






Chemical–Physical Characterization of PET-G-Based Material for Orthodontic Use: Preliminary Evaluation of micro-Raman Analysis

Fabiana Nicita¹ Cesare D'Amico¹ Vincenzo Filardi² Donatella Spadaro³ Emidio Aquilio⁴
Maura Mancini¹ Luca Fiorillo^{1,5}

¹Department of Biomedical and Dental Sciences and Morphofunctional Imaging, University of Messina, via Consolare Valeria, Messina, Italy

²D.A. Research and Internationalization, University of Messina, Via Consolato del mare 41, Messina, Italy

³CNR-IPCF, Institute for Physical Processes, Messina, Italy

⁴Lineo Aligners, Torino, Italy

⁵Multidisciplinary Department of Medical-Surgical and Dental Specialties, University of Campania Luigi Vanvitelli, Naples, Italy

Address for correspondence Fabiana Nicita, Department of Biomedical and Dental Sciences and Morphofunctional Imaging, University of Messina, via Consolare Valeria, 1, 98125 Messina, Italy (e-mail: fabnicita@unime.it).

Eur J Dent 2024;18:228–235.

Abstract

Objectives Orthodontic treatment with clear thermoplastic aligners is in great demand by patients especially for aesthetics. Any alterations in the chemical composition of the thermoplastic material for aligners, subjected to the oral environment and exposure to various commonly used substances, could influence the desired orthodontic movement decreasing the predictability of the treatment. The objective of this study was to determine the chemical–physical characterization by micro-Raman spectroscopy of a thermoplastic material based on polyethylene terephthalate glycol (PET-G) used for the manufacture of Lineo aligners (Micerium Lab, Avegno, Italy) subjected to different staining beverages and cleaning agents.

Materials and Methods Twenty-two thermoformed PET-G samples were immersed to various substances of daily use for 10 and 15 days (coffee, tea, Coca-Cola, red wine, colloidal silver disinfectant, nicotine, artificial saliva, cigarette smoke, and different combinations of saliva with some of the previous solutions). Subsequently, the chemical–physical characterization was investigated by micro-Raman spectroscopy.

Results The analysis of the spectra acquired for all the specimens showed no difference in the exposure to the different solvents at 10 and 15 days. Furthermore, having ascertained the heterogeneous surface morphology of the PET-G material due to thermoforming, various deposits were present on all the samples whose consistency and concentration depended on the substance used.

Conclusion The spectroscopic investigations have provided a precise and detailed analysis of the qualitative and structural data of the PET-G material under examination. No significant structural modifications of the thermoplastic polymer were found after immersion in different solutions in the exposure times adopted.

Keywords

- ▶ clear aligners
- ▶ PET-G
- ▶ thermoplastic materials
- ▶ staining substances
- ▶ chemical–physical characterization
- ▶ micro-Raman spectroscopy.

article published online
May 29, 2022

DOI <https://doi.org/10.1055/s-0043-1764424>.
ISSN 1305-7456.

© 2022. The Author(s).

This is an open access article published by Thieme under the terms of the Creative Commons Attribution License, permitting unrestricted use, distribution, and reproduction so long as the original work is properly cited. (<https://creativecommons.org/licenses/by/4.0/>)

Thieme Medical and Scientific Publishers Pvt. Ltd., A-12, 2nd Floor, Sector 2, Noida-201301 UP, India

Introduction

Current computer-aided design and manufacturing (-CAD/CAM) techniques are widely used in the manufacture of clear thermoplastic aligners for the treatment of various types of dental malocclusion.¹⁻⁴ The biomechanical characteristics of commercial clear aligners are influenced by the properties of the thermoplastic material used, the forming process,^{2,5} and the precise aligner-teeth fitting.⁶

The thermoplastic polymers currently most used are based on polyurethanes (PU) or polyesters such as polyethylene terephthalate glycol (PET-G).⁷⁻⁹ These materials have good mechanical and physical properties, biocompatibility, chemical stability, excellent aesthetic characteristics, good formability, and are of low cost,¹⁰ but also have various limitations such as low strength and poor wear resistance.¹¹ In particular, PET-G materials are structurally amorphous polymers that possess an irregularly arranged molecular structure with poor packaging.¹² These polymers are transparent because they are passed through by visible light and their degree of crystallization after thermoforming is negligible.¹³

However, the thermoforming could cause variations in the morphological and mechanical properties of the polymer.⁵ Furthermore, during their use, thermoplastic aligners are continuously subjected to mechanical loads, temperature changes inside the oral cavity, and the influence of saliva and food pigments.¹⁴ These factors could lead to abrasions, surface alterations, color changes, and delamination of the polymer.¹⁴⁻¹⁶ Chemical cleaning methods may also alter the structural integrity of the thermoplastic material. These degradations lead to a significant loss of mechanical strength and transparency of the aligner, an essential requirement in an invisible orthodontic treatment.^{13,17}

Although clinicians recommend removing aligners before eating and drinking, patient compliance is still insufficient. Therefore, it is necessary to simulate the intraoral clinical conditions, even with the use of staining substances and agents such as nicotine and cigarette smoke, to better evaluate any structural and/or optical changes of the orthodontic aligners. The aim of this research is to characterize the PET-G-based thermoplastic material used for Lineo aligners (Micerium Lab) after exposure to various commonly used staining and disinfecting agents. In detail, micro-Raman spectroscopy was used to identify any changes in the chemical composition with consequences on the morphology and/or structure of the polymer in question.

Materials and Methods

Preparation of PET-G Samples

Four sheets of thermoplastic material in PET-G with a thickness of 0.8 mm were selected for the study. Three of these slabs were thermoformed, while the fourth was not subjected to hot molding techniques. A truncated pyramid-shaped mold was prepared and placed in the thermoforming machine. A thermoforming quota of 20 mm and an angle of 11 degrees was applied for less friction in extraction. The applied temperature is 160 to 165°C. The models obtained after thermoforming

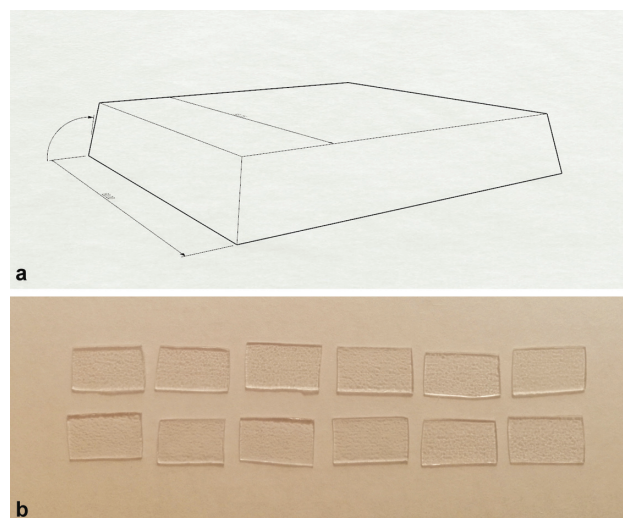


Fig. 1 Preparation of thermoformed polyethylene terephthalate glycol (PET-G) samples. (a) Truncated pyramid model used in the thermoforming phase. (b) Some of the thermoformed samples cut from the horizontal surface of the model obtained.

were removed and the horizontal surface was used to obtain samples with dimensions of 1 × 1.5 cm ($n = 23$; ► **Fig. 1**). A nonthermoformed sample of 1 × 1.5 cm was obtained from the fourth sheet, which will be used to evaluate the influence of thermoforming on the PET-G material.

Treatment of PET-G Samples with Commonly Used Substances

It is essential to evaluate whether the intake of beverages or the use of certain substances or detergents used in cleaning the aligners can influence the chemical-physical characterization of the thermoplastic PET-G material under analysis. Twenty-two thermoformed samples were used for this purpose. Each specimen was placed in a plastic container containing 5 mL of one of the following solutions: (1) 6 g of coffee powder (Nescafé Classic, Switzerland) was added to 200 mL of boiling deionized water; (2) sugar-free tea (30 mg/150 mL, Earl Grey Twinings, London, England); (3) Coca-Cola (Coca-Cola Company, Atlanta, Georgia, United States); (4) undiluted red wine (San Crispino, Cantina Ronco Romagna, Italy); (5) disinfectant based on colloidal silver; (6) the nicotine solution was obtained by infusing cigarette filters into deionized water and then filtered; (7) 120 mL of artificial saliva (Bi-tène Oral Balance, GlaxoSmithKline Consumer Healthcare S. p.A.) were diluted in 480 mL of deionized water; (8) cigarette smoke (a certain amount of smoke produced by cigarettes); (9) saliva and smoke; (10) solution of saliva and nicotine in a 1:1 ratio; and (11) a solution of saliva and coffee in a 1:1 ratio.

All specimens were maintained in immersion in a water bath at $T = 37^{\circ}\text{C}$ and were randomly divided according to the immersion time in the chosen solvents ($n = 11$ up to 10 days; $n = 11$ up to 15 days). The samples were rapidly rinsed with deionized water (Milli-Q) every 24 hours before being reimmersed in fresh solution.

As for the colloidal silver-based disinfectant, the two thermoformed samples, up to 10 and 15 days, were treated

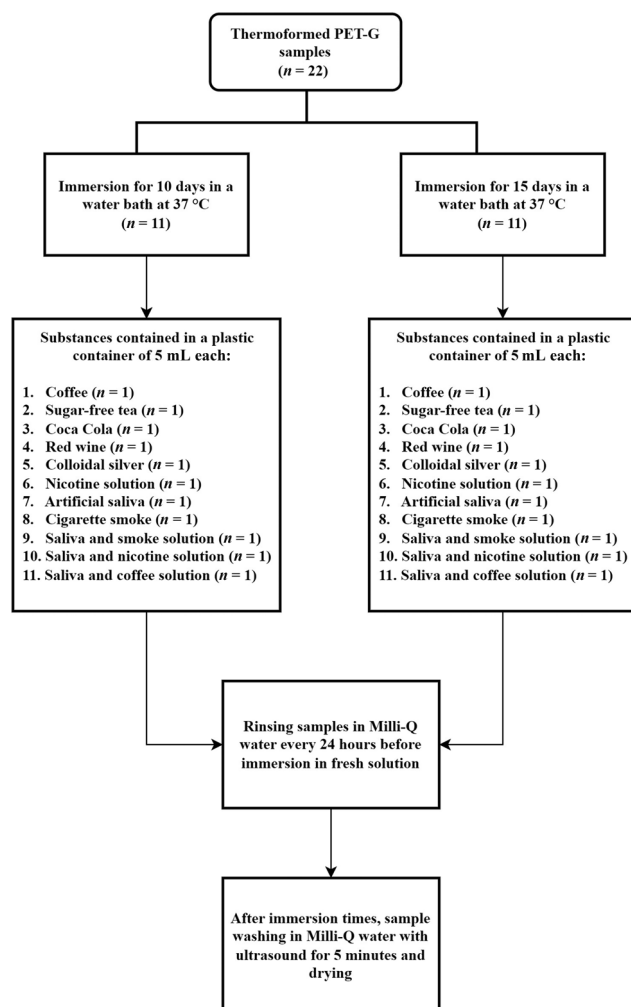


Fig. 2 Flowchart of the protocol adopted for the treatment of polyethylene terephthalate glycol (PET-G) samples immersed in staining substances.

for a maximum of 3 hours a day to simulate the aligner cleaning methods.

After 10 and 15 days, all the samples were washed by immersion in Milli-Q water, kept in ultrasound for 5 minutes and adequately dried before being analyzed for the physico-chemical characterization (► **Fig. 2**).

Micro-Raman Spectroscopy Analysis

Raman spectroscopy analysis was performed to investigate the chemical composition of the samples in PET-G. The measurements were carried out with a micro-Raman spectrometer (XploRA Plus, Horiba) using a laser source with a wavelength of 785 nm with a 100X objective, 1,200 g/mm reticle, with 10-second acquisition time for five accumulations in a range between 200 and 3,200/cm.

Results

Influence of the Thermoforming Process

The peaks characteristic of the vibrational modes of PET-G¹⁸ are shown in ► **Table 1**. To assess the influence of the thermoforming process in the physicochemical characteri-

Table 1 The assignment of observed micro-Raman bands of polyethylene terephthalate glycol (PET-G)

Raman (per cm)	Assignment
3,082 w	CH stretching
3,068 w	CH stretching
3,000 w	CH stretching
2,960 w	CH ₂ stretching
1,730 m	C=O stretching
1,615 s	C=C stretching (ring)
1,450 w	CH deformation
1,412 vw	C-C stretching (ring)
1,370 vw	CH ₂ wagging
1,282 m	C-C stretching (ring), C-O stretching
1,270 m	C-C stretching (ring), C-O stretching
1,245 sh, w	C-C stretching (ring), C-O stretching
1,175 w	CH in plane bending (ring)
1,117 w	CH in plane bending (ring), C-O stretching
1,038 vw	C-C stretching (glycol)
890 vw	CH ₂ rocking
853 w	C-C stretching (ring breathing), C-O stretching
797 w	CH out of plane bending (ring)
633 s	CCC in plane bending (ring)
407 vw	Asymmetric ring torsion
272 w	C-C stretching (ring), CCC bending (ring)

Abbreviations: m, moderate; s, strong; sh, shoulder; w, weak; v, very.

zation, two PET-G samples were compared ($n=1$ thermoformed and $n=1$ nonthermoformed). The preliminary investigation shows that the structure of the polymer used is not altered by the thermoforming process (► **Fig. 3**). However, the morphological analysis shows that the surface of the thermoformed sample is characterized by roughness, holes, and scratches in comparison with the uniform and homogeneous surface of the one not subjected to thermoforming (► **Fig. 4**).

Aging Treatments

From the analysis of the Raman spectra acquired for all the samples immersed in the different substances ($n=22$), no differences were found between those treated for 10 and 15 days (► **Fig. 5**). Therefore, the results shown are comparable to the single solvent or agent used regardless of the duration of the treatment itself.

The micro-Raman analysis shows that in all the samples the acquired spectra are those of the PET-G polymer, whatever the agent used in the treatments at both 10 and 15 days. Only in the samples dipped in nicotine were areas of burns and morphological changes of the polymer detected. Furthermore, in all the samples, different fluorescence

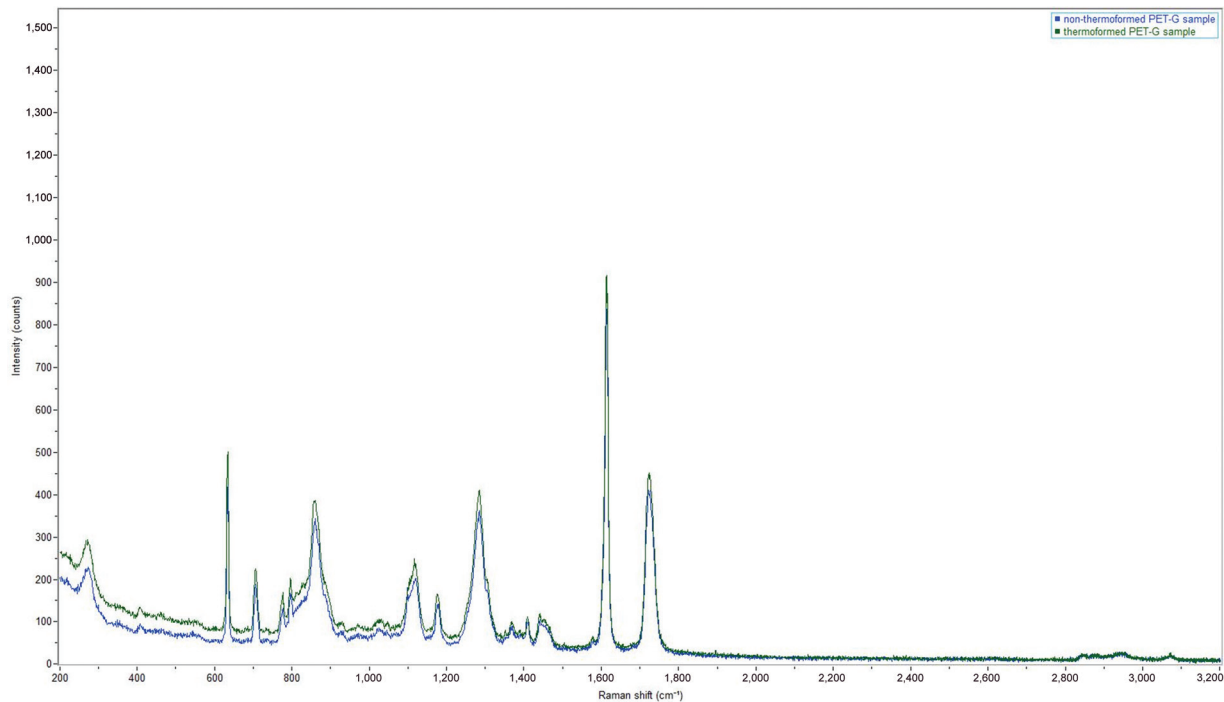


Fig. 3 Raman spectra of non-thermoformed (blue) and thermoformed (green) polyethylene terephthalate glycol (PET-G) samples at 785 nm. The characteristic peaks belong to the PET-G polymer and there is no change in the signals when heat treatment is carried out.

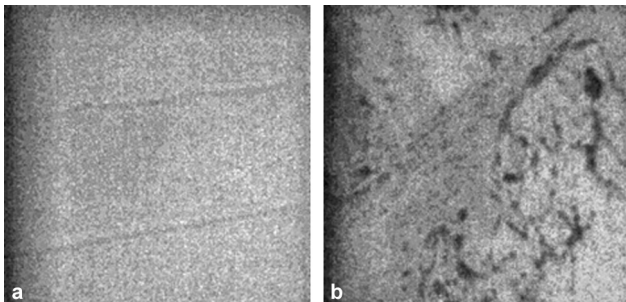


Fig. 4 Morphological analysis under an optical microscope at 100x magnification. (a) Smooth and homogeneous non-thermoformed surface and (b) thermoformed surface with scratches and roughness.

phenomena are found due to residues of substances accumulated in correspondence with the asperities and scratches of the thermoformed material (► **Figs. 6–12**). There are also fibrous residues of accidental origin attributable to cotton fibers on the surface of the samples immersed in the saliva and coffee solution, at 10 and 15 days, and treated with colloidal silver disinfectant for 15 days (► **Fig. 13**).

Discussion

The qualitative properties of clear orthodontic aligners are strictly related not only to the material used and the molding process for manufacturing but also to modifications related to the oral environment. The thermoforming process applied to thermoplastic materials involves a heating cycle followed by forming under vacuum or pressure, which could cause morphological alterations of the polymer.⁵ Furthermore, these materials in the

form of aligners inserted inside the oral cavity can also be subject to surface and color alterations due to factors such as humidity, temperature variations, and coloring agents.^{5,13,19} Despite clinicians' recommendations to wear aligners full-time except when eating, drinking, or for oral hygiene maneuvers,²⁰ many patients take coloring agents (red wine, coffee, tea, Coca-Cola) or smoke with their orthodontic devices.^{21,22}

This *in vitro* study reports the chemical–physical characteristics of PET-G, widely used for the fabrication of orthodontic aligners (Lineo, Micerium Lab), which has undergone various aging treatments. Micro-Raman spectroscopy is a nondestructive chemical analysis technique that provides detailed information on the chemical structure, phases, and polymorphy and molecular interactions. It is integrated with an optical microscope, which, by focusing the laser on the sample, allows the analysis of small regions.²³

The originality of this work consists in the chemical–physical characterization of the thermoplastic material that occurs after its exposure to substances for common use for a prolonged time (15 days) equal to the period of use of a single aligner during complex orthodontic treatment. This has great relevance in observing the structural behavior of the polymer during intraoral aging.

Although the micro-Raman analysis did not reveal any changes in the chemical structure of PET-G (► **Fig. 3**), the thermoforming process used to manufacture the aligners caused evident surface alterations of the polymer including roughness, holes, and scratches (► **Fig. 4**). Also, Porojan et al²⁴ noted an increase, albeit insignificant, in the roughness of this material. In contrast, the study by Zhang et al²⁵ showed a smoother PET-G surface after thermoforming.

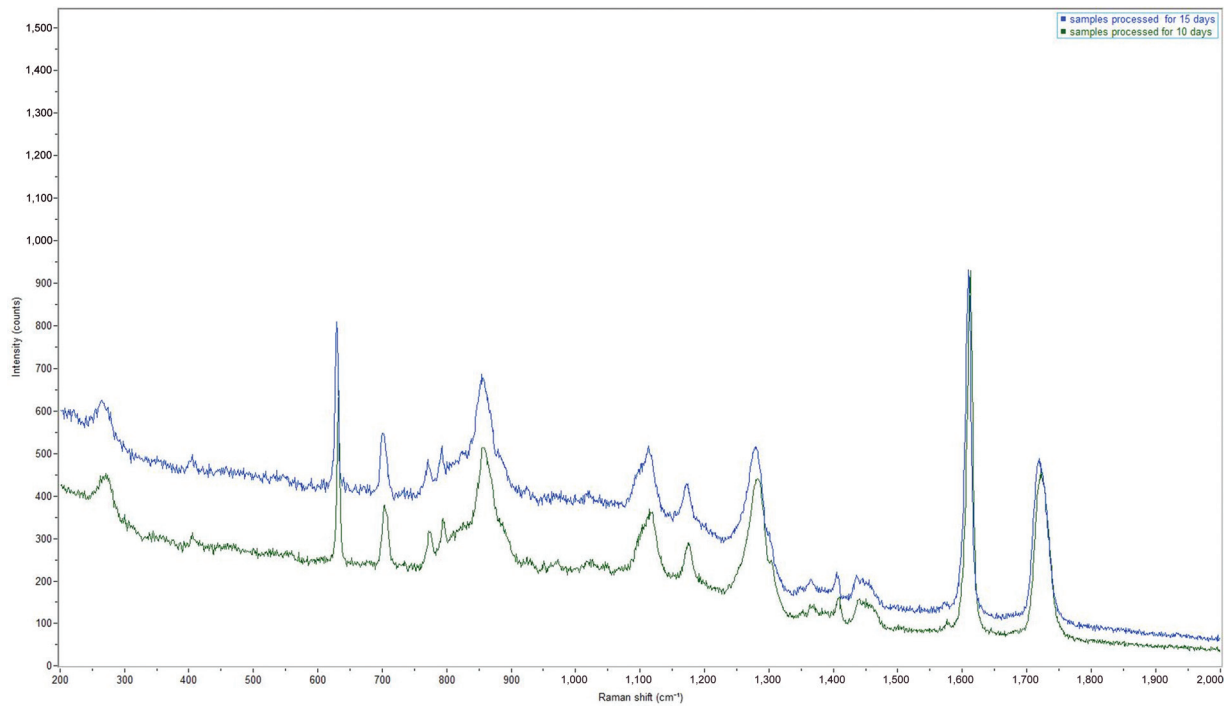


Fig. 5 Raman spectra representative of the signals found on the surface of the samples subjected to the different treatments for 10 (green) and 15 days (blue). Peaks found are those characteristics of the polyethylene terephthalate glycol (PET-G) polymer and are stackable with each other.

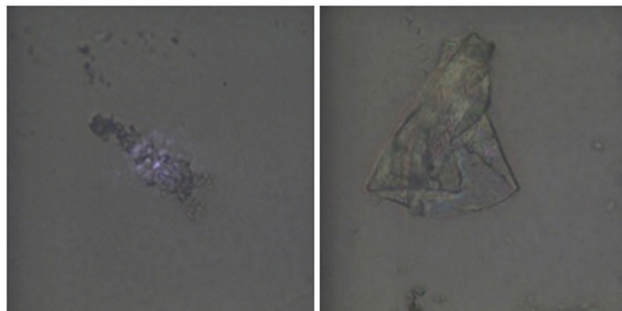


Fig. 6 (a,b) Morphological analysis of polyethylene terephthalate glycol (PET-G) samples immersed in a coffee solution. There is presence of residues with a discrete diffuse fluorescence.

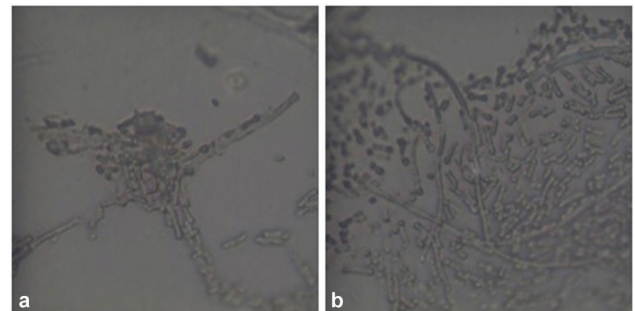


Fig. 7 (a,b) Morphological analysis of polyethylene terephthalate glycol (PET-G) samples immersed in a sugar-free tea. There is presence of highly fluorescent tree structures.

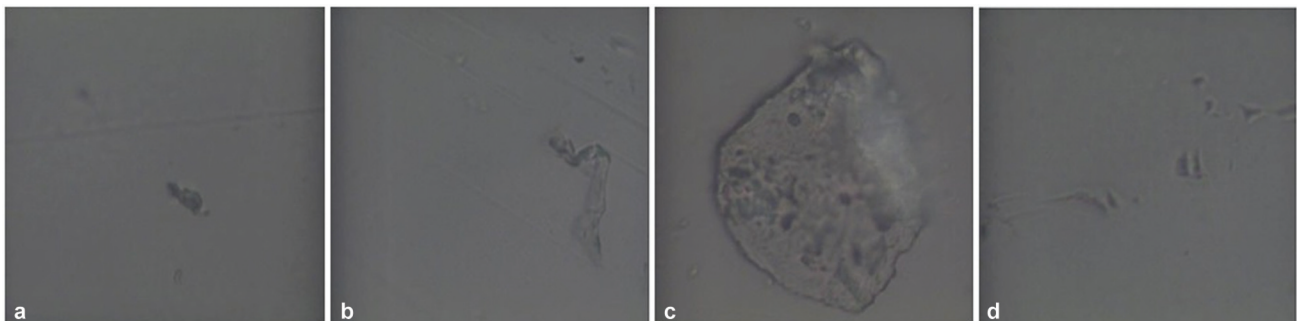


Fig. 8 Morphological analysis of polyethylene terephthalate glycol (PET-G) samples immersed in (a,b) Coca-Cola and (c,d) red wine. There are no structures and no fluorescence.

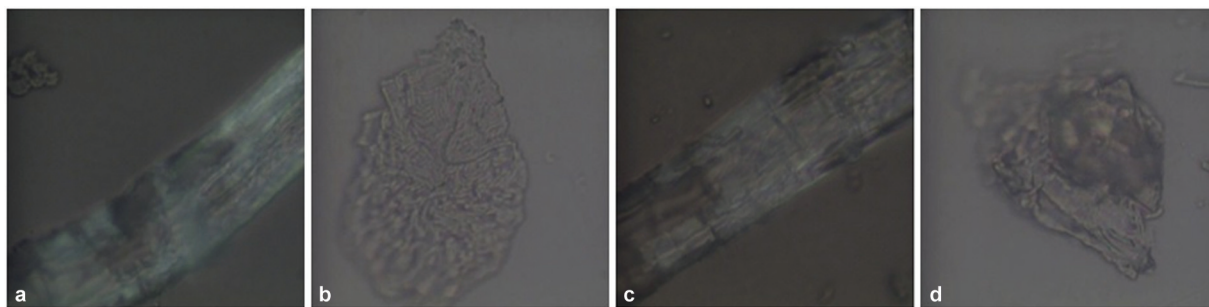


Fig. 9 Morphological analysis of polyethylene terephthalate glycol (PET-G) samples immersed (a,b) in a silver colloidal and (c,d) in the solution of artificial saliva and coffee. Along with the usual structures, large nonfluorescent cottonlike fibrous structures are present.

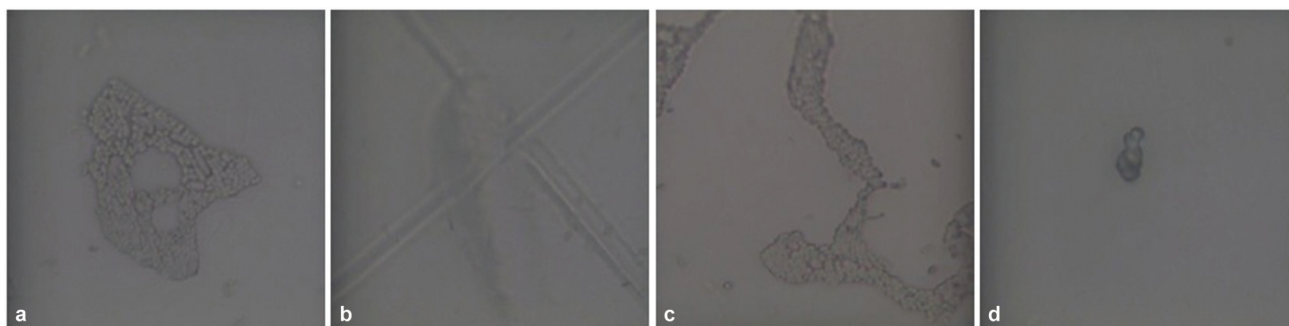


Fig. 10 Morphological analysis of polyethylene terephthalate glycol (PET-G) samples immersed (a,b) in a pure nicotine and (c,d) in the solution of artificial saliva and nicotine. There is presence of carbon deposits and rodlike structures, which cause less fluorescence.

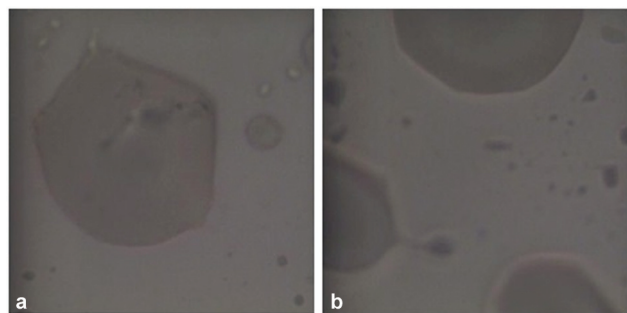


Fig. 11 (a,b) Morphological analysis of polyethylene terephthalate glycol (PET-G) samples immersed in an artificial saliva and saliva with cigarette smoke. There is presence of almost regular circular spots without fibrous or rodlike structures.

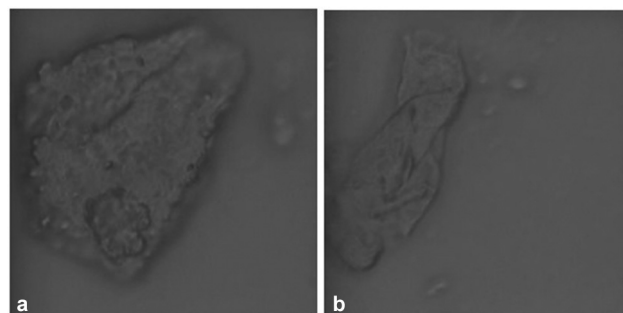


Fig. 12 (a,b) Morphological analysis of polyethylene terephthalate glycol (PET-G) samples immersed in cigarette smoke. There is presence of deposits with little fluorescence, without fibrous structures or rods or circular spots.

Alterations in the physical properties of PET-G have also been reported after intraoral exposure.²⁵ The micro-Raman analysis performed after immersion in different solvents for up to 10 and 15 days has shown that the structure of PET-G is not altered and that the fluorescence phenomena found are due only to the accumulation of residues of the substances used (►Figs. 6–12). The only morphological changes were detected in the nicotine-treated samples as the interaction between the micro-Raman laser and the remaining carbon residues resulted in local burn areas of the material. Furthermore, in the samples immersed in the solution of saliva and coffee and in those treated with colloidal silver disinfectant, accidental foreign bodies of a fibrous nature were detected,

whose composition and characteristic peaks are probably related to cotton fibers (►Fig. 13).²⁶

Transparency represents another important property possessed by thermoplastic materials.²⁷ Any color changes have been associated with the absorption or penetration of the coloring substances that come into contact with the surface of the material within the oral environment.^{17,28,29} The surface characteristics of the thermoformed materials could accelerate the accumulation of pigment with consequent loss of transparency.³⁰ Daniele et al⁹ found alterations in the aesthetic characteristics of aligners made of PET-G and PU, especially after immersion in coffee or red wine, with a consequent loss of transparency due to impurities deposited

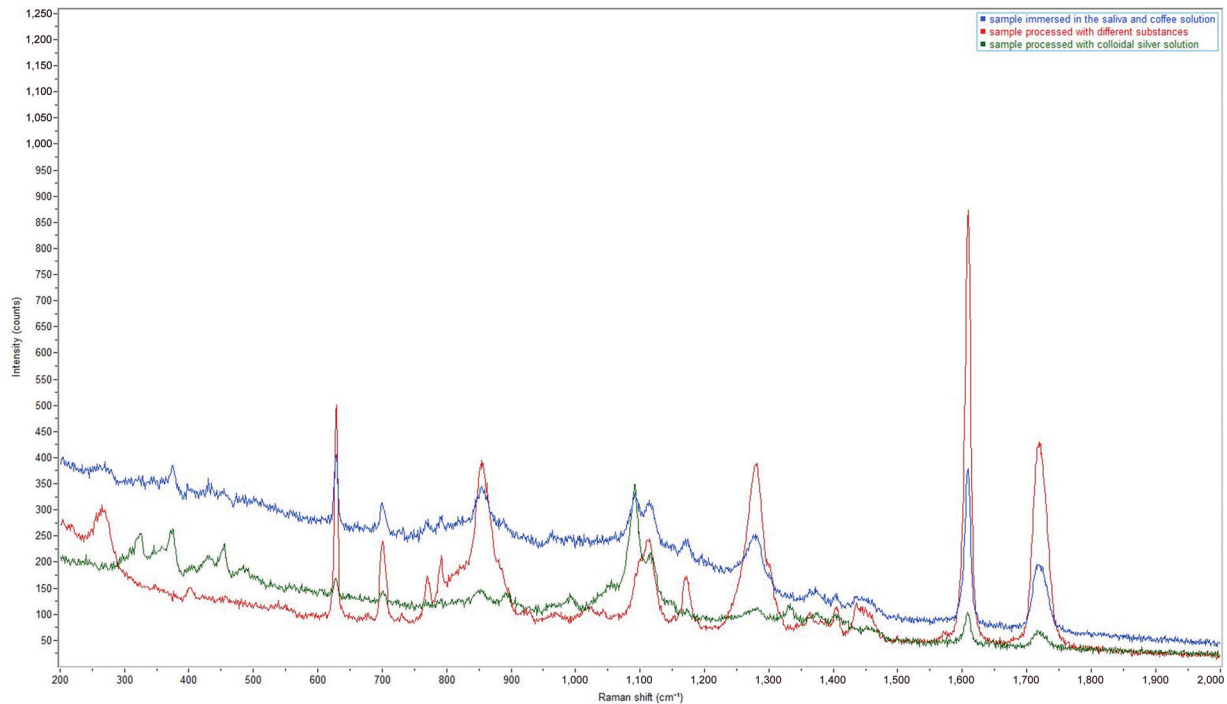


Fig. 13 Raman spectra representative of some signal types found on the surface of the polyethylene terephthalate glycol (PET-G) samples. The observed peaks correspond to those of cotton-fiber-like foreign bodies found on the surface of samples immersed in saliva and coffee solution (blue) and in those treated with colloidal silver (green) in comparison with a representative Raman spectrum of treated samples with other substances (red).

on the surface. However, Porojan et al²⁴ have shown that color variations of the PET-G samples do not depend so much on the surface roughness but on the penetration inside the material itself.

In the present study, no substantial variations in the colorimetric level were found; however, the spectroscopic technique used in this study does not have the ability to detect any changes of this type. Therefore, in future research, it would be appropriate to evaluate transparency changes and colorimetric variations of PET-G with the length of time used in this study (10 and 15 days) with more suitable instruments.

Conclusions

After thermoforming and aging treatments, there are no structural or color variations on the PET-G material used for the manufacture of Lineo aligners produced by Micerium Lab.

The heterogeneous morphological surface, which could suggest a loss of transparency and aesthetic properties, depends on the intraoral exposure and on the contact with coloring pigments deriving from beverages, nicotine, or cigarette smoke, which determine the accumulation of deposits in the rough surface and scratches due to thermoforming. Therefore, the surface characteristics of the PET-G samples found on the scanning electron microscope (SEM) images after 10 and 15 days of immersion times are attributed exclusively to the staining substances used.

Conflict of Interest
None declared.

References

- Weir T. Clear aligners in orthodontic treatment. *Aust Dent J* 2017; 62(Suppl 1):58–62
- Martorelli M, Gerbino S, Giudice M, Ausiello P. A comparison between customized clear and removable orthodontic appliances manufactured using RP and CNC techniques. *Dent Mater* 2013;29 (02):e1–e10
- Simon M, Keilig L, Schwarze J, Jung BA, Bourauel C. Erratum: Forces and moments generated by removable thermoplastic aligners: incisor torque, premolar derotation, and molar distalization. *Am J Orthod Dentofacial Orthop* 2014;146(04):411
- Ben Gasseem AA. Does clear aligner treatment result in different patient perceptions of treatment process and outcomes compared to conventional/traditional fixed appliance treatment: a literature review. *Eur J Dent* 2022;16(02):274–285
- Ryu JH, Kwon JS, Jiang HB, Cha JY, Kim KM. Effects of thermoforming on the physical and mechanical properties of thermoplastic materials for transparent orthodontic aligners. *Korean J Orthod* 2018;48(05):316–325
- Dasy H, Dasy A, Asatrian G, Rózsa N, Lee HF, Kwak JH. Effects of variable attachment shapes and aligner material on aligner retention. *Angle Orthod* 2015;85(06):934–940
- Alexandropoulos A, Al Jabbari YS, Zinelis S, Eliades T. Chemical and mechanical characteristics of contemporary thermoplastic orthodontic materials. *Aust Orthod J* 2015;31(02):165–170
- Sifakakis I, Zinelis S, Eliades T. Aligners for orthodontic applications. In: Eliades T, Brantley WA, eds. *Orthodontic Applications of Biomaterials: A Clinical Guide*. Amsterdam: Woodhead Publishing; 2017

- 9 Daniele V, Macera L, Taglieri G, et al. Thermoplastic disks used for commercial orthodontic aligners: complete physicochemical and mechanical characterization. *Materials (Basel)* 2020;13(10):2386
- 10 Condo' R, Pazzini L, Cerroni L, et al. Mechanical properties of "two generations" of teeth aligners: change analysis during oral permanence. *Dent Mater J* 2018;37(05):835–842
- 11 Barone S, Paoli A, Neri P, Razionale AV, Giannese M. Mechanical and geometrical properties assessment of thermoplastic materials for biomedical application. *Lect Notes Mech Eng* 2017: 437–446
- 12 Michler GH, Lebek W. Electron microscopy of polymers. In: Guo G, ed. *Polymer Morphology: Principles, Characterization, and Processing*. Hoboken, NJ: John Wiley & Sons; 2016:37–53
- 13 Liu CL, Sun WT, Liao W, et al. Colour stabilities of three types of orthodontic clear aligners exposed to staining agents. *Int J Oral Sci* 2016;8(04):246–253
- 14 Schuster S, Eliades G, Zinelis S, Eliades T, Bradley TG. Structural conformation and leaching from *in vitro* aged and retrieved Invisalign appliances. *Am J Orthod Dentofacial Orthop* 2004; 126(06):725–728
- 15 Ryokawa H, Miyazaki Y, Fujishima A, Miyazaki T, Maki K. The mechanical properties of dental thermoplastic materials in a simulated intraoral environment. *Orthod Waves* 2006;65(02):64–72
- 16 Memè L, Notarstefano V, Sampalmieri F, Orilisi G, Quinzi V. Atr-ftir analysis of orthodontic invisalign® aligners subjected to various *in vitro* aging treatments. *Materials (Basel)* 2021;14(04):1–10
- 17 Lombardo L, Arreghini A, Maccarrone R, Bianchi A, Scalia S, Siciliani G. Optical properties of orthodontic aligners: spectrophotometry analysis of three types before and after aging. *Prog Orthod* 2015;16(01):41
- 18 Bistričić L, Borjanović V, Leskovic M, et al. Raman spectra, thermal and mechanical properties of poly(ethylene terephthalate) carbon-based nanocomposite films. *J Polym Res* 2015;22(03):39
- 19 Meto A, Colombari B, Castagnoli A, Sarti M, Denti L, Blasi E. Efficacy of a copper-calcium-hydroxide solution in reducing microbial plaque on orthodontic clear aligners: a case report. *Eur J Dent* 2019;13(03):478–484
- 20 Moshiri M, Eckhart J, Mcshane P, German DS. Consequences of poor oral hygiene during clear aligner therapy. *J Clin Orthod* 2013; 47(08):494–498
- 21 Tsomos G, Ludwig B, Grossen J, Pazera P, Gkantidis N. Objective assessment of patient compliance with removable orthodontic appliances: a cross-sectional cohort study. *Angle Orthod* 2014;84 (01):56–61
- 22 Lombardo L, Martini M, Cervinara F, Spedicato GA, Oliverio T, Siciliani G. Comparative SEM analysis of nine F22 aligner cleaning strategies. *Prog Orthod* 2017;18(01):26
- 23 Mariani MM, Day PJR, Deckert V. Applications of modern micro-Raman spectroscopy for cell analyses. *Integr Biol* 2010;2(2–3):94–101
- 24 Porojan L, Vasiliu RD, Porojan SD, Birdeanu MI. Surface quality evaluation of removable thermoplastic dental appliances related to staining beverages and cleaning agents. *Polymers (Basel)* 2020; 12(08):1736
- 25 Zhang N, Bai Y, Ding X, Zhang Y. Preparation and characterization of thermoplastic materials for invisible orthodontics. *Dent Mater J* 2011;30(06):954–959
- 26 Puchowicz D, Giesz P, Kozanecki M, Cieślak M. Surface-enhanced Raman spectroscopy (SERS) in cotton fabrics analysis. *Talanta* 2019;195:516–524
- 27 Dupaix RB, Boyce MC. Finite strain behavior of poly(ethylene terephthalate) (PET) and poly(ethylene terephthalate)-glycol (PETG). *Polymer* 2005;46(13):4827–4838
- 28 Fang D, Zhang N, Chen H, Bai Y. Dynamic stress relaxation of orthodontic thermoplastic materials in a simulated oral environment. *Dent Mater J* 2013;32(06):946–951
- 29 Zafeiriadis AA, Karamouzou A, Athanasiou AE, Eliades T, Palaghias G. *In vitro* spectrophotometric evaluation of Vivera clear thermoplastic retainer discolouration. *Aust Orthod J* 2014;30(02): 192–200
- 30 Jindal P, Juneja M, Siena FL, Bajaj D, Breedon P. Mechanical and geometric properties of thermoformed and 3D printed clear dental aligners. *Am J Orthod Dentofacial Orthop* 2019;156(05): 694–701