normally detected in the reversing heat flow curve [19]. On the other hand, the occurrence of polymer crystallization, which is a nonreversible event, is shown in the nonreversing heat flow curve. The peak for polymer melting can occur both in the nonreversing and reversing heat flow curves [20], because this process is initially reversible in the early stages but subsequently becomes irreversible. Analysis of these two TMDSC heat-flow components has provided new insight about structural transformations in dental elastomeric impression materials [21] and nickel–titanium orthodontic wires [22] that are not possible with conventional DSC.

Published laboratory testing of mouthguard materials appears to have been almost exclusively performed at room temperature [8,23–26], although mouthguards are used at close to body temperature. It is important to know if the properties of these materials are substantially different at room and body temperatures and to determine the most appropriate in vitro temperature for impact testing that would mimic clinical usage. The purpose of this study was to employ conventional DSC and TMDSC to investigate the transformation processes and temperature ranges for three representative commercial mouthguard materials in order to provide insight into their reported energy absorption characteristics. Scanning electron microscopy (SEM) was used to examine differences in mouthguard materials due to processing or impact testing. It was hypothesized that the thermal analyses and SEM observations would reveal differences in the mouthguard materials that would account for their differences in impact resistance.

2. Materials and methods

2.1. *Mouthguard materials*

Three commercially available mouthguard materials were selected for study: a conventional ethylene vinyl acetate (EVA) (T&S Dental and Plastics, Myerstown, PA), which served as the control; Pro-form™ (Dental Resources Inc, Delano, MN), another commercial EVA-type of thermoplastic material; and PolyShok™ (Sportsguard Laboratories, Kent, OH), a new EVA product containing polyurethane. Specific information about the polymer compositions and strategies for preparing these materials is proprietary with the manufacturers.

2.2. *Test sample groups and processing of mouthguard materials*

Two groups of test samples for thermal analysis were obtained from the processed and unprocessed mouthguard materials.