

Original Article

Effects of various cleaning agents on polypropylene and copolyester thermoplastic orthodontic retainer materials



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المخلص

أهداف البحث: لتقييم ومقارنة معامل الانحناء ونفاذية الضوء بين مادة البولي بروبيلين ومادة الكوبوليستر البلاستيكية الحرارية وبين عوامل التنظيف الأربعة على كل مادة بعد التعرض طويل الأمد لطرق التنظيف المختلفة.

طرق البحث: تم استخدام مائة وعشرين قطعة موحدة من مادة المثبتات البولي بروبيلين والكوبوليستر في هذه الدراسة بعد تشكيلها بالحرارة. تم تقسيمها بالتساوي إلى ست مجموعات فرعية: (كما وردت، اللعاب الاصطناعي، الكلور هيكسدين، غسول الفم الكحولي وغير الكحولي، وحبوبات تنظيف المثبت). خضعت هذه القطع لعملية تنظيف بموجب البروتوكول التالي: 15 دقيقة غمر، ثلاث مرات اسبوعياً، لمدة ثلاثة أشهر. بعد ثلاثة أشهر، تم قياس معامل الانحناء ونفاذية الضوء لجميع العينات باستخدام اختبار الانحناء بثلاث نقاط ومقياس الطيف الضوئي على التوالي. تم تطبيق اختبار تحليل التباين الأحادي الاتجاه واختبار تي المستقل لمقارنة الوسائل، وتم استخدام اختبار التوكي عندما كان هناك فرق كبير.

النتائج: أظهرت النتائج الإحصائية لكل نوع من أنواع المثبتات أن قيم معامل الانحناء لمثبت الكوبوليستر تختلف إحصائياً عن مادة البولي بروبيلين في غسول الفم الكلور هيكسدين، وغسول الفم الكحولي، وحبوبات تنظيف المثبت. بينما كان للكوبوليستر فرق معنوي في نفاذية الضوء من البولي بروبيلين في جميع الظروف. لم يكن هناك فرق معنوي في قيم معامل الانحناء بين الظروف المختلفة، بينما كان هناك فرق معنوي في نفاذية الضوء بين غسول الفم الكحولي والظروف المختلفة لمادة البوليستر.

الاستنتاجات: بناءً على هذه النتائج، يمكن استخدام أي عامل تنظيف بأمان لكتات المادتين دون التأثير على معامل المرونة. ومع ذلك، فإن غسول الفم الكحولي قلل من نفاذية الضوء لنوع مثبت الكوليستر.

الكلمات المفتاحية: الخاصية الفيزيائية؛ البولي بروبيلين؛ منظف مثبت تقويم الأسنان؛ مثبت تقويم الأسنان المشكل بالتقريع الحراري؛ النفوذية

Abstract

Objectives: This study aimed to evaluate and compare the effects of four cleaning agents on the flexural modulus and light transmittance properties of polypropylene and copolyester thermoplastic retainer materials after long-term exposure.

Methods: A total of 120 pieces of standardized copolyester and polypropylene retainer materials were tested after being thermoformed. They were divided equally into six subgroups: as-received, artificial saliva, chlorhexidine, alcohol-based and alcohol-free mouthwashes, and Retainer Brite®. The pieces were subjected to a cleaning process involving 15 minute immersion three times weekly for 3 months. The flexural modulus and light transmittance were then measured for all specimens with three point bending tests and spectrophotometry, respectively. One-way ANOVA and independent samples t-test were applied to compare the means, and Tukey's post hoc test was used in cases of significant differences. The threshold for significance was 0.05.

Results: For each retainer type, the statistical results revealed that the flexural modulus values of the copolyester retainer material significantly differed from those of polypropylene material under chlorhexidine mouthwash, alcohol-based mouthwash, and Retainer Brite® conditions. Copolyester and polypropylene showed significant differences in light transmittance under all conditions. No significant difference in flexural modulus values was observed among conditions, whereas

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significant differences in light transmittance were observed between alcohol-based mouthwash and the other conditions for copolyester material.

Conclusions: According to our results, any cleaning agent can be safely used for both materials without affecting the elastic modulus. However, alcohol-based mouthwash decreases the light transmittance of copolyester retainer material.

Keywords: Physical property; Polypropylene material; Retainer cleaning; Thermoplastic retainer; Translucency

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Introduction

After orthodontic treatment is completed, and orthodontic appliances are removed, teeth have a tendency to revert back to their original positions.¹ In general, stability can be achieved through a retention protocol using permanent or removable retainers, or combinations thereof.²

Vacuum formed retainers (VFR) are widely used removable retainers produced from thermoplastic materials by vacuum or air pressurized machines.³ Because of their esthetic and translucent characteristics, clear thermoplastic retainers have increased in popularity.^{4–6}

Intraoral temperature changes, as well as cyclic deflections, have been found to alter the physical properties of thermoplastic retainers.⁷ Previous studies have shown that orthodontic appliances have poor wear resistance and durability after short service periods; additionally, similar studies on mouth guards made from comparable thermoplastic orthodontic materials have indicated that aging causes various dimensional changes, depending on the material and processing techniques.⁸ Polyester, polypropylene, and polyurethane are common polymers used to construct thermoplastic retainers. Polyethylene terephthalate is a polyester that is present as an amorphous non-crystallizing substance. Because of its outstanding creep properties, fatigue resistance, and dimensional stability, polyethylene terephthalate is the most commonly used thermoplastic material for clear orthodontic appliances.⁹

Because retainers are required to avoid orthodontic relapse, to enable long-term use of the retainers, an efficient cleaning procedure is crucial. Several drawbacks are associated with the long-term use of transparent retainers, including loss of translucency and integrity of the material, discoloration, and retention of plaque and calculus.^{10,11}

Although clear retainers have grown in popularity because of their aesthetic appeal, their proper cleaning and maintenance pose challenges. Transparent retainers can be cleaned in two ways: mechanically or chemically. Tooth brushing and/or the use of an ultrasonic system are examples of mechanical cleaning. Chemical washing, in contrast, entails immersing retainers in antimicrobial/refreshing solutions.¹²

To our knowledge, no studies have compared the effects of chlorhexidine (CH) mouthwash, alcohol-based (AL) and alcohol-free (ALF) mouthwashes, and Retainer Brite® (RB) and the effects of artificial saliva (AS) only on two materials. Thus, the aims of this study were to evaluate and compare the light transmittance (T%) and flexural modulus among the four cleaning agents on polypropylene and copolyester thermoplastic retainer materials after long-term exposure to various cleaning methods.

The null hypothesis was that copolyester and polypropylene would not show differences in flexural modulus and light transmittance before (as-received; AR) and after being subjected to the above conditions.

Materials and Methods

Sheets of the thermoplastic materials copolyester (Clear Advantage™ Series I Clear Retainer Material, OrthoTechnology-Tampa, Florida, USA) and polypropylene (Clear Advantage™ Series II Durable Retainer Material, OrthoTechnology-Tampa, Florida, USA) were thermoformed with a pressure molding machine device (BIOSTAR®, Scheu Dental, Iserlohn, Germany). First, the sheets of copolyester and polypropylene were heated at 220 °C for 40 and 60 sec, respectively. They were then pressed and vacuumed over a stainless-steel block with dimensions of 55 mm × 18 mm × 6 mm (Figure 1). The thermoformed sheets were cut into rectangular pieces with standard dimensions of 50.8 mm × 12.7 mm × 1.0 mm with a computerized numerical control cutting machine (CNC, Zhejiang Kaida Machine Tool Co., Ltd, Zhejiang, China). Measurements were performed according to the “Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials” (ASTM D790), which specifies alternative test specimen sizes for materials less than 1.6 mm thick¹³ (Figure 2). Because the sheets used to create the specimens were thinner than the standard thickness provided in ANSI/ADA Standard No. 139, “Dental Base Polymers,” this ASTM standard was used instead of Standard No. 139.¹⁴

A total of 120 pieces (60 from each thermoplastic material) were prepared. The samples were randomly divided into six subgroups (with ten pieces per subgroup) as follows: 1. AL mouthwash (Listerine® Cool Mint Mouthwash™, Johnson & Johnson Consumer, Inc.; New Brunswick, NJ, USA), 2. ALF mouthwash (Listerine® Cool Mint Zero Alcohol Mouthwash™, Johnson & Johnson Consumer, Inc.; New Brunswick, NJ, USA) (ALF), 3. CH mouthwash (Corsodyl® original mouthwash, GlaxoSmith Kline, Brentford, UK), 4. RB (OrthoTechnology-Tampa, Florida, USA), 5. AS (active control), and 6. AR, which served as the baseline condition.

The AS formula was a modified Carter’s solution as follows¹⁵: 1.5 g NaHCO₃, 1.2 g KCl, 0.7 g NaCl, 0.26 g Na₂HPO₄, 0.2 g K₂HPO₄, 0.13 g urea, and 0.33 g KSCN.

The samples were stored in glass containers separately containing AS inside the incubator at 37 °C throughout the study. The samples of subgroups 1, 2, 3, and 4 were removed from the AS, rinsed with distilled water, and subjected to a cleaning procedure with the indicated cleaning agents for 15 min three times weekly for 3 months^{16–18} (Figure 3). After

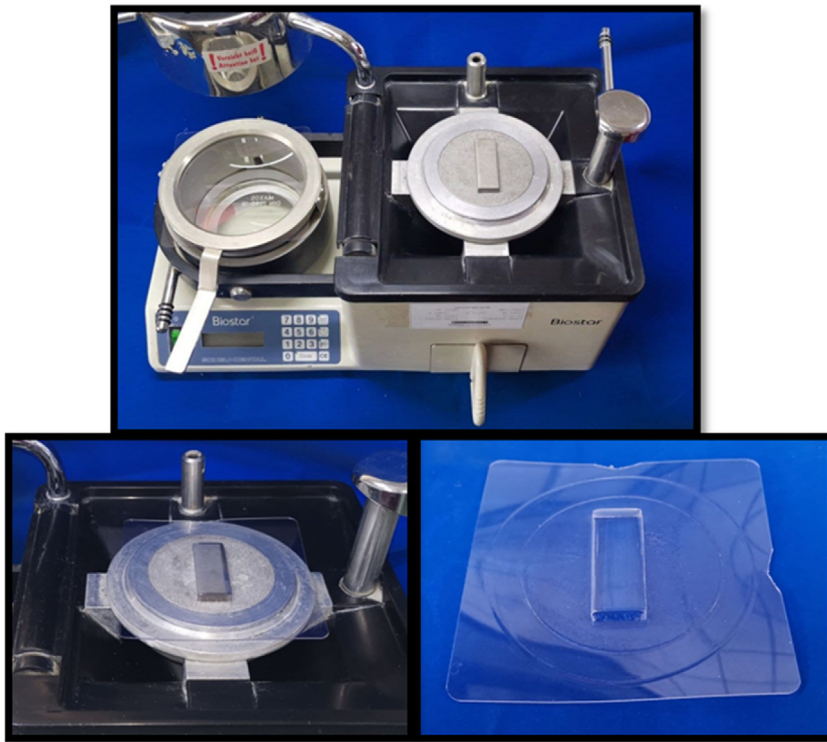


Figure 1: Thermoforming of clear retainer sheets.



Figure 2: Thermoformed plastic material after being cut to the required dimensions.

immersion, each sample was rinsed with distilled water and stored in AS at 37 °C. All specimens were then subjected to tests for flexural modulus and light transmittance (T%).

Abbreviations: Vacuum formed retainer (VFR), Light transmittance (T%), Alcohol-based mouthwash (AL), Alcohol-free mouthwash (ALF), Chlorhexidine mouthwash (CH), Retainer Brite® (RB), Artificial saliva (active control) (AS), As received (AR).

Three point bending tests

Three point bending tests were used to evaluate the load-deflection properties of VFR, because they accurately model

the clinical practice of VFR insertion into a patient's mouth.^{16–18}

An Instron universal mechanical testing machine (H50KT, A Tinius Olsen, Salfords, UK) was used to conduct three-point bending tests of the specimens to measure the flexural modulus.

Before the testing, the name, width, and thickness of each specimen were entered into QMat Material Testing and Analysis software (version 4.53, A Tinius Olsen, Salfords, UK). Each specimen was loaded at a 1 mm/min cross-head speed, below the yield strength of the material in the linear-elastic area of its stress/strain curve^{16–18} (Figure 4).



Figure 3: Sample storage. CP: Copolyester. PP: Polypropylene. AR: As received. AS: Artificial saliva. CH: Chlorhexidine mouthwash. AL: Alcohol-based mouthwash. FAL: Free-alcohol.

Light transmittance ($T\%$) tests

$T\%$ tests were performed with a double-beam pathway UV/visible spectrophotometer (LAMBDA™ 365, PerkinElmer Inc., Waltham, USA). After the specimen was placed in the sample cell compartment, the light beam from the source was passed through the monochromator, and then the light beam was split into a double beam with the beam splitter; each beam was passed through one of two sample compartments: the reference cell compartment containing air and the sample cell compartment containing the specimen (Figure 5).

The $T\%$ of each wavelength, from 380 nm to 740 nm, was measured automatically after being calibrated and integrated in UV Win Lab Software (version 7.0, PerkinElmer Inc., Waltham, USA) through division of the intensity of the light leaving the sample (I) by the intensity of the light entering the sample (I^0). Finally, the overall $T\%$ for each specimen was calculated as the average for all integrated $T\%$.

Statistical analysis

A computer program (SPSS, version 26, Chicago, USA) was used to perform the statistical analysis. The mean and

standard deviation (SD) were calculated for each data set. The normality of the distribution and the equality of variances between groups were tested with Shapiro–Wilk and Levene tests. Because the data were normally distributed, parametric tests (one-way ANOVA and unpaired T-test) were used. A p -value <0.05 was considered statistically significant.

Results

The means and SDs of the flexural modulus values for copolyester and polypropylene retainer materials in AR form and after immersion in different agents is presented in Table 1.

Generally, for the copolyester material, the highest mean value of the flexural modulus was observed in the RB

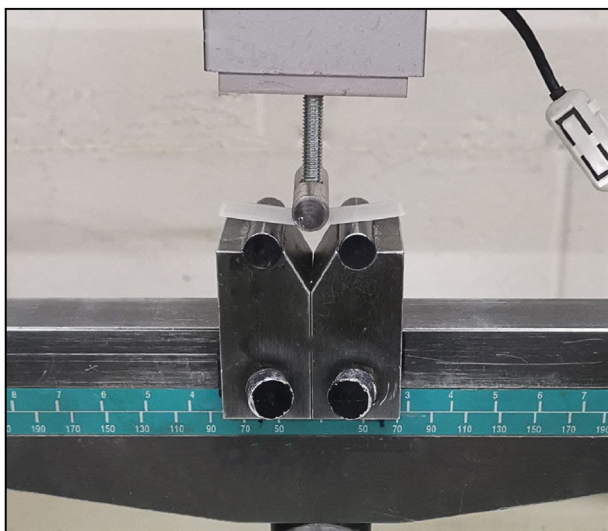


Figure 4: Three point bending test.



Figure 5: Color measurement test.

Table 1: Mean values, standard deviations and comparison of the flexural modulus between copolyester and polypropylene retainer materials as received and after exposure to different conditions.

Conditions	Copolyester		Polypropylene		Comparison	
	Mean	SD	Mean	SD	t-test	P-value
AR	1264.50	±156.180	1230.70	±178.506	0.451	0.658
AS	1289.30	±105.883	1229.60	±170.461	0.941	0.362
CH	1306.10	±112.390	1009.00	±171.407	4.584	0.000**
AL	1276.50	±87.897	1072.00	±232.463	2.602	0.024*
ALF	1289.10	±139.254	1206.90	±206.612	1.043	0.311
RB	1325.30	±121.228	1127.80	±163.386	3.070	0.007**
F-test	0.309		2.383			
P-value	0.905		0.050			

(* Significant difference ($p \leq 0.05$) (** Highly significant difference ($p \leq 0.01$)).

AR: As received. AS: Artificial saliva. AL: Alcohol-based mouthwash.

CH: Chlorhexidine mouthwash. ALF: Alcohol-free mouthwash. RB: Retainer Brite®.

Table 2: Mean values, standard deviations and comparison of T% between copolyester and polypropylene retainer materials as received and after exposure to different conditions.

Conditions	Copolyester		Polypropylene		Comparison	
	Mean	SD	Mean	SD	t-test	P-value
AR	86.20	±1.55	16.40	±2.01	86.949	0.000**
AS	86.31	±1.15	16.40	±2.36	83.925	0.000**
CH	86.129	±2.50	18.40	±3.17	52.996	0.000**
AL	75.00	±4.62	17.54	±1.63	37.091	0.000**
ALF	86.34	±2.59	17.40	±1.57	72.134	0.000**
RB	87.20	±1.55	17.70	±1.94	88.344	0.000**
F-test	26.611		1.282			
P-value	0.000**		0.285			

(* Significant difference ($p \leq 0.05$) (** Highly significant difference ($p \leq 0.01$)).

AR: As received. AS: Artificial saliva. AL: Alcohol-based mouthwash.

CH: Chlorhexidine mouthwash. ALF: Alcohol-free mouthwash. RB: Retainer Brite®.

subgroup followed by CH, and the lowest mean value was observed in the AR subgroup, but the difference was non-significant ($p > 0.05$).

For the polypropylene material, the highest flexural modulus was recorded in the AR group followed by the AS group, and the lowest mean value was observed in the CH group, but the difference was non-significant ($p > 0.05$).

The effects of various cleaning agents on the flexural modulus values of the two retainer materials were subsequently tested. Copolyester had a significantly higher flexural modulus than polypropylene in the CH, AL, and RB subgroups only (Table 1).

The means and standard deviations of T% for the copolyester and polypropylene retainer materials in the AR condition and after exposure to the cleaning conditions are presented in Table 2.

In general, the T% mean value for copolyester retainer material type was highest under the RB condition and lowest under the AL condition, and the difference was significant ($p \leq 0.05$). Post hoc Tukey's HSD tests revealed a significant difference in T% between the AL subgroup and other conditions (Table 3).

A higher T% mean value for polypropylene material was recorded in the CH condition, and the lowest mean values

Table 3: Post hoc Tukey's HSD test for multiple comparisons among groups.

Material	Condition	Mean difference	p-value	
Copolyester	AR	AS	-1.00	1.000
		CH	0.08	1.000
		AL	11.20	0.000**
		ALF	-0.14	1.000
		RB	-1.00	0.955
	AS	CH	0.19	1.000
		AL	11.30	0.000**
		ALF	-0.03	1.000
		RB	-0.89	0.972
		CH	11.11	0.000**
	CH	ALF	-0.22	1.000
		RB	-1.08	0.939
AL		11.34	0.000**	
AL	ALF	-11.34	0.000**	
	RB	-12.20	0.000**	
ALF	RB	-0.85	0.977	

(**) High significant difference ($p \leq 0.01$).

AR: As received. AS: Artificial saliva. AL: Alcohol-based mouthwash.

CH: Chlorhexidine mouthwash. ALF: Alcohol-free mouthwash. RB: Retainer Brite®.

were observed in the AR and AS groups, but the differences were non-significant ($p > 0.05$).

The effects of various conditions on the T% of different retainer materials was then investigated. Copolyester had a significantly higher T% than polypropylene materials under all conditions (Table 2).

Discussion

Orthodontists can now choose from a variety of thermoplastics for retainer appliances. Furthermore, patients can now use a variety of cleaning agents to keep their retainers clean. Transparent retainers' excellent aesthetics and fatigue resistance are the most appealing features to patients and orthodontists in this regard. Therefore, the goal of this study was to evaluate both the light transparency and the flexural modulus of various thermoplastic materials after cleaning with various cleaning agents.

The statistical results demonstrated that both the copolyester and polypropylene materials, before being exposed to different cleaning agents, had comparable flexural modulus values. This finding contradicts Wible's¹⁹ claim that the flexural modulus values of both materials differ at baseline. However, according to Ryokawa et al.²⁰ and Zhang et al.,²¹ the difference between these findings might be due to the production process.

Except for ALF, all cleaning conditions resulted in differences in the flexural modulus of the two materials, making the copolyester material stiffer and the polypropylene material more flexible.

Glycerol, benzoic acid, and citric acid, which are present in CH, AL, and RB mouthwashes, respectively, may contribute to increasing the stiffness of copolyester by degrading or damaging the material.²² However, most polymers, including copolyester, are altered dramatically over time by oxidation and degradation after exposure to oxygen, heat, light, and the production process, thus leading to increased stiffness, as described by Piiroja and Lippmaa,²³ Kholodovych,²⁴ Sepe,²⁵ and the Polymer Properties Database.²⁶ In contrast, low hydrolytic stability, wherein water hydrolysis produces physiochemical changes, results in swelling and irreversible degradation, as described by Modjarrad and Ebnesajjad.²⁷ This finding may also explain the increased stiffness.

CH mouthwash contains glycerol plasticizers. Plasticizers are typically used to give polymers more flexibility and toughness. Polypropylene's molecular organization is affected by morphological modifications, such as cross linking. Therefore, glycerol increases the crystallinity of polypropylene and decreases the flexural modulus, as described in earlier studies.^{28–33}

According to Sawalha et al.,³⁴ the inclusion of citric acid, which also serves as a plasticizer, in RB causes a loss in strength and elasticity, while increasing flexibility as the crystallinity increases. According to European Plasticisers,³⁵ AL containing benzoic acid also acts as a plasticizer that increases the flexibility of polypropylene.

The increase in the stiffness or flexibility of the tested materials after exposure to the various conditions, in comparison with the AR condition, is considered unacceptable. A higher elastic modulus implies higher rigidity and a steeper slope. Therefore, although a higher elastic modulus will

improve retention, it will increase the difficulty in wearing and removing the appliance. Low modulus material, in contrast, can facilitate easy insertion and removal of the appliance, but cannot provide sufficient forces to achieve tooth retention.³⁶ In the current study, the changes in the elastic modulus were not statistically significant for each material. However, greater exposure time to the cleaning agents might cause these effects to become statistically significant; thus, further investigations may be required.

The statistical results also revealed no differences in flexural modulus among the conditions for each material type. This result is in agreement with Wible et al.'s¹⁸ and Brehove's³⁷ findings that AL and RB have no effect on the flexural modulus. Whereas the findings of the former were based on the flexural modulus of polypropylene, the findings of the latter were based on both polyethylene terephthalate (copolyester) and polypropylene materials. These findings contradict those of Wible et al.¹⁷ and Agarwal.³⁸ The former found that AL and RB increase the stiffness of copolyester material, whereas the latter found that AL also increases the stiffness of copolyester material. These studies have indicated that the stiffness of copolyesters increases as a result of the material's oxidative deterioration and limited hydrolytic stability, both of which affect the polymer's structure and mechanical characteristics. This discrepancy may be attributable to two factors. First, the previous studies exposed specimens to cleaning agents for 6 months, twice per week, thus resulting in 48 exposures per specimen, whereas the current study exposed the specimens to cleaning agents for 3 months, three times weekly, thus resulting in 36 exposures for each specimen. Second, a difference in the manufacturing process might have influenced the results, as reported by Ryokawa et al.²⁰ and Zhang et al.²¹

Before being subjected to any condition, the T% values for copolyester and polypropylene materials were substantially different: copolyester materials were more transparent than polypropylene materials. This conclusion is consistent with those of Wible,¹⁹ who has found that the T% of copolyester materials is higher than that of polypropylene materials at baseline. The differences in composition may explain these findings. According to the OrthoTechnology catalog,³⁹ polypropylene is slightly opaque in transparency, whereas copolyester is highly clear. Furthermore, Ryokawa et al.²⁰ have shown that polypropylene's crystalline nature makes it appear opaque. The initial difference in T% between materials was not affected by exposure to the cleaning agents.

The statistical results demonstrated that the cleaning agents did not influence the T% of polypropylene material, whereas the AL condition affected the T% of copolyester material, in agreement with the results of Agarwal,³⁸ Wible et al.,¹⁷ and Brehove.³⁷ According to Eastman Chemical Company,⁴⁰ the reason for the decrease in T% for copolyester material may be the presence of ethanol in AL components, which can create a yellowish discoloration of copolyester material. Zafeiriadis et al.¹¹ have demonstrated color changes in clear retainers after exposure to wine, thus implying that alcohol may cause color changes in retainer thermoplastics. Wible et al.,¹⁸ in contrast, have shown that the T% of polypropylene material is decreased by AL and RB, and have attributed this decrease to ethanol, sodium carbonate, and citric acid having minor effects on the plastic

materials. This conclusion contradicts the findings of the current study. This discrepancy may be explained by the differences in protocols between investigations, as previously indicated. According to Ryokawa et al.,²⁰ a change in the production process might also have been a factor.

According to our results, the null hypothesis for flexural modulus and light transmittance was rejected.

The use of flat specimens in this study were a study limitation, because they did not show the real shape of thermo-plastic retainers. However, flat standard specimens with uniform cross-sectional areas were required for the flexural modulus and light transmittance measurements in this study, and they have provided standard data that could be used in future research. Despite being flat, the specimens were processed (heat-vacuum formed) in the same manner as orthodontic retainers; therefore, the processing step was not a limitation in the study. In the future, the following research directions might be highly beneficial in this field. 1. A similar study could be performed to assess additional properties, for example, inhibition of microorganisms, of retainer thermo-plastics over a longer period. 2. A similar study could be conducted with different retainer material types and/or different mouthwashes or cleaning agent types. 4. A randomized clinical trial could be conducted to evaluate the effects of these cleaning agents on the light transmittance and roughness properties of these materials.

Conclusions and recommendations

The copolyester retainer material has a higher flexural modulus than polypropylene under CH, AL, and RB conditions. However, the flexural modulus is unaffected after exposure to the four tested cleaning agents.

Before and after cleaning with various cleaning agents, the copolyester retainer type had a far higher light transmittance than the polypropylene retainer type. Furthermore, the T% of copolyester retainer material was decreased by AL mouthwash.

According to the results, the clinical recommendations of the present study are as follows:

1. For both copolyester and polypropylene retainer types, any cleaning agent (AL, ALF, CH, or RB) can be used without altering the material's flexibility or stiffness factor.
2. For polypropylene retainers, any of the cleaning agents (AL, ALF, CH, or RB) can be used without altering the light transmittance.
3. Because of their negative effects in terms of the light transmittance and yellowish discoloration of copolyester retainer types—such as thermoplastic retainers, particularly when used for longer periods—cleaning agents containing ethanol, such as AL mouthwash, should be avoided.

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Conflict of interest

The authors have no conflict of interest to declare.

Ethical approval

No ethical approval was applicable, because this was an experimental laboratory study.

Authors contributions

AMH conceptualized and designed the study; performed research; provided research materials; collected and organized the data; and was responsible for project administration, resources, software, data analysis, investigation, and the initial draft of the article. **HSM** was responsible for project management, monitoring, visualization, validation, supervision, and the final draft. **IIA** contributed to the creation, planning and design of the study, and supervision. All authors have critically reviewed and approved the final draft and are responsible for the content and similarity index of the manuscript.

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