Characterization of Mouthguard Materials: A Comparison of a Commercial Material to a Novel Thiolene Family

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ABSTRACT: The goal of this study is to compare the thermal and mechanical properties of a commercial mouthguard material with a novel class of thermoset polymers based on thiolene "click" chemistry. Ternary thiolene systems modified with urethane or acrylate [urethane-modified thiolene network (UMTEN) and acrylate-modified thiolene network (AMTEN), respectively] were synthesized and their properties compared with commercially available Polyshok™. Durometer hardness (ASTM D2240-05), water absorption [ASTM D570-98 (2005)], tear strength (ASTM D624-00), and impact attenuation [ASTM D6110-06f (modified)] were measured for physical property comparison. Differential scanning calorimetry and dynamic mechanical analysis were used as a means to compare thermal properties. One-way analysis of variance and independent t tests were used to test for differences between Polyshok™, AMTEN and UMTEN samples. It was found that the novel thiolene networks exhibit higher impact attenuation at intraoral temperature compared with Polyshok™, although Polyshok™ demonstrates lower water absorption and hardness, as well as higher tear strength. With further modification, this family of thiolene materials may provide a platform for developing next-generation mouthguard materials. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40402.

INTRODUCTION

The use of mouthguards in sports has been shown to provide a protective effect against injury to the orofacial complex decreasing the likelihood of injury between 1.6 and 1.9 times in users compared to nonusers.[1–14] Although this is a compelling statistic, the majority of commercially available mouthguards are composed of some variation in ethylene vinyl acetate (EVA), a thermoplastic polymer known to have mechanical and thermal property limitations.[15,16] The most notable of these is an impact resistance that falls below the threshold set by the American National Standards Institute (ANSI) or Standards Australia International (SAI).[15–18] To overcome limitations of commercially available EVA, researchers have focused their efforts either on identification of possible improvements within existing materials systems by new design or the creation of novel systems that can alternatively meet safety standards such as those containing hard laminate inserts, air inclusions and even new material choices including photocurable materials.[3,9,19–23]

The current ASTM standard for mouthguards categorizes these devices by material type (i.e., thermoplastic vs. thermosetting) and by fabrication class (i.e., vacuum-formed, mouth-formed,

pressure formed, or pressure laminated).[24] Thermoplastic polymers can be highly deformable, which aids in energy absorption but over long periods of time these materials can become thinner. Compressive pressure from teeth clenching and repetitive impacts will eventually reduce the thickness of mouthguard, compromising the protective ability of a mouth protector, leading to inadequate levels of protection. This is a common phenomenon among many users.[9,25] Unlike thermoplastics, polymer chains of thermosets are interconnected by chemical bonds therefore generally shape is permanent and even if deformation occurs the material will return to its original shape in most instances. Cross-linked materials like butyl rubber (car tires), epoxies, and foams are common thermosets that have resilient and highly variable properties which can be controlled by various factors such as starting material structure, molecular weight between cross-links, curing conditions and cross-link density lending them to be highly elastic and pliable or rigid and stiff.[26] To date, no known published research exists that investigates the potential thermosetting materials may have as a mouthguard material. Moreover, no commercially available thermosetting materials are known to be used in either the off-the-shelf or custom mouthguard markets. Due to published
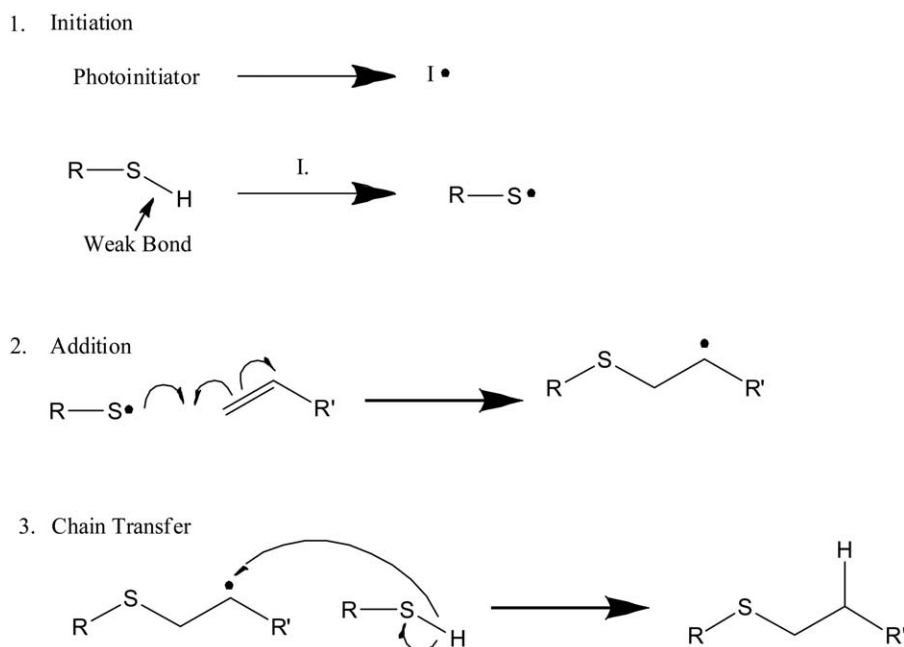
Scheme 1. Schematic representation of a typical photoinitiator-induced thiolene polymerization. For monomers having multiple reactive groups, the final product is a 3-D network containing many thioether linkages.

accounts of thermosets that suitably management impact energy,[22,27,28] our intent is to explore novel synthesized thermosetting material systems manufactured via simple and efficient techniques.

One class of novel thermoset systems suitable for such an application is thiolene networks (TENs).[29,30] Thiolene networks are readily formed from a specified "click" reaction between a thiol functional group and an ene or vinyl functional group. This reaction is one among a minuscule list of reactions meeting the qualifications of "click" categorization based on high reaction efficiency, versatility and nonreactivity with atmospheric water and oxygen.[31–37] Thiolene coupling reactions (TECRs) begin with ultraviolet (UV) irradiation to generate thiol radicals which subsequently add across vinyl groups producing carbon-centered radicals. In traditional chain polymerization, these carbon radicals would add across other vinyl groups, but in thiolene polymerization these radicals abstract hydrogen from other thiol groups, restarting the cycle again of a rather unique chain-transfer step-growth polymerization (Scheme 1). The resulting bonds from such reactions are flexible anti-Markovnikov thioether linkages that are interconnected when choice starting materials are multifunctional.[29,33,34] Amazingly this entire process approaches quantitative conversions within a matter of seconds to yield networks that are highly uniform, low-stress, optically advantageous, have minimal chain ends and most importantly high mechanical energy damping capabilities.[29,32–34,38–40]

In an effort to not only further abate dental injury but also broaden the scope of available end-use mouthguard materials which potentially improve upon the current functional capabilities of thermoformed EVA, we explore a thermoset type material that is known to possess high energy dampening capacities

and glass transition temperature (temperature where maximum damping occurs) approaching intraoral temperatures (i.e., 37°C). As such, the purpose of this study was to synthesize two formulations of novel TENs and compare their physical, mechanical and thermal characterizations to a representative commercial, EVA-based, mouthguard material, Polyshok[TM].

MATERIALS AND METHODS

Commercial Mouthguard Material
Polyshok[TM] (Dentsply Raintree Essix, Sarasota, FL) is a popular commercially available EVA thermoplastic material used for custom mouthguard fabrication. Polyshok[TM] has slightly superior properties compared with similar EVA commercial materials and thus best represents this family of materials as a comparison baseline for this study.[15] All tests on this material were conducted on a single batch of material from the manufacturer.

Experimental Mouthguard Materials
Thiolene mouthguard materials were synthesized from several monomers listed below (Scheme 2). Trimethylolpropane diallyl ether 90 (TMPDE90), isophorone diisocyanate (IPDI), dibutyl-tin dilaurate, allyl pentaerythritol (APE), and trimethylolpropane tris(3-mercaptopropionate) (Trithiol) were purchased from Sigma Aldrich. Dimethoxy-2-phenylacetophenone (DMPA) was received from Ciba Specialty Chemicals. Propoxylated glycerol tricarylate (PGTA) was obtained from Sartomer. All chemicals were used as received from the manufacturer.

Synthesis of Urethane-Modified Thiolene Network
Synthesis and monomer characterization were performed according to previous published methods.[26] Urethane-modified thiolene network (UMTEN) was synthesized in two parts. The first reaction was synthesis of a tetrafunctional ene via the nucleophilic addition of an alcohol to an isocyanate, reacting a
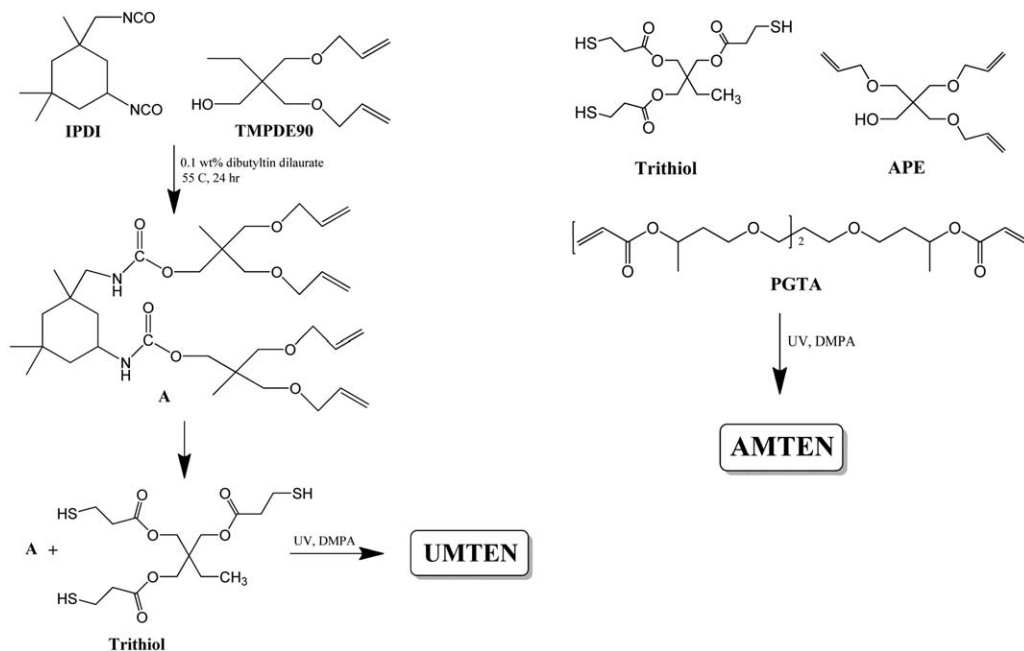
Scheme 2. Schematic representation of chemical reactions leading to (left) UMTEN and (right) AMTEN. UMTEN is formed from an ene monomer containing urethane groups, the network synthesized with this monomer consequently contains urethane linkages in the backbone. AMTEN is the acrylate-containing thiolene network. Total mole percentage of acrylate functional groups in AMTEN is 50%.

2 : 1 mixture of TMPDE90 and IPDI. First 0.1 wt % (of the total weight) dibutyltin dilaurate was added to TMPDE90 under a nitrogen purge and mixing. While the temperature of the first mixture was lowered to 0°C via ice bath, IPDI was added slowly from a second container, also under nitrogen purge, over a 30-min period. The slow addition of IPDI prevents heat build-up and side reactions, however, after this period, the reaction temperature was slowly increased to 55° and continued stirring for 24 h under inert atmosphere (N_2) to afford a tetrafunctional ene whereby urethane groups have been incorporated into the backbone (**A**) [Scheme 2(a)]. The reaction product was verified via nuclear magnetic resonance technique.

In the second reaction, an efficient photoinitiated TECR proceeded between a trifunctional thiol and tetrafunctional urethane-modified ene (**A**) [Scheme 2(a)]. UMTEN was then synthesized by reacting (**A**) with Trithiol in stoichiometrically equivalent amounts, based on functional groups of thiol and ene, utilizing a highly efficient photo initiated thiolene reaction. The photoinitiator, DMPA was initially dissolved in the thiol component, prior to mixing in the ene component (**A**). Thin (0.5 mm) and thick (4–6 mm) films were synthesized utilizing 1 wt % and 0.02 wt % of UV initiator DMPA. All samples were cured using a 9 mW/cm^2 ($\lambda = 354$ nm) light source for 30 min.

Synthesis of Acrylate-Modified Thiolene Network
Methods similar to those previously published were used for making ternary thiolene/acrylate networks.[27] Stoichiometrically equivalent ratios of Trithiol and APE were used while an additional 50 mol % (based on functional groups) of PGTA was added to the system. DMPA was first dissolved into Trithiol followed by addition of APE. The addition of the PGTA followed

directly after blending the thiolene-catalyst system [Scheme 2(b)]. Complete mixing of all materials was achieved by mechanical stirring. Again, to make thin films (0.5 mm), 1 wt % of DMPA was utilized. A lower percentage (0.02 wt %) of DMPA was added to make thick (4–6 mm) thermoset samples. All samples were cured using a 9 mW/cm^2 ($\lambda = 354$ nm) light source for 30 min. Intermittent light was used for acrylate-modified thiolene network (AMTEN) synthesis to minimize heat build-up from the highly exothermic acrylate reaction.

Thermal Analysis of Materials
The glass transition, melting, and crystallization temperatures were obtained using differential scanning calorimetry (DSC; TA Instruments Q200, New Castle, DE) calibrated against an indium standard using an N_2 purge (50 mL/min). Standard aluminum pans and specimens having mass of 8.0 ± 1 mg were used to create effective heat flow within the chamber and good contact with the pan bottom. Each specimen was initially cooled to -70°C and allowed to equilibrate for 10 min. Following initial cooling, the specimens were heated at a rate of 10°C/min to 150°C and annealed for 10 min to erase the thermal history. The specimens were then cooled at 10°C/min to -70°C and reheated to 150°C. Glass transition values (taken via the inflection point method) were calculated from the second heating curve, whereas crystallization temperatures were taken from the cooling curve. This process was repeated on a total of 15 samples (3 materials × 5 replicates) and all relevant thermal values were averaged.

Storage modulus, loss modulus, and tan δ values were obtained by dynamic mechanical analysis (DMA; Rheometric Scientific MK V, New Castle, DE). Instrument calibration was performed

before testing as per the manufacturer's instructions for both force and temperature. Measurements were conducted in the vertical tension mode on samples with dimensions of ca. 10 mm $\times$ 5 mm $\times$ 0.50 mm ($L \times W \times T$). The samples were cooled to $-50°C$ and then heated at 5°C/min under a sinusoidal strain of frequency 1 Hz with 0.05% strain up to a final temperature of 150°C. This process was repeated on a total of 15 samples (3 materials $\times$ 5 replicates) and the glass transition, loss modulus, storage modulus, and tan δ values were averaged.

Physical and Mechanical Analysis Methods

Shore A Hardness was used as the standardized test for comparison of novel thiolene materials to commercially available Polyshok[TM]. The durometer hardness was measured according to ASTM guideline D2240-05 to measure the resistance toward indentation.[41] The calibrated device is composed of a spring-based scale (0–100) on an indenter having a tip with dimensions (tip = 0.031 $\pm$ 0.001 mm; taper = 35 $\pm$ 0.25°, and shaft=1.40 $\pm$ 0.005 mm). All tested materials were at least 12 mm in length and 6 mm thick. A thickness of 6 mm was achieved by plying two 3 mm sheets. Shore A hardness was measured at five locations per sample by carefully placing the indenter on the material without shock, followed by a firm press into the sample while on a solid, horizontal surface. The indenter was held for one second and the highest reading was recorded at both room temperature 23 $\pm$ 2°C (73.4 $\pm$ 3.6°F) and intraoral temperature 37$\pm$2°C (98.6 $\pm$ 3.6°F).

Water absorption was measured for all samples according to ASTM guideline D570-98.[42] From this test, the percentage of mass increase due to absorption of water and rate of absorption can be determined. In previous water absorption studies of commercial materials, the 24 h procedure in combination with repeated 24 h immersion test (Section 7.3 of ASTM D570-98) was utilized for a total of 9 h or 3 days.[42] In this study, this same procedure was used for thiolene samples but for a significantly longer time period, approximately 20 days. This time allowed the desired test endpoint requirements to be achieved. Samples were molded into discs of diameter 50.8 $\pm$ 0.3 mm and thickness 3.2 $\pm$ 0.3 mm. The discs were conditioned for 24 h in an oven and cooled in a desiccator prior to the first weighing. The samples were weighed to the nearest 0.001 gram to determine conditioned weight and placed upright in distilled water at the appropriate temperature. The TENs, AMTEN, and UMTEN, were weighed every 24 h until the weight increase remained unchanged (to 0.001 g) for two consecutive days. Five samples of each type were tested at room temperature 23 $\pm$ 2°C (73.4 $\pm$ 3.6°F) and a separate set of five were tested at intraoral temperature 37 $\pm$ 2°C (98.6 $\pm$ 3.6°F). Percentage of weight increase was calculated and reported according to the following equation and reported to the nearest 0.01%:

$$\%increase = \frac{\text{wet weight} - \text{conditioned weight}}{\text{conditioned weight}} \times 100\% \qquad (1)$$

Tear Strength Methods

Failure of a mouthguard due to a tear is highly likely. Sharp edges of teeth may cause minor voids or imperfections to spread, progressing to a larger area of material, eventually leading to equipment failure. ASTM test procedure D624-00 (die shape C) was used to determine tear strength, of novel thiolene materials.[43] This ASTM test calls for measuring the tear strength of conventional vulcanized rubber and thermoplastic elastomers. While this test is appropriate for commercial EVA, thermoset materials are not a conventional material. This test, however, provides us with a method for direct comparison with previously published data on commercial materials. The tear strength is calculated by the following equation, where F is the average maximum force required to propagate the tear, and d is the sample thickness.

$$T_s = F/d \qquad (2)$$

Sample thickness was recorded as an average of three measurements, one taken directly and the notch and the others slightly left and right. A universal material testing machine (Model 3300 Instron, Norwood, MA) was calibrated prior to the study and used to determine tear strength. Samples were placed consistently and deeply into the grip to lessen the chance of slippage. The test grips were separated at a rate of 500 $\pm$ 50 mm/min for five separate samples. Higher temperature 37 $\pm$ 2°C, was achieved by water bath equilibration.

Impact Testing Methods

The method used to measure impact absorption energy was a modified ASTM test for determination of impact resistance of notched specimens, ASTM D 6110.[44] The full modification description is consistent with previously published literature, and readers are directed to Ref. 16 for a more thorough explanation. A pendulum style apparatus was used to measure impact absorption energy. A pendulum of known weight was set to a height corresponding to 1.13 J. Upon release, the pendulum swings and strikes the sample normal to the surface with a standard radius Charpy style tup. Care was taken to ensure material energy dissipated by material flexion was negligible by layering two, 4-mm thick bars and mounting them to a steel plate. A total thickness of 8 mm further helps ensure minimal influence of the steel plate on the impact measurement.

Statistical Analysis

Values from each sample set were analyzed using the Statistical Package for Social Sciences (SPSS, v. 16.0; SPSS, Chicago, IL). Values in the tables are representative of the mean and the standard deviation. The independent variables for this study were temperature (23°C and 37°C) and material (Polyshok[TM], AMTEN, and UMTEN). The dependent variables of interest include mean Shore A hardness, water absorption, tear strength, and impact resistance values for the mechanical variables. For the DSC and DMA thermal measurements, the dependent variables include mean glass transition temperatures and tan δ at 37°C (only for DMA). Several 2 (temperature) $\times$ 3 (material) factorial analysis of variances were conducted to test for differences between the materials on the mean mechanical and thermal properties of interest. To determine whether the glass transition temperatures of the materials could be considered statistically different from intraoral temperature, series one-sample t tests were conducted. Due to the number of one-sample t tests performed, the Bonferroni correction factor was
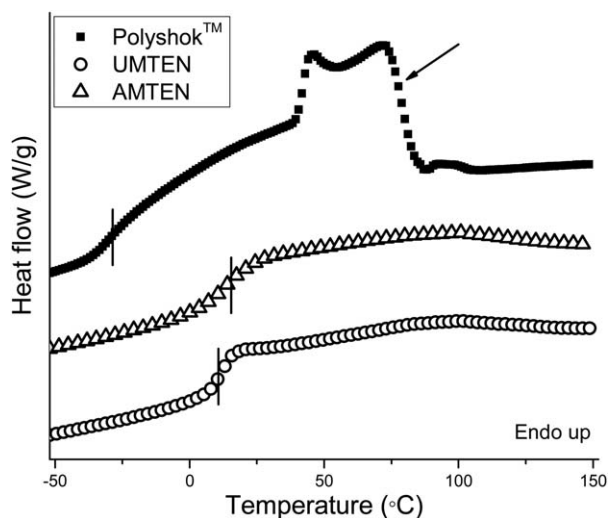
Figure 1. DSC first heating scans of commercial EVA (Polyshok[TM]) (■), AMTEN (Δ), and UMTEN (○) materials heated at a rate of 10°/min. Glass transition temperatures are indicated by the vertical black line and crystallization by an arrow.

applied to the type I error rate and set a priori at $P = 0.008$ (0.05/6).

RESULTS

Differential Scanning Calorimetry

Figure 1 shows the thermograms from the first heating scan of the three tested materials. Heating from an initial temperature of $-70°C$ to $150°C$, glass transitions (T_gs) are present for all three systems. Polyshok[TM] has the lowest T_g ($-28°C$) of all systems. The T_gs for UMTEN and AMTEM were comparable with one another ($13°C$). There was also evidence of trace post T_g activity within all the samples. Three endothermic peaks are present in the Polyshok[TM] samples at approximately 44°C, 73°C, and 95°C, indicated melting of crystalline domains or similar processes. UMTEN and AMTEN also exhibited subtle post T_g activity as evidenced by a very broad, low intensity, endothermic peak having a maximum around 100°C.

Upon the second heating cycle, it becomes apparent that the network morphology of UMTEN and AMTEN was affected by the first annealing step. The average glass transition temperature increased 6°C for UMTEM, and 7°C for AMTEN systems. In contrast, the T_g of Polyshok[TM] was shifted lower, to $-31°C$. The width of the glass transition region varied between samples. Qualitatively, the transition region for Polyshok[TM] samples was very broad. UMTEN had a very narrow transition region of about 9°C, typical of a thiolene network. AMTEN had a broader transition region (ca. 20°C) compared with UMTEN, but still much lower than Polyshok[TM]. A statistical difference ($F_{2,12} = 10119.64$, $P < 0.05$) in mean glass transition temperature as measured by DSC was noted between the materials. A Tukey honest significant difference (HSD) *post hoc* test revealed two homogeneous subsets with Polyshok[TM] as sole membership in one group and AMTEN and UMTEN as members of the second group. The one-sample *t* test revealed that the glass transition temperature of all of the samples tested were statistically

Table I. Thermal Analysis of Materials

	T_g[a]	E' at 37°C[b]	E'' at 37°C[c]	DSC T_g (1st heating)	DSC T_g (2nd heating)	Tan δ at 37°C[d]	Tan δ_{max}[e]	FWHM[f]
	(°C)	(Mpa)	(Mpa)	(°C)	(°C)			
Polyshok[TM][g]	9.1 (1.91)	20 (4.02)	1.15 (0.07)	−28.4 (0.33)	−30.87 (0.83)	0.059 (0.004)	0.31 (0.006)	38.6 (0.85)
UMTEN	38.07 (0.82)	110.0 (27.1)	111.0 (20.7)	12.8 (0.54)	18.99 (0.55)	1.02 (0.066)	1.05 (0.035)	16.2 (0.866)
AMTEN	37.84 (0.50)	213.2 (23.7)	110.0 (9.71)	13.1 (0.42)	19.95 (0.52)	0.524 (0.009)	0.529 (0.008)	26.3 (0.609)

[a] Temperature at tan δ maximum.
[b] Storage modulus at 37°C.
[c] Loss modulus at 37°C.
[d] Tan δ value at 37°C.
[e] Maximum value of tan δ
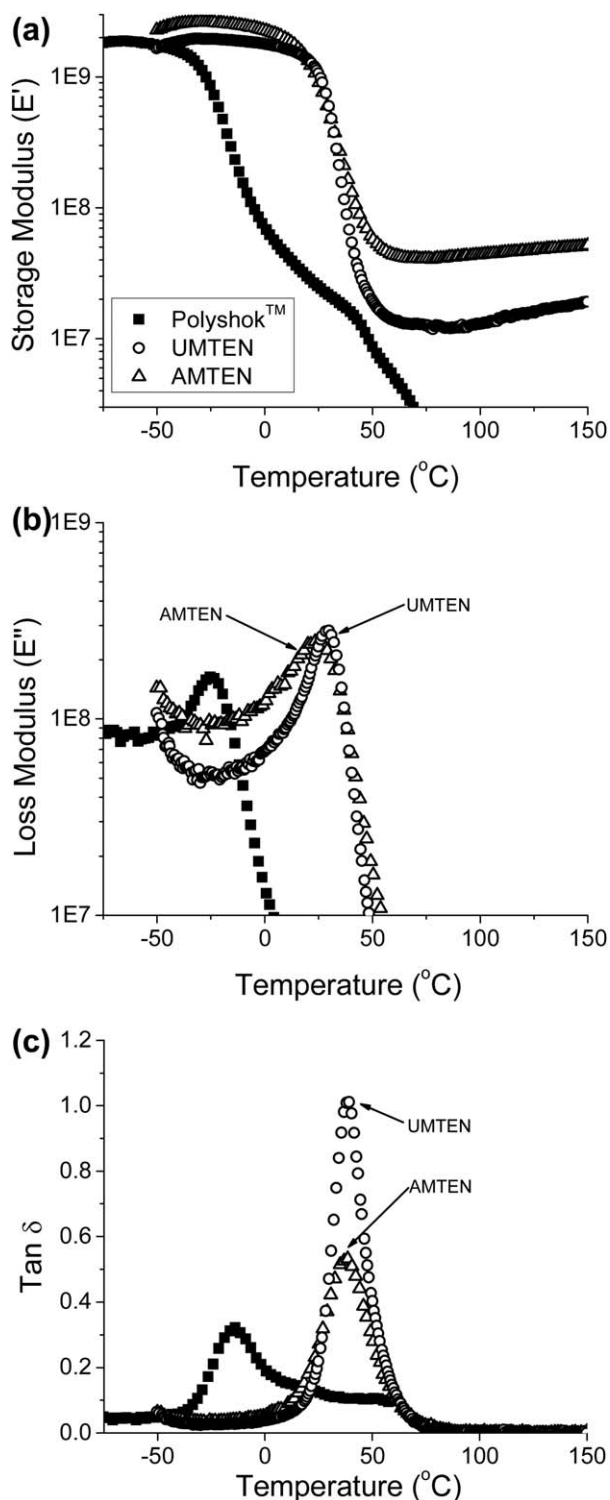[f] Full width at half maximum of tan δ.
[g] Values reported from Ref. 17.

Figure 2. DMA traces from tests conducted at a 5°C/min heating rate at 1 Hz with 0.05% strain. (a) Storage modulus (E') of commercial Polyshok^{TM} (■), UMTEN (○), and AMTEN (Δ). (b) Loss modulus (E'') for each system, and (c) tan δ plots of three systems with peaks corresponding to glass transition temperatures.

different from intraoral temperature ($P < 0.008$). Mean and standard deviations for DSC measurements of T_g for all samples upon both first and second heating are presented in Table I.

Dynamic Mechanical Analysis

Using DMA, several thermomechanical characteristics [i.e., storage modulus (E'), loss modulus (E'') and tan δ] were obtained as a function of temperature (Figure 2). At 37°C (intraoral temperature) the storage moduli of UMTEN and AMTEN were on average 110 MPa and 213 MPa, respectively. In contrast, Polyshok^{TM} had a significantly lower storage modulus (20 MPa) at the same temperature. A decrease in storage modulus observed for Polyshok^{TM} around −40°C indicates an earlier onset of the glass transition. UMTEN and AMTEN maintained high moduli until a much higher temperature (ca. 20°C), corresponding to a later onset of T_g.

In a DMA experiment, the maximum value of the tan δ versus temperature curve is indicative of T_g. Subsequently, as local segmental motion increases, there is a concomitant mechanical loss. In addition, when the tan δ value is highest, materials exhibit maximum damping properties and the loss modulus versus temperature curve will exhibit a peak corresponding to this transition. Upon heating AMTEN and UMTEN, the maximum in the tan δ versus temperature occurred at approximately 38°C for both samples. These values were confirmed by peaks in the E'' versus temperature graphs for both materials. The value of tan δ at the maximum temperature for AMTEN and UMTEN were 0.53 and 1.0, respectively, indicative of a high mechanical loss and energy dissipation In contrast, Polyshok^{TM} samples showed only a maximum tan δ value of 0.31 at a much lower temperature (−9°C) according to a previous study.[15] The full width at half maximum of the AMTEN and UMTEN tan δ versus temperature curves coincide with DSC results for the width of the transition region mentioned above (Table I).

A statistical difference ($F_{2,12} = 3911.13$, $P < 0.05$) in mean glass transition temperature as measured by DMA was noted between the materials. A Tukey HSD *post hoc* test revealed two homogeneous subsets with Polyshok^{TM} as sole membership in one group and AMTEN and UMTEN as members of the second group. Another statistical difference between materials was noted for tan δ at 37°C ($F_{2,12} = 784.38$, $P < 0.05$) with the same group membership previously noted. The one-sample t test revealed that the glass transition temperature of the Polyshok^{TM} sample was statistically different from intraoral temperature ($P < 0.008$), but not the AMTEN and UMTEN samples. Mean and standard deviations for DMA measurements of T_g for all samples upon both first and second heating are presented in Table I.

Shore A Hardness

Mean hardness values at room and intraoral temperatures are presented in Table II. At room temperature AMTEN had a Shore A hardness of 80, slightly greater than the industry standard Polyshok^{TM} which is reported to be about 77. UMTEN registered the highest room temperature hardness of the three systems at 85. The hardness for AMTEN and UMTEN declines to 68 and 70, respectively, at intraoral temperature. Polyshok^{TM} follows the same trend, decreasing to approximately 68 (intraoral) from 77 (room temperature). A statistical interaction ($F_{2,24} = 20.29$, $P < 0.05$, $f = 1.29$) between material and temperature indicated that mean hardness decreased at a greater rate for UMTEN than

Table II. Physical and Mechanical Properties

23°C ± 2°C	Shore A hardness [a]	Water absorption [b]		Tear strength [c]		Impact resistance [d]
		Water absorption 24 h	Water absorption 96 h	Max tear (kN m^{-1})	Max strain (% length)	
		% Water absorption	% Water absorption			% Joules absorbed
Polyshok™	77.2 (4.2)	0.37(0.001)	0.46 (0.041)	30.4 (1.06)	161.13 (18.85)	60
UMTEN	85 (3.3)	0.29 (0.030)	0.53 (0.055)	28.11 (1.61)	18.1 (2.3)	92 (0.01)
AMTEN	80 (1.6)	0.68 (0.043)	1.27 (0.067)	8.35 (0.756)	4.18 (0.29)	86 (0.004)
37°C ± 2°C						
Polyshok™	67.6 (0.54)	0.56 (0.004)	0.58 (0.019)	21.5 (0.89)	161.43 (67.25)	66
UMTEN	69.8 (1.5)	0.58 (0.1)	1.1 (0.2)	11.4 (1.8)	18.5 (4.7)	85 (4)
AMTEN	68.2 (1.3)	1.3 (0.2)	2.1 (0.2)	3.75 (0.40)	3.76 (0.92)	57 (5)

[a] ASTM D2240-05 standard test method for rubbery property-durometer hardness.
[b] ASTM D570-98 (2005) standard test method for water absorption of plastics.
[c] ASTM D624–2000 (2007) standard test method for tear strength of vulcanized rubber and thermoplastic elastomers.
[d] Modified ASTM D6110-06 standard method for determining the Charpy impact resistance of notched specimens of plastics.
[e] Values reported from Ref. 16.

it did for either AMTEN or Polyshok™ at approximate intraoral temperature. An additional implication of this interaction is that the three systems (while demonstrating statistically different mean room temperature hardness values) demonstrate equivalent mean hardness values at higher temperatures.

Water Absorption Studies
Mean water absorption values at room and intraoral temperatures are presented in Table II. There was no visible warping, cracking,

Figure 3. Percentage of water absorption for thiolene networks UMTEN (top) and AMTEN (bottom) at room temperature (open symbols) and 38°C (filled symbols). Each point is an average of five samples and standard deviations are represented by error bars.

or change in physical appearance due to water immersion for any of the tested materials during the length of the test. Figure 3 shows percentage of water absorption versus time for AMTEN and UMTEN at room and intraoral temperature. All thiolene-based systems appear to demonstrate identical behavior overall, characterized by rapid uptake of water within the first five days, a slower increase in mass, and finally reaching a terminal saturation. At room temperature 24 h after immersion, the percentage of mass increase for AMTEN and UMTEN was 0.68% and 0.29%, respectively. These water absorption values increased over the same time frame at 37°C to 1.3% and 0.58%, respectively, approximately double the room temperature water uptake. The 96-h values were 1.27% and 0.53% for AMTEN and UMTEN, respectively, at room temperature and 2.1% and 1.1% at 37°C. Compared to Polyshok™, the percentage of water absorption was slightly higher for the modified TENs. At room temperature Polyshok™ has been reported to have water absorption of 0.37–0.46%. These values are higher at intraoral temperature, 0.56–0.58%. A statistical interaction ($F_{2,24} = 43.77$, $P < 0.05$, $f = 1.91$) between material and temperature indicated that the rate of uptake and maximum percentage of mass varied between the samples and was accelerated at intraoral temperature. Additionally, this analysis further indicates that the increased rate of water absorption between temperatures is equivocal for UMTEN and Polyshok™ and higher for AMTEN. Note that none of the samples studied exhibited a significant mass increase (due to water uptake) under any testing conditions.
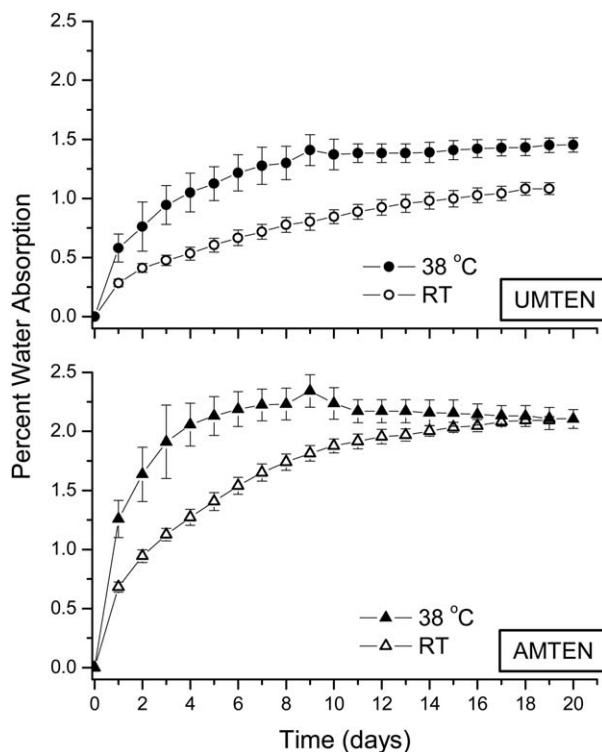
Tear Strength Studies
Mean tear strength and % strain at room and intraoral temperatures are presented in Table II. At room temperature, the average tensile modulus for AMTEN and UMTEN was 18.3 MPa and 24.4 MPa respectively. These values decreased appreciably at higher temperatures to 10.7 MPa and 7.43 MPa, respectively, at intraoral temperatures. Tear strength, defined as the ratio of peak load to sample thickness, was 8.35 kN·m^{-1} and 28.1 kN·m^{-1} for AMTEN and UMTEN, respectively. At 37 ± 2°C, tear strength values decreased to 3.75 kN·m^{-1} and 11.43 kN·m^{-1} for AMTEN and
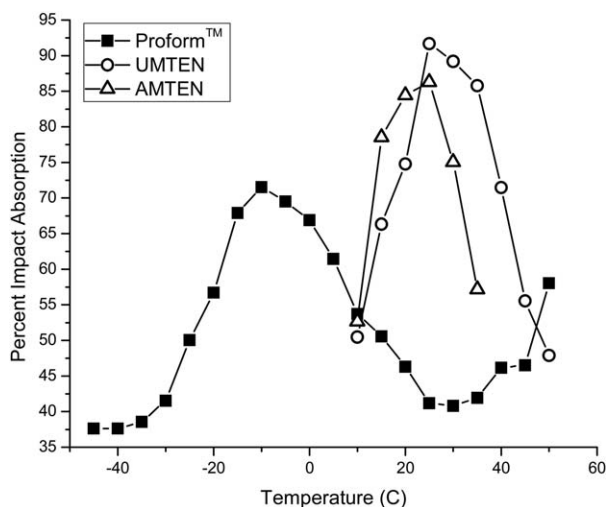
Figure 4. Graphs of impact absorption as a function of temperature for each system: commercial EVA-based (Proform; ■) and two novel, modified thiolene networks UMTEN (○) and AMTEN (△). Each point for AMTEN and UMTEN represents an average of five tests. Data for Proform is taken from Ref. 16.

UMTEN samples. Polyshok[TM] has a reported tear strength of 30.4 $kN \cdot m^{-1}$ at room temperature and 21.5 $kN \cdot m^{-1}$ at intraoral temperature. A statistical interaction ($F_{2,24} = 67.75$, $P < 0.05$, $f = 2.38$) between material and temperature indicated that the rate of mean tear strengths decreased at the elevated temperature for all samples. However, this analysis further indicates that the rate of decrease in tear strength was more profound for UMTEN than for AMTEN or Polyshok[TM]. There were slight variations in strain % values for AMTEN at room temperature (4.18%) compared to intraoral temperature (3.76%) while UMTEN was essentially unaffected (18.1% vs. 18.5%, respectively). There was no statistical difference in the strain % for UMTEN at room and intraoral temperature.

Impact Resistance Studies
Impact resistance properties of these materials were measured by a modification of the ASTM D6110-06f method. Mean percentage of impact resistance at room and intraoral temperatures are presented in Table II. At approximately 37°C, the percentage of impact resistance for AMTEN and UMTEN was 57% and 86%, respectively. Polyshok[TM] has the smallest reported value, ca. 42% at 37°C.[16] To investigate energy absorption properties of these materials in more detail, percentage of impact resistance was measured as a function of temperature between 10°C and 50°C for UMTEN and between 10°C and 35°C for AMTEN for comparison with Polyshok[TM]. Figure 4 shows percentage of impact versus temperature for UMTEN, AMTEN and Polyshok[TM]. In general, a plot of percentage of impact versus temperature mimics a plot of tan δ versus temperature and is consistent with previous literature reports.[16] A statistical interaction ($F_{2,24} = 113.65$, $P < 0.05$, $f = 3.07$) between material and temperature indicated that mean impact resistance decreased for Polyshok[TM] and increased for AMTEN and UMTEN materials at approximate intraoral temperature. Additionally, this analysis

further indicates that the rate of increase in impact resistance was more profound for AMTEN than for UMTEN.

DISCUSSION

It is the intention of these studies to compare the physical and thermal properties of novel thiolene based thermosets with a commercial EVA-based material specific to end-use parameters associated with mouthguard materials. The materials tested in the current study represent two distinct classifications of polymers, thermoplastic (EVA, Polyshok[TM]) and thermosets (AMTEN and UMTEN). Our findings demonstrated similarities and differences between the various classes of materials from a polymer perspective as well as industrial standards for the intended applications. The following discussion will focus on comparing properties of these materials specifically for mouthguard applications.

Thermal Characterization Comparison
DSC thermograms (Figure 1) revealed similarities in the thermal behavior of Polyshok[TM] to previous literature. In particular, thermal analysis reveals a relatively low T_g and several endothermic peaks corresponding to melting of crystalline domains, all of which melt below 100°C. A large percentage of EVA-based mouthguards are formed to fit the mouth by heating in boiling water (i.e., "boil and bite"); therefore, melting of crystalline regions in EVA has proven beneficial with regards to ease of mouthguard fit. This process, however, leads to uncontrolled thinning in several regions, which may lead to less than ideal protection. Our novel TENs lack crystalline regions. During the first heating, there was a broad endothermic transition. This is a common phenomenon for thermoset materials that have not reached full cure. As molecular weight builds during polymerization, chain mobility decreases as viscosity rapidly increases. This can frustrate mobility of uncross-linked chains causing vitrification. When the system is supplied with heat (as with a DSC experiment) unreacted monomers gain enough energy and mobility to complete the curing reaction. This endotherm is therefore not reversible and is only present upon the first heating; once the system becomes fully cured, there is no additional reaction. As a result, the T_g of the second heating cycle is higher than the first. For all of the materials studied, T_g was below intraoral temperature, although T_g for AMTEN and UMTEN were much closer to 37°C. As such the T_gs, or temperature where a polymer would absorb maximum energy, was measured to be closer to intraoral temperature for AMTEN and UMTEN compared to Polyshok[TM], which exhibited T_gs at subzero temperatures. A higher value of T_g is clearly more ideal for a mouthguard material.

DMA (Figure 2) provides valuable information about the viscoelastic properties of polymer materials as a function of temperature and revealed important structural differences between the materials studied. Because EVA is a thermoplastic material, polymer chains in Polyshok[TM] are not chemically bound to one another; rather the crystalline domains act as physical cross-links and polymer chain entanglements, chain interactions and crystallinity are the dominant source of material properties. If sufficient thermal energy is provided (i.e., $T > T_g$), long-range segmental motions of the polymer chains are possible and chains can slip past adjacent chains lending the material

deformable. For Polyshok™ this energy is minimal to overcome and is low enough that heat from ones mouth can cause the material to soften, rendering the mouthguard less protective due to thinning. In contrast, covalently cross-linked networks such as in AMTEN and UMTEN exhibit different behaviors because all chains are chemically bound forming one large, single network. The same segmental motions then require more energy and are constrained by chemical connections. Heating a thermoset does not cause chain slippage from local motions, and with further heating the entire network will remain intact until the system degrades.

Damping characteristics of the networks (quantified by tan δ) demonstrated typical behavior for each class of material over a broad range of temperatures. Polyshok™ demonstrates only modest damping (quantified by the amplitude of the tan δ peak) over the entire temperature range, with a maximum at subzero temperatures. The stiffness (E') decreased rapidly for Polyshok™ at temperatures approaching 0°C from this tan δ maximum at −20°C. This is detrimental for a mouthguard material given that stiffness possibly leads to bridging effects whereby energy concentrated in one area can spread throughout the entire dental bridge. This tan δ peak is broad and asymmetric, extending toward higher temperatures likely due to the presence of crystalline domains within the system. In contrast, AMTEN and UMTEN have maxima in tan δ at much higher temperatures than Polyshok™, with UMTEN exhibiting superior damping properties compared with the other two materials. The former case AMTEN is chemically composed of three monomers; thiol, ene and acrylate. While the ene is only able to react with a thiol, the acrylate can react with thiol as well as with itself. The ability for both homo and cross-polymerization means that at least two distinct domains are formed within the network, one soft (thiolene rich) and the other hard (acrylate rich). This biphasic network exhibits one T_g, potentially because the distinct domains are small (2–3 nm), but the damping capacity suffers due to a discontinuous system. In contrast, UMTEN exhibited superior properties compared with all other systems with regard to the temperature and amplitude of maximum damping. UMTEN is different from AMTEN in that urethane groups are built into the monomer, which may facilitate greater damping character. The sequential reaction of the urethane ene monomer with a thiol, is strictly between thiol and ene functional groups, leading to homogeneous networks with excellent damping character, typical of thiolene thermosets. Consistency of the networks leads to high tan δ_{max} values and consequently favorable damping behavior at intraoral temperatures. As mentioned previously, the temperature where the damping effects are greatest lie much closer to intraoral temperature for AMTEN and UMTEN (38°C) compared with Polyshok™ (−9°C), which is a significant property advantage for internal protective equipment.

Physical Characterization Comparison

The comfort level of the mouthguard material is important for the intended application, as these materials inevitably will contact soft tissues of the mouth such as the cheeks and gums. From a materials standpoint, the Shore A hardness is a measure of the ability for the material to deform when in compressive contact with another object. While there are a number of poten-tial variables in actual use, Shore A hardness is a good approximation for the material response during clenching. As such, the softer the material is under compression, the more comfortable it will likely feel while in contact with soft tissues. Shore A hardness of the materials at room and intraoral temperatures were measured and compared. The scale of the Shore A Hardness ranges from 0 to 100, where 0 is the softest and 100 the hardest. The test is highly subjective and leaves room for significant error between testers. Nonetheless, it was determined that all of the materials tested fell within the range 77–85 at room temperature. At intraoral temperatures, the hardness was lower as expected, and the range was much smaller, only a 68–70, for all three materials. It was observed that UMTEM softened at a faster rate than AMTEN or Polyshok™. Interestingly, from a comfort standpoint at room temperature there might be a noticeable difference, but inside the mouth all three materials could very well feel the same.

The mouth is a very humid and moist environment, so water uptake is important for the intended application of these materials. ANSI and SAI guidelines call for the water absorption in mouthguard materials to be less than 0.5% by weight. Of the three materials studied, only Polyshok™ was compliant with this value. AMTEN had the highest equilibrium water absorption, measuring about four times the recommended amount (Figure 3). This may be explained chemically due to the fact that the acrylate component consists of ethylene oxide groups that modestly attract water. UMTEN exhibited slightly less water absorption compared with AMTEN, but still had values that are three times the guideline amount. Although at first these results may seem discouraging, two important factors should be considered: (1) The initial rate of water uptake was much slower for AMTEN and UMTEN compared to Polyshok™. For example, thiolene materials took ca. 3 days of constant submersion in water to reach 0.5% water absorption. Given that in typical use the mouthguard will not be in constant contact with water for more than a few hours at a time, the increase in equilibrium water absorption will not likely have an impact on end use. (2) Changes in the physical properties under saturated conditions will likely be less dramatic for networks such as AMTEN and UMTEN compared with thermoplastics such as Polyshok™ and EVA.

Tear strength measurements are meant to mimic contact with the sharp points of teeth that could cause significant damage to the mouthguard over time. The tear strength of UMTEN and Polyshok™ at room temperature were similar, 28 kN·m^{-1} and 30 kN·m^{-1}, respectively. At higher temperatures all systems show a decrease in tear strength; however, the difference in tear strength between Polyshok™ and UMTEN widened to the point that UMTEN was only half as resistant to tear at intraoral temperatures. It is expected that at room temperature and intraoral temperature, Polyshok™ is well beyond its T_g and is in an equilibrium state, whereas AMTEN and UMTEN are in a transition region. This means that small fluctuations in temperature can have large effects on tear strength.

Key differences in the tear behavior between thermoplastic versus thermoset mouthguard materials are exemplified in the strain percentage at tear. The strain percentage at tear was 161% for

Polyshok™ compared with 18% and 4.2% for UMTEN and AMTEN, respectively. This result was not totally unexpected, as thermosets characteristically exhibit low strains and brittle failure. Tensile loading, as in a tear strength test of thermoplastics, causes chains to rearrange and align in pulling direction. In cross-linked networks, this rearrangement is not possible and the same load quickly breaks covalent bonds, leading to material failure. Surprisingly, the strain percentage at tear for UMTEN is unchanged at higher temperatures. We speculate that the increased urethane content in UMTEN provides a mechanism for additional material reinforcement through hydrogen bonding. For real applications, a high strain percentage at tear is not necessary for mouthguard materials because strains are miniscule during use.

Arguably, the impact absorption energy of a mouthguard material is the most important physical property in terms of the potential end-use applications. Impact energy denotes the amount of energy the material is capable of managing, and it can be measured at various temperatures. Logically, any decrease in the amount of force transmitted through the mouthguard into the substrate (tooth/jaw/skull) is an important factor toward injury prevention. Our findings verify that the thermosets UMTEN and AMTEN absorb much more impact energy than the thermoplastic Polyshok™ material at intraoral temperatures (Figure 4). Ostensibly, greater than 90% of impact energy is absorbed for both TENs close to intraoral temperatures. This result is unmatched by any EVA-based commercial material and is perhaps the most advantageous property of the thiolene system.

Although the material properties of UMTEN and AMTEN are promising, there are some important considerations with regards to the optimization and deployment of these systems. Along with other important thermal and mechanical properties yet to be measured (cyclic loading or hysteresis and *in vivo*), the fabrication of mouthguards out of thermoset materials necessitates an appropriate manufacturing technique. In addition, there are potential toxicity issues for *in vivo* use of materials containing acrylates and isocyanates. With the increasing prevalence of three-dimensional (3-D) printing, both of these issues will be alleviated. From the fabrication standpoint, it is now common to use 3-D printing for custom dental restoratives. We would propose the same fabrication method here. In addition, it would be possible to create layered structures whereby the TEN would be sandwiched between layers of FDA-approved polymer (perhaps even EVA). As this technology evolves, there appears to be an opportunity to meet this manufacturing need via deploying UV curable thermosets. Ultimately, it is of great importance to continue making strides in novel material development and testing to offer the best protection possible. The material–human interface remains an important aspect of the sports world and this study represents only a small part of a very large challenge.

CONCLUSIONS

Urethane-based TENs are highly promising as mouthguard material and have matched or exceeded values obtained by commercial EVA-based mouthguard materials in multiple facets of physical, mechanical, and thermal tests. Thermally, UMTEN demonstrates a T_g around intraoral temperature and, although DSC shows postcuring effects, this is typical of networks and may be resolved by a simple annealing procedure. DMA confirms the findings of DSC and show that the monomer-up design approach leads to thiolene behaviors typical of other TENs (i.e., high tan δ_{max} values and narrow glass transition regions).

From a physical testing standpoint, water absorption for EVA systems is lower than AMTEN and UMTENs, but the rate of water uptake is remarkably slower for the thiolene networks. UMTEN, AMTEN and Polyshok™, have comparable tear strengths at room temperature, but at intraoral temperature, Polyshok™ excelled. It may be possible to increase the tear strength of such thiolene networks using a bottom-up approach consisting of careful monomer selection. In other studies, efforts have been made to incorporate urethane and thiourethane linkages into thiolene networks. This could offer tunability of T_g and increased tear strength at all temperatures. UMTEN exhibits excellent impact resistant properties at intraoral temperatures and may be the single system set apart from the others, as this factor has important implications for mouthguard applications. Having more than 90% absorption proximal to intraoral temperature, UMTEN was the best performing material in this regard.

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