Dynamic stress relaxation of orthodontic thermoplastic materials in a simulated oral environment

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Mechanical properties are crucial for screening orthodontic thermoplastic materials for invisible aligners. However, most of previous studies were carried out within laboratory conditions which limit our understanding of the mechanical behaviors of aligners within oral environment. In this study, we studied the dynamic stress relaxation of thermoplastic materials by combination of Bose ElectroForce and a homemade temperature-controlled water bath. The 3-h stress relaxation curves of five orthodontic thermoplastic materials were measured within 37°C water bath as well as comparatively in ambient atmospheric environment (~20°C). The percentage residual stress at 0, 30, 60, 90, 120, 150, and 180 min was selected for statistical analyses. As expected, the experimental results showed that the residual stress within all five materials decreased with time, and that this process was significantly accelerated in the 37°C water bath ($p < 0.05$). Compared with other materials, Erkodur and Masel exhibited slower relaxing rates in the 37°C water bath ($p < 0.05$).

Keywords: Orthodontic thermoplastic materials, Stress relaxation, Invisible aligners, Home-made devices, Simulated oral environment

INTRODUCTION

Thermoplastic materials have been widely used in dental medicine as orthodontic retainers, temporomandibular joint splints, periodontal splints, mouth guards, and bleaching trays due to their outstanding formability, superior shape-memory properties, and excellent esthetic characteristics^{1–4}. Thanks to the development of computer-aided design/computer-aided manufacturing techniques in the past two decades, transparent thermoplastic materials have been precisely designed and fabricated into a series of clear, removable tooth aligners for orthodontics^{5,6}. This orthodontic treatment modality, the most renowned of which is Invisalign, becomes more and more attractive than traditional fixed appliances because it offers a number of advantages including less pain, fewer office visits, virtually transparent, and can be removed for eating and brushing⁷. Despite being increasingly accepted by patients, the mechanical properties and tooth-moving process of orthodontic thermoplastic appliances remains unclear^{8,9}.

Clinically, an archwire, when inserted and deformed, will deliver a corresponding force (*i.e.*, orthodontic force) and move a target tooth towards its memorized position. Over time, the tooth moves, the archwire recovers its shape, and the force decreases until it falls below the ‘threshold’¹⁰. Within its elastic limit, an archwire generally delivers orthodontic force proportional to its deformation (with the exception of certain nickel-titanium wires). Therefore, tooth movement can be predicted and controlled relatively well. In contrast, the stress within thermoplastic materials induced by initial deformation tends to cause the deterioration of mechanical properties with time

because they are viscoelastic¹¹. Such a phenomenon, called stress relaxation, results in additional loss of the ability of a thermoplastic appliance to move a tooth over time, which makes predicting orthodontic forces and tooth movement much more challenging. The time course of stress relaxation of thermoplastic materials within the oral environment is crucial, not only for screening materials intended for dental applications, but also for better understanding the mechanism and process of Invisalign orthodontics.

In the past two decades, several studies have been performed on the mechanical properties of various dental thermoplastic products^{12–15}. These previous studies have shown that the mechanical properties including elastic modulus, tensile yield stress, and stress relaxation depend on the type of thermoplastic material, the measuring technique (*e.g.*, the amount of strain), and testing environment (*e.g.*, temperature and moisture). However, most of previous studies were carried out on the thermoformed samples pretreated by immersing in distilled water at 37°C to simulate intraoral environment. This limits our understanding of the mechanical behaviors of orthodontic thermoplastics within mouth, where both temperature and moisture play a role for a relatively long period. Here, we designed a temperature-controlled water bath that was used to study the dynamic stress relaxation of thermoplastic materials in a simulated oral environment. The 3-h stress relaxation of five commercial orthodontic thermoplastic materials was measured in a water bath at 37°C, as well as in an ambient atmospheric environment. The stress-strain behavior of different materials within different testing environments was compared and further discussed.

MATERIALS AND METHODS

Materials

Five commercial orthodontic thermoplastic materials were used in the present study (Table 1). For stress relaxation testing, all the samples were fabricated into dumbbell-shaped specimens according to the ISO standard 527-3 type 5¹⁶⁾. Briefly, the specimen is 115 mm long, 1.0 mm thick, 25.0 mm wide at both ends, and 6.0 mm wide in the narrow middle part. The narrow middle part of the specimen is ~33.0 mm long. In general, such a configuration will induce deformation or breakage occurring in the middle area (~25.0 mm long) of the specimen when it is stretched from the two ends¹⁷⁾.

Set-up of the temperature-controlled water bath system

To simulate oral environment, we set up a temperature-controlled water bath system that was adapted to the Bose ElectroForce test instrument (ELF 3100, Bose Corp., Framingham, MA, USA). The ELF 3100 is the smallest instrument in the ElectroForce product family and well-suited for micro-characterization of biomaterials and tissues. As shown in Fig. 1, this experimental set-up is composed of three interconnected parts: (1) a glass chamber, 50.0 mm in diameter and 75.0 mm in height, designed to accommodate testing specimens, with one water jacket inlet and outlet located in the upper right and lower left walls, respectively; (2) a water bath that serves as a reservoir, offering temperature-controlled distilled water for the glass chamber and recycling the effluent water from it as well; and (3) a flow control pump that is used to connect the water bath with the glass chamber and regulate fluid flow velocity.

Before experiments, two parallel rectangular openings (~27.0 mm long and ~2.0 mm wide) were cut on the top and bottom of the glass chamber; subsequently, the bottom one was sealed with silicon sealant, dried for 48 h, then cut by a sharp knife across the axis of the sealant. The sealant slit is elastic, thereby producing a squeezing force after the dumbbell-shaped specimen is passed through. To further avoid water leakage during experiments, the possible

fissure between the specimen and slit was wrapped with Parafilm M. A small hole was drilled on the top of the glass chamber across which a thermometer was installed for real-time monitoring of the temperature of the fluid inside the glass chamber.

Once the specimen was loaded, the water bath, flow control pump, and specimen-loaded glass chamber were interconnected, as shown in Fig. 1. An iron support stand and an extension clamp were used to fix the glass chamber, and the specimen was held vertically by the upper (loading) and lower (fixing) clamps of the ELF 3100 equipment. The experiment began once the glass chamber was filled with temperature-controlled water from the water bath. The temperature of the

Fig. 1 Schematic diagram of the temperature-controlled water bath and mechanical testing of the orthodontic thermoplastic materials in a simulated oral environment.

Table 1 Characteristics and description of the materials used in this study

Product name	Thickness	Manufacturer	Item number	Component (MSDS) ^a
Erkodur	1.0 mm	Erkodent Erich Kopp, Pfalzgrafenweiler, Germany	521210	Polyethyleneterephthalat-Glycol Copolyester (PETG)
Biolon	1.0 mm	Dreve Dentamid, Unna, Germany	D-42396	Polyethylene terephthalate
Masel ^b	1.0 mm	Ortho Organizers Inc., Carlsbad, CA, USA	2032-081	Copolyester
Keystone ^b	1.0 mm	Keystone Industries, Myerstown, PA, USA	9615060	Copolyester
Duran	1.0 mm	Scheu-dental, Iserlohn, Germany	3415	PETG

^a Component as obtained from the manufacturers' Material Safety Data Sheet.

^b The name of manufacturer is used as no specific product name is found.

water within the glass chamber was controlled by regulating the temperature of the water reservoir and the fluid velocity through the pump. The idea is to keep the water within the glass chamber nearly full and regulate the fluid recycling so it is as slow as possible (for less disturbance and for economic reasons), which allows the specimen to be measured within water bath at target temperature.

Stress relaxation testing and statistics

Stress relaxation testing was carried out at 37°C within the water bath, and in an ambient atmospheric environment (~20°C), with the ELF 3100 equipment. Each test consisted of three parts; 15 s for stretching the specimen up to 1.25 mm (*i.e.*, 5 mm/min of tensile-velocity and a total ~5% of strain), 5 s for system stabilization, and 3 h for stress relaxation. Three specimen duplicates were measured for each material in both test environments. Stress values were recorded at 0.02 s intervals. For each specimen, the percentage residual stress was calculated as $(N_n/N_0) \times 100$, where N_n is the residual stress value at relaxing time T_n , and N_0

is the initial stress value at zero minutes. It should be clarified that the 5% strain was selected here because it was about 50% of the yield strain, which was previously determined to be 9–10% for those batches. To minimize intra-sample variance, stress relaxation curves were drawn based on the percentile of residual stress.

To compare the differences between the two testing conditions and among different materials, the residual stress percentiles at 0, 30, 60, 90, 120, 150, and 180 min were selected and analyzed with the statistical software SPSS v17.0 (SPSS Inc., Chicago, IL, USA). Repeated-measures analysis of variance (ANOVA), independent *t* test, multi-way ANOVA, and Bonferroni's test were used to determine the presence of statistically significant differences.

Additionally, initial stress at 5% strain of above 30 specimens, with and without glass-chamber-loading, was comparatively measured to confirm whether or not the physical fixing of the specimen in the glass chamber would affect the stress measurement. As shown in Tables 2 and 3, the initial stress values are

Table 2 Comparison of initial and residual stress of the different materials in the atmospheric environment

Materials	Initial stress (MPa)	Residual stress, % (SD)						
		0 min	30 min	60 min	90 min	120 min	150 min	180 min
Erkodur	41.66 (1.63)	100.00 (0.00)	94.58 (1.92)	93.48 (2.08)	92.71 (2.26)	92.32 (2.13)	92.01 (1.86)	91.88 (1.72)
Biolon	35.29 (1.68)	100.00 (0.00)	93.50 (1.56)	92.11 (1.89)	91.26 (2.00)	90.54 (2.00)	89.93 (2.19)	89.51 (2.21)
Masel	41.33 (6.51)	100.00 (0.00)	93.67 (2.43)	92.14 (2.65)	91.17 (2.91)	90.50 (3.02)	89.82 (3.20)	89.35 (3.52) ^a
Keystone	45.67 (0.56)	100.00 (0.00)	91.62 (1.07)	89.82 (1.67)	88.56 (1.64)	87.52 (1.44) ^a	86.76 (1.49) ^a	86.10 (1.66) ^a
Duran	40.39 (1.38)	100.00 (0.00)	91.22 (1.48)	89.41 (1.58)	88.09 (1.69) ^a	87.29 (1.58) ^a	86.50 (1.82) ^a	85.80 (1.59) ^a
Average	40.87 (4.36)	100.00 (0.00)	92.92 (1.43)	91.39 (1.72)	90.36 (1.96)	89.63 (2.16)	89.01 (2.33)	88.53 (2.56)

SD, standard deviation.

^a Significantly different from Erkodur at the same time point by Bonferroni's test.

Table 3 Comparison of the initial and residual stress of the different materials in the 37°C water bath

Materials	Initial stress (MPa)	Residual stress, % (SD)						
		0 min	30 min	60 min	90 min	120 min	150 min	180 min
Erkodur	37.26 (2.55)	100.00 (0.00)	85.82 (2.17)	78.93 (2.29)	74.49 (2.26)	71.73 (2.19)	69.10 (2.09)	66.49 (2.21)
Biolon	37.70 (2.64)	100.00 (0.00)	73.16 (2.15) ^{a,b}	62.02 (3.22) ^{a,b}	58.65 (3.45) ^{a,b}	57.36 (4.09) ^{a,b}	54.69 (2.92) ^{a,b}	53.24 (3.19) ^{a,b}
Masel	41.46 (1.87)	100.00 (0.00)	83.25 (1.77)	77.45 (2.17)	73.26 (2.40)	69.39 (2.63)	67.51 (2.66)	65.27 (2.51)
Keystone	42.24 (4.30)	100.00 (0.00)	72.94 (3.64) ^{a,b}	64.15 (4.03) ^{a,b}	58.99 (3.59) ^{a,b}	56.05 (3.93) ^{a,b}	52.64 (3.97) ^{a,b}	50.22 (4.14) ^{a,b}
Duran	37.32 (2.47)	100.00 (0.00)	77.12 (4.38) ^{a,b}	69.96 (5.28) ^{a,b}	65.56 (5.32) ^{a,b}	60.73 (5.01) ^{a,b}	57.12 (4.20) ^{a,b}	55.48 (5.00) ^{a,b}
average	39.20 (3.33)	100.00 (0.00)	76.62 (4.82)	68.40 (6.91)	64.12 (6.88)	60.88 (6.00)	57.99 (6.61)	56.05 (6.51)

SD, standard deviation.

^a Significantly different from Erkodur at the same time point by Bonferroni's test.

^b Significantly different from Masel at the same time point by Bonferroni's test.

39.20±3.33 MPa and 40.87±4.36 MPa with and without chamber loading, respectively. No obvious difference (independent *t* test, *p*=0.209) was found, indicating that the potential influence of physical fixing on the stress behavior is rather weak or negligible. This result is consistent with the previous assumption that the deformation and, therefore, the stress originate from the middle narrow part of the dumbbell-shaped specimen^{16,17}, and also indicates that the differences in stress relaxation observed here should result from the testing environments (*i.e.*, temperature and moisture) or/and material types.

RESULTS

Experiments show that under an ambient atmospheric environment, the temperature in the glass chamber could be well controlled at ~37.0°C when the temperature setting of the water reservoir was 38.0°C and the flow velocity was ~28.0 mm/min (data not shown).

Figure 2 and Tables 2 and 3 show the stress relaxation curves and statistical results, respectively. It is clear that in both environments, all materials exhibit time-dependent stress-strain behavior as expected. The residual stress at each selected time

Fig. 2 Stress relaxation curves of the five tested materials (a–e) and average residual stress (%) at selected time points (f) under both environments.

For each material, the stress relaxation curves were averaged from three individual specimens; and only the standard deviation values at 30, 60, 90, 120, 150, and 180 min were shown for comparison with the selected average residual stress values of different materials. Compared with those within ambient atmospheric environment, the stress relaxation curves obtained within 37°C-water bath are a little noisy, possibly due to mechanic disturbance of water flow.

*Significantly different from the average residual stress at the same time point in the ambient atmospheric environment.

point is significantly lower than the previous one ($p < 0.05$). However, stress-strain behavior in the 37.0°C water bath was significantly different from that in the ambient atmospheric environment ($p < 0.05$, material type not included as a variable). Specifically, at each selected time point, residual stress in the former environment was significantly lower than the latter ($p < 0.05$; material type not included as a variable). These results confirm that a hygrothermal aging environment can accelerate stress relaxation of thermoplastic materials^{18–21}.

The stress relaxation behavior also differs among different materials within the same testing environment ($p < 0.05$). More specifically, within the ambient atmospheric environment, Erkodur shows the slowest relaxing rate. Its residual stress is significantly higher than Duran from 90–180 min, Keystone from 120–180 min, and Masel at 180 min ($p < 0.05$). In contrast, in the 37.0°C water bath, Erkodur and Masel had much slower stress relaxation than the other three materials, *i.e.*, the residual stress of Erkodur and Masel is higher than the other materials at all selected time points (except at zero min).

It should be noted that there was no obvious plateau of stress relaxation for all materials, especially for those under the simulated oral environment. A reasonable interpretation might be short duration or/and relatively small deformation (5% strain) used in the present study.

DISCUSSION AND CONCLUSIONS

The mechanical properties of thermoplastic materials are known to strongly depend on the material types and environmental conditions in which they are used^{14,15}. Understanding the mechanical behaviors of orthodontic thermoplastics within an oral environment is an essential requisite for screening materials for appliances. Such a study is also crucial to better understand the orthodontic mechanism and process of Invisalign. In the past decade, various approaches or specific instruments have been developed to study the mechanical properties (including instantaneous forces and moments) of different thermoplastic materials in clinically-relevant situations^{22–24}. This study developed a practical and economical temperature-controlled water bath system, which holds the specimen under a controllable environment. Through a combination of commercial testing equipment (ELF 3100), dynamic stress relaxation of thermoplastic materials can be measured within a simulated oral environment (*e.g.*, water bath at 37.0°C as in this study). Furthermore, if needed this system can also be used to characterize the mechanical properties of thermoplastic materials at various temperatures and in fluid environments by regulating the temperature of the water bath or/and changing the circulated liquid (*e.g.*, artificial saliva).

The present study clearly shows that the hygrothermal aging environment can significantly accelerate the stress relaxation of orthodontic

thermoplastic material, but the mechanism is still unclear. Numerous studies indicate water absorption may contribute to the stress relaxation of thermoplastic materials. Bao *et al.*¹⁸ found that in bismaleimide resin, absorbed water accelerated the relaxation of the matrix through a process called plasticization. Boubakri *et al.*^{19,20} confirmed this irreversible phenomenon in thermoplastic polyurethane and pointed out that the nature of plasticization was increased mobility of chains' macromolecular segments. The authors believed that water absorption may induce a breakup of the intrachain and/or interchain hydrogen bonds and modify the free volume of the polymers. Hollande *et al.*²¹ also observed that absorbed water may wash out soluble substances in polymers, which accelerates the degradation process. On the other hand, thermal aging was found to increase mechanical properties like Young's modulus and the tensile stress of polymers. However, in a hygrothermal aging environment, temperature promoted water diffusion in polymers, therefore accelerating degradation¹⁹. In our study, significant differences between materials arises since 90 min in the atmospheric environment, whereas it is observed from the start in the 37°C-water-bath environment. This confirms that the process of water absorption and temperature discriminately taxes different materials, probably owing to their different susceptibilities to water and/or the amount of water intake.

The ideal orthodontic force should be a 'light, continuous force', as stated by Proffit¹⁰. For tipping movement, the ideal force is suggested as 35–60 g. This study indicates that both material type and the environment where they are used should be considered in clinical situations. For instance, materials delivered only 42.29–66.56% of their initial forces after immersion in the 37°C water bath for 3 h. Therefore, the 'ideal' initial force might be unable to activate the biochemical process in the periodontal ligament (PDL) over time. Moreover, compared with the 37°C water bath used in this study, the *in vivo* oral environment is much more complicated, not only in chemistry but also in periodic removal and reinsertion of aligners. Therefore, further experiments dedicated to studying the mechanical properties of orthodontic thermoplastics within more temperature, duration, and chemical environments, *i.e.*, periodically altered temperature, weekly or monthly duration, artificial saliva, and various thickness of specimen, are extremely needed.

Based on this study performed in a simulated oral environment, Masel and Erkodur are relatively less affected among the five materials, showing a slower stress relaxation rate with time in the hygrothermal aging environment than the other three materials. A further comparative study on the chemical composition and molecular structure of these five materials is needed in the near future to understand the relationship between the mechanical properties and the chemico-physical features. Nevertheless, this study set up a temperature-controlled water bath system which can be used to study the mechanical properties

of orthodontic thermoplastic materials within temperature, liquid, and time-controlled environments. From a clinical perspective, Masel and Erkodur might be good candidates for delivering more stable forces to target teeth.

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REFERENCES

- 1) Sheridan JJ, Ledoux W, McMinn R. Essix technology for the fabrication of temporary anterior bridges. *J Clin Orthod* 1994; 28: 482-486.
- 2) Sheridan JJ, Armbruster P. Bleaching teeth during supervised retention. *J Clin Orthod* 1999; 33: 339-344.
- 3) Oh WS, Wang C. Use of thermoplastic vacuum-formed matrix for emergency management of crown-root fracture. *J Prosthet Dent* 2007; 98: 335-336.
- 4) Lloyd T, Nightingale C, Edler R. The use of vacuum-formed splints for temporary intermaxillary fixation in the management of unilateral condylar fractures. *Br J Oral Maxillofac Surg* 2001; 39: 301-303.
- 5) Joffe L. Invisalign: early experiences. *J Orthod* 2003; 30: 348-352.
- 6) Rosvall MD, Field HW, Ziuchkovski J, Rosenstiel SF, Johnston WM. Attractiveness, acceptability, and value of orthodontic appliances. *Am J Orthod Dentofacial Orthop* 2009; 135: 276-288.
- 7) Jeremiah HG, Bister D, Newton JT. Social perceptions of adults wearing orthodontic appliances: a cross-sectional study. *Eur J Orthod* 2010; 33: 476-482.
- 8) Kravitz ND, Kusnoto B, BeGole E, Obrez A, Agran B. How well does Invisalign work? A prospective clinical study evaluating the efficacy of tooth movement with Invisalign. *Am J Orthod Dentofacial Orthop* 2009; 135: 27-35.
- 9) Kuncio D, Maganzini A, Shelton C, Freeman K. Invisalign and traditional orthodontic treatment postretention outcomes compared using the American Board of Orthodontics objective grading system. *Angle Orthod* 2007; 77: 864-869.
- 10) Proffit WR, Fields HW, Sarver DM. Contemporary orthodontics. 4th ed. St. Louis: Mosby; 2007.
- 11) Tricca R, Li C. Properties of aligner material Ex30. In: Tuncay OC. The invisalign system. Philadelphia: Quintessence; 2006. p. 177-186.
- 12) Zhang N, Bai Y, Ding X, Zhang Y. Preparation and characterization of thermoplastic materials for invisible orthodontics. *Dent Mater J* 2011; 30: 954-959.
- 13) Goldberg AJ, Libler SA, Burstone CJ. Viscoelastic properties of an aesthetic translucent orthodontic wire. *Eur J Orthod* 2010; 33: 673-678.
- 14) Ryokawa H, Miyazaki Y, Fujishima A, Miyazaki T, Maki K. The mechanical properties of dental thermoplastic materials in a simulated intraoral environment. *J Orthodontic Waves* 2006; 65: 64-72.
- 15) Gould TE, Piland SG, Shin J, Hoyle CE, Nazarenko S. Characterization of mouthguard materials: Physical and mechanical properties of commercialized products. *Dent Mater* 2009; 25: 771-780.
- 16) ISO 527-3. Plastics —Determination of tensile properties— Part 3: Test conditions for films and sheets. ISO; 1995.
- 17) ISO 527-1. Plastics —Determination of tensile properties— Part 1: General principles. ISO; 1993.
- 18) Bao LR, Yee AF, Lee CYC. Moisture absorption and hygrothermal aging in a bismaleimide resin. *Polymer* 2001; 42: 7327-7333.
- 19) Boubakri A, Haddar N, Elleuch K, Bienvenu Y. Impact of aging conditions on mechanical properties of thermoplastic polyurethane. *Mater Design* 2010; 31: 4194-4201.
- 20) Boubakri A, Elleuch K, Guermazi N, Ayedi HF. Investigations on hygrothermal aging of thermoplastic polyurethane material. *Mater Design* 2009; 30: 3958-3965.
- 21) Hollande S, Laurent JL. Weight loss during different weathering tests of industrial thermoplastic elastomer polyurethane-coated fabrics. *Polym Degrad Stabil* 1998; 62: 501-505.
- 22) Hahn W, Dathe H, Fialka-Fricke J, Fricke-Zech S, Zapf A, Kubein-Meesenburg D, Sadat-Khonsari R. Influence of thermoplastic appliance thickness on the magnitude of force delivered to a maxillary central incisor during tipping. *Am J Orthod Dentofacial Orthop* 2009; 136: 12.e1-e17.
- 23) Hahn W, Engelke B, Jung K, Dathe H, Fialka-Fricke J, Kubein-Meesenburg D, Sadat-Khonsari R. Initial forces and moments delivered by removable thermoplastic appliances during rotation of an upper central incisor. *Angle Orthod* 2010; 80: 239-246.
- 24) Barbagallo LJ, Shen G, Jones AS, Swain MV, Petocz P, Darendeliler MA. A novel pressure film approach for determining the force imparted by clear removable thermoplastic appliances. *Ann Biomed Eng* 2008; 36: 335-341.