Mechanical properties of "two generations" of teeth aligners: Change analysis during oral permanence

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Aim of this *in vitro* study was to analyze structural properties of two different polymeric orthodontic aligners, Exceed30 (EX30) and Smart Track (LD30), before and after use. Forty patterns of aligners were randomly selected: 20 LD30 and 20 EX30, worn intra-orally for 14±3 days, 22 h/day. From each aligner, 10 specimens were prepared from buccal surfaces of the incisor region by the cutting of samples 5×5 mm under a stereomicroscope. All samples were subjected to Fourier transform infrared spectroscopy, micro-Raman spectroscopy, X-ray diffraction, tensile and indentation strength test. LD30 appeared more homogeneous, with a crystalline fraction lower than EX30 and exhibited a higher elastic behavior and a lower tendency to warp after use than EX30. LD30 demonstrated better adaptability to the dental arch and greater consistency of application of orthodontic forces than produced with EX30. However, both materials showed structural modifications that resulted in increased sample hardness and hyper-plasticity.

Keywords: Invisalign®, Indentation and tensile strength test, Fourier transform infrared spectroscopy, Micro-Raman spectroscopy, X-ray diffraction

INTRODUCTION

The development of computer-aided design/computer-aided manufacturing techniques has permitted the use of thermoplastic materials to fabricate clear and removable tooth aligners for orthodontics[1,2]. Thermoplastic polymers have good physical, chemical and mechanical properties, such as low stiffness, good deformability, biocompatibility and dimensional stability. They are widely used for orthodontic retainers, temporomandibular joint splints, night guards and bleaching trays[3,4]. This wide range of applications is derived from excellent esthetic characteristics, better formability and low cost[2-5].

Polyester, polyurethane and polypropylene are the dominant thermoplastic materials in polymer mixtures used for the manufacture of clear orthodontic appliances[6]. To date, a considerable body of literature has been published on various blends of thermoplastic materials, such as the mixture of polycarbonate and polypropylene, rather than polyurethane and polycarbonate[7-9].

Amorphous polymers possess an irregularly arranged molecular structure, and molecular packing has been found to be poor. Conversely, some polymers exhibit a regularly arranged molecular structure, the chemical structure of which allows the polymer chains to fold on themselves and pack together in an organized manner. All crystalline polymers retain, in their structure, amorphous regions that connect crystalline regions; hence, crystalline polymers are often called semi-crystalline polymers[10].

Clear thermoplastic removable appliances are produced by CAD/CAM technology, in this way, it is possible to produce the movements required for comprehensive orthodontic treatment and, at the same time, to create more esthetic appeal than traditional stainless steel or esthetic brackets and wires[11,12].

Polyurethane, is one of the most versatile engineering thermoplastics, with excellent physical properties, chemical resistance, abrasion resistance, and ease of processing[13,14]. However, polyurethane is not an inert material and is affected by heat, moisture and prolonged contact with salivary enzymes[15-17].

Before September 2001, Invisalign® (Align Technology, San Jose, CA, USA) aligners were made with a material called Proceed30 (PC30), a polymer mixture that did not meet all the physical-chemical and clinical requirements for orthodontic tooth movement. Many disadvantages have been outlined which, in some cases, have limited the usage of these clear aligners[18,19].

In 2013, Invisalign® aligners were made with the polymer material Exceed30 (EX30), an implantable medical-grade polymer made of polyurethane methylene diphenyldiisocyanate 1,6-hexanediol, tested for safety and biocompatibility in accordance with the United States Pharmacopeia, Class IV[17]. The EX30 material exhibited elasticity 1.5 times greater than that of PC30, thus removal and insertion were easier, in addition

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the aligners were four times more adaptable than that produced with PC30. Between the two materials, there is a significant difference in the stress-strain curves, at equal deflection, the thinner material (EX30) is able to develop a greater force[20]. However, orthodontists reported that 70 to 80% of their treatments required midcourse correction, case refinement or conversion to fixed appliances before the end of treatment[21,22].

From 2013, EX30 has been replaced by a new innovative polymer called Smart Track (LD30), a multilayer aromatic thermoplastic polyurethane/co-polyester. The material's features that provide better performance include a gentle and more constant force, a more long-term action and improved adhesion thanks to the elasticity of the material, as well as convenience and ease of use for the patient. This new technology, LD30 has three main advantages compared with EX30: greater consistency of application of orthodontic forces, greater elasticity, chemical stability and an even more precise and comfortable aligner fit[23,24].

Aim of this study was to investigate and compare main technical and morphological features of Invisalign® aligners made with two different polymer blends: EX30 and LD30 to better understand from a chemical-physical point of view the properties that make it the current ideal mixture for fabricating orthodontic clear aligners. Both materials have been analyzed with the Fourier transform infrared spectroscopy (FTIR analysis) and with micro-Raman spectroscopy to evaluate the chemical structure of the two different polymers. Afterwards the degree of crystallinity was investigated, by using X-ray diffraction (XRD) technique in order to evaluate, compare and analyze crystalline phases in the two materials and then identify the physical-chemical properties describing their mechanical behaviors before and after clinical use.

Subsequently to verify and proof the mechanical characteristics of the two polymer blends, tensile strength and indentation tests have been carried out, with the aim to compare possible differences in the mechanical behavior starting from samples with the same geometry (realized in the same mold).

MATERIALS AND METHODS

Forty Invisalign® aligners were selected for experimental *in vitro* tests, 20 LD30 aligners and 20 EX30 aligners, each group was divided in two subgroups, never used and intra-orally aged (Table 1). The clinically used aligners worn intra-orally for two weeks, approximately 22 h each day.

From each aligner, 10 specimens were prepared from buccal surfaces of the incisor region by the careful cutting of samples approximately 5×5 mm under a stereomicroscope. Two specimens of each aligner were analyzed.

FTIR analysis
Since the exact constituents of the aligners are unknown, a material that could be reasonably used as a reference

Table 1 List of samples

Sample label	Description
LD30N	Smart Track never used
LD30U	Smart Track used
EX30N	Exceed30 never used
EX30U	Exceed30 used

was needed. After comparison of EX30 and LD30 spectra with other known spectra reported in the literature, polyurethane (PU) was selected for the analysis of FTIR data. The front tooth mold was selected for its planarity with respect to the other aligner regions. FTIR analysis was performed with a Perkin Elmer Spectrum 1000 FTIR device in transmittance mode (Perkin Elmer, Waltham, MA, USA).

Micro-Raman spectroscopy analysis
Raman spectroscopy analysis was performed to investigate the chemical composition of the samples and to compare these results with those from the FTIR tests. The measurements were carried out with a Thermo Fisher Scientific DXRxi Raman Imaging Microscope. A 532-nm laser was powered at 1 mW, and the samples were irradiated with an exposure time of 2 s for 500 accumulations. The spectra were acquired in the range from 50 to 3,000 cm^{-1} with a 20× objective, by the selection of two different focal depths for both materials.

XRD characterization
XRD is used for analyzing crystalline phases in solid materials, determining the extent of crystallinity and identifying crystalline structure. The crystalline parts give sharp narrow diffraction peaks, while the amorphous component gives a very broad peak (halo). The ratio between these intensities can be used to calculate the degree of crystallinity in the material. The intensity of X-ray scatter from the entire sample corresponds to the total area under the diffraction pattern. XRD patterns were recorded at room temperature by means of a Philips X'Pert diffractometer equipped with a CuK$_\alpha$ radiation source (λ=0.1542 nm). Data were collected by the step-scanning mode with steps of 0.02° (step time, 2 s)[25]. Intensity of the diffracted beam from the crystalline zone (Ic) was the area under the sharply resolved peaks, whereas the remaining area under the curve was the intensity of the diffracted beam from the amorphous zone (Ia). The degree of crystallinity was determined as: $\theta_C=[I_C/(I_C+I_A)]\times100$, where I_C is the intensity of diffracted beam from crystalline part[23], corresponding to the area under the peak at higher 2θ, and I_A is the area under the second peak. The degree of crystallinity of the samples was determined from the deconvolution of XRD patterns, allowing to compare the intensity of the peak centered at 2θ=17° with that of the peak centered at 2θ=27°. The position of the main peak shifted toward lower 2θ values for EX30N (17.3° compared with 21°). The other

peak centered on 44° for both samples. The main peak was analyzed with 2-peak fit (Gaussian). The degree of modification (θ_{MOD}) of the XRD pattern was evaluated as follows:

$$\theta_{MOD}=[\theta_U-\theta_N]\times100$$

where θ_U and θ_N are the percentage ratios between the area under the peak at 20° and the total area, for used and new materials, respectively. All reported data such as peak intensity and crystalline degree were evaluated as an average of at least ten spectra of the same set of samples.

Tensile strength test
Maxillary dental arch aligners were used and the first three molar tooth cavities of both sides filled with a filler resin to create two planar grab pads that could be clamped into the tensile vise of the tensile machine, a Testometric with a load cell of 250 N. Due to the characteristic arch geometry of the aligners, two samples of each group were tested in a C-ring tensile test configuration (Fig. 1). To investigate the elastic properties of the two materials and their creep behavior, samples of each group were placed under a load of 65 N at a velocity of 5 mm/min until they reached their elastic limit. Subsequently, a
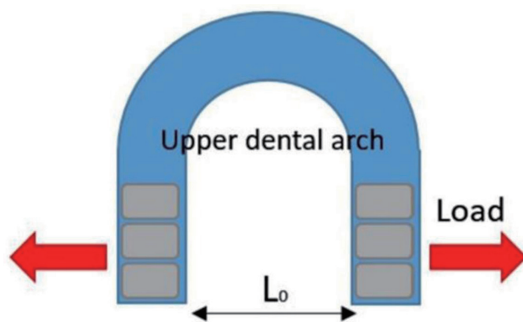

Fig. 1   c-Ring set-up.
The scheme used for testing the tensile strength of the aligner, where L_0 represents the resting position.

second load at the maximum value was applied for 10 min to reach the creep behavior. The test was repeated twice to determine the creep-elastic properties after an initial severe cycle.

Indentation strength test
Samples of each aligner was obtained from the incisive region because of its planarity with respect to the other aligner regions. The hardness of the materials was calculated with a Vickers indenter as the deepness of the imprint caused by the Vickers tip over the samples:

$$Hv=\frac{LOAD\times1.8544}{Project\ Imprint\ Area}$$

Project Imprint Area=diagonal^2
The load applied was 1 kg. The calculated final hardness was determined by the average of ten different indentation experiments on the same set of samples.

RESULTS

In Fig. 2, FTIR analysis is reported, no perceptible differences were appreciated when the FTIR profiles of the LD30 samples were compared with those of EX30 (new and used). The list of detected peaks is reported in Table 2 the measured spectra are comparable with the polyurethane-based spectra found in the literature[26].

Analysis of the Raman data (Table 3) indicated that EX30 aligners had a single spectrum profile, whereas the LD30 aligners exhibited two profiles, one corresponding to a deeper focus and the other registered focusing on the surface of the material. The deeper spectrum measured in the LD30 samples was the same as observed for the EX30, indicating that the LD30 aligners are made of two compounds, one of them also being present in the EX30 material. In Figs. 3a–b, it is possible to appreciate the two different spectral features registered for the LD30 samples, as well as the similarity of the exterior spectra of LD30 and EX30 samples. When the spectra obtained on the surfaces of both aligners were compared, no differences caused by usage were observed in both materials, demonstrating the absence of significant
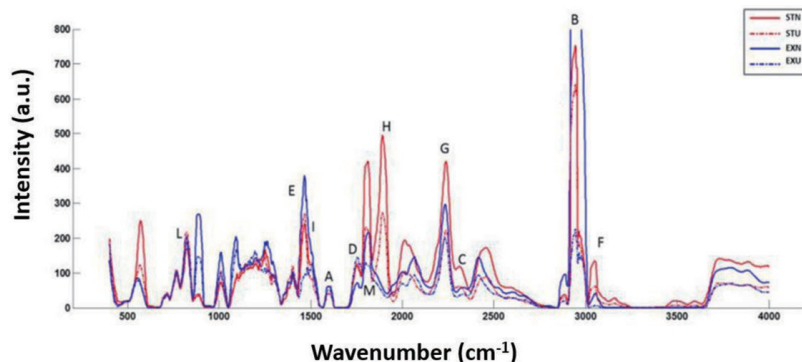

Fig. 2   FTIR traces registered for LD30 and EX30 samples of used and new aligners.

Table 2   List of detected peaks found in EX30 and LD30 spectra

Peak	Wavenumber (cm⁻¹)	Assignments	Movement	Group
A	1,600	v(C=C) vibration C-C=C	Sym stretching	Aromatic
B	2,800–3,000 (s)	C-H bond vibration CH_2 and CH_3	Sym stretching	Alkanes
C	2,312 (w)	C-H bonds	—	Isocyanates
D	1,750–1,735 (w)	C=O Non-bonded	Stretching	Urethanes
E	1,450–1,550	N-H bonds	Bending	—
F	3,000–3,100	C=C-H	Asym stretching	Alkenes
G	2,210–2,260	C≡N stretch	Stretching	Nitriles
H	1,800–1,890	C=O bonds	—	—
I	1,470–1,450	C–H bond	Bending	Alkanes
L	1,000–1,650	=C–H bond	Bending	Alkenes
M	1,950–1,750	3 or 4 small humps	—	Aromatic

Table 3   Percentage of correlation with preloaded materials present in the materials library

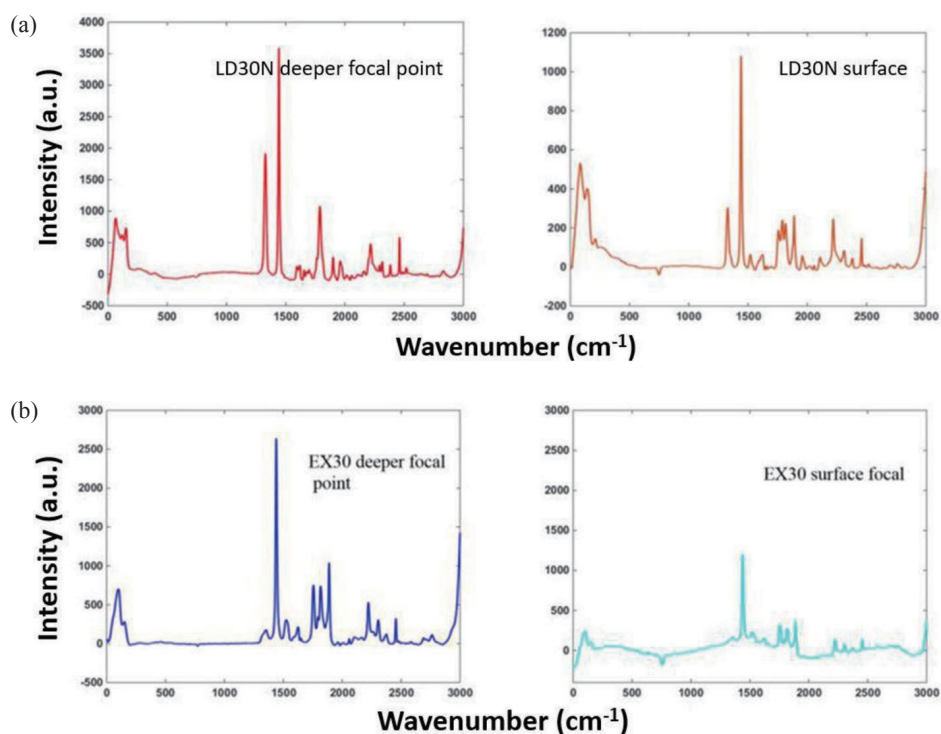| Materials	Correlation
EX30	MDI-PU-ADHESIVE 67% (polyurethane) Poly trimethyl exanethilene terephthalanide 73%
LD30	MDI-PU-ADHESIVE 67% (polyurethane) Poly trimethyl exanethilene terephthalanide 73% Poly ethylene terephthalate 82%

Fig. 3   Micro-Raman spectroscopy analysis of LD30 (a) and EX30 (b).
On the left, the Raman spectrum corresponds to the deeper focal point; on the right, the spectrum registered on the surface of the same sample.

contaminants on the aligners after usage.

Figure 4 shows the peak analysis of never-used samples of EX30 (EX30N) and LD30 aligners (LD30N) (XRD). The total intensity scattered from the entire sample was divided into two zones: crystalline and amorphous.

Both diffractograms exhibits broad peaks at 2θ angles around 18°, 27°, and 43° which can be assigned to the scattering from polyurethane chains with regular interplanar spacing[25]. It indicates some degree of crystallinity: the higher the degree of crystallinity, the greater is the intensity of the peak at 17°[27].

The degree of crystallinity was reported in Table 4, where it was found that EX30N has a crystallinity of 37%, while θ_C of LD30N was found to be lower (28%).

XRD analysis of EX30 and LD30 before and after use revealed a modification of both materials after treatment (Fig. 5). Deconvolution methodology could not be applied to the XRD patterns of used materials, since the peak became sharper and the shoulder disappeared, so it was not possible to identify two contributions at 19° and 26°, and therefore the deconvolution in this area
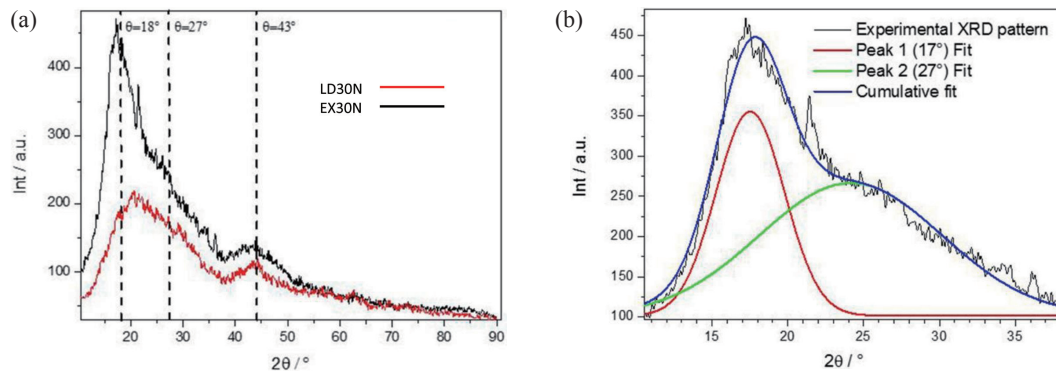

Fig. 4 (a): Peak analysis of never-used samples of EX30 (EXN) and Smart Track (LD30N) aligners.
(b): Deconvolution of XRD patterns of EXN with 2-peak fit (gauss)

Table 4 Degree of crystallinity of EX30N and LD30N samples

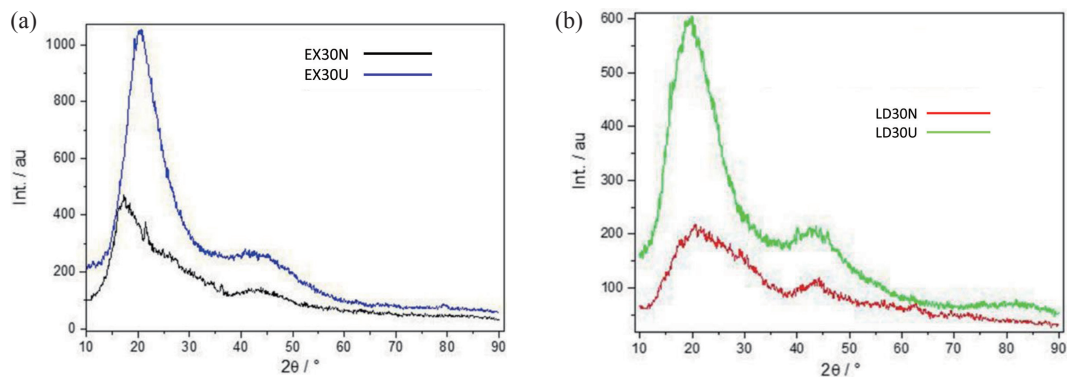| Sample	I_C	I_A	I_T	θ_C/%
EX30N	1,436	2,490	3,926	36.6
LD30N	789	2,041	2,830	27.9

Fig. 5 (a): XRD patterns of EX30 and LD30 (b): Before and after use.

Table 5 Degree of modification of new and used samples

Sample	θ_N/%	θ_U/%	θ_{MOD}/%
xxN	47	58	23
xxU	29	36	24

was meaningless. In both cases, the peak at 20° became sharp and its intensity was much more predominant with respect to the intensity of the peak at 43°. The degree of modification (θ_{MOD}) of the XRD pattern reported in Table 5 demonstrated a similar value for both samples (θ_{MOD} was 23–24%).

The oral aging increased intensity of the peak at lower 2θ for both samples, as a result of increased crystallinity.

When the results obtained by the tensile strength test were compared for the two materials at the first run, the elastic properties of both EX30 and LD30 materials appeared to be similar, taking into account the approximations of the C-ring set-up.

The comparison between the second run of both materials confirmed the differences in the creep region.
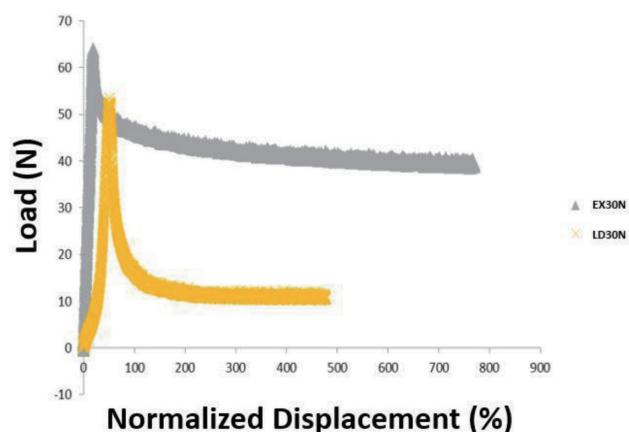

Fig. 6   Tensile test.
          First run. LD30N (yellow trace) and EX30N (grey trace).

In fact, due to the hardening effect of the first run, these differences were more evident. The LD30 material showed a reduced plastic capability and a greater elastic recovery, whereas the EX30 showed a greater residual deformation (Fig. 6). Otherwise, the creep properties were markedly different. Specifically, the elastic recovery of the LD30 results was greater than that of the EX30, with subsequent residual deformation results smaller for the LD30 material. When the first and second runs of the tensile tests of LD30 samples were compared, it was possible to appreciate the repeatability in the behavior. As expected in the second run, a small hardening was noted, due to the application of the load in the first run.

During the indentation test, only the EX30 material showed a traditional residual imprinting, whereas the LD30 sample cracked, and its imprints were smaller (Fig. 7), indicating, according to the results of the tensile strength tests, that the LD30 material was more rigid than the EX30. In Table 6, the measured values are reported. In addition, for evaluation of the mechanical properties after usage, some tests were performed on used samples of EX30 and LD30 materials. In this case, the indentation load (1 kg) did not leave any imprinting on the samples, thus indicating that both materials were inclined to become harder with age and usage, changing their initial properties.

DISCUSSION

Previous studies of Invisalign® have covered primarily technical aspects, materials studies and case reports[28,29]. The efficacy of clear aligner treatment in controlling orthodontic tooth movement has been widely assessed by scientific evidence[30]. With regard to the methods of production, the orthodontic appliance Invisalign® operates with a sophisticated digital study model and treatment planning software called ClinCheck.
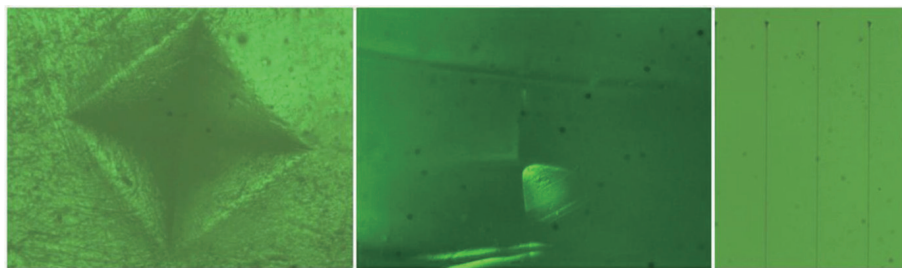

Fig. 7   Vickers imprint over the EX30 material (left) and the LD30 sample (center).
          On the right is the reference line spacing of 10 µm. The maximum error in the measurements is the range of 10%.

Table 6   Elasticity and hardness values measured (HV-Vickers test)

	LD30	EX30
Elasticity	1.83 (N/displ_norm %)	2.48 (N/displ_norm %)
Hardness (HV)	53±5	14±0.7

The software makes it easier to manipulate factors such as tooth proportions to diagnostically evaluate different treatment outcomes prior to commencing treatment. This also allows for excellent communication among clinicians for interdisciplinary treatment planning which can then be relayed to the patient[31].

Most common commercial polymers are a mixture of different states and constituents, such as the two materials examined in our work: EX30 and LD30. Both polymer mixtures are polyurethane-based, and both have a particular scientific formulation, not well-specified for commercial reasons.

Actually, there are few articles in the scientific literature regarding the technical characteristics of the new polymer blend LD30[23,24,32-34]. Only a pilot study has been published in the corporate archives of Align Tech. This study concluded that the new technology has three main advantages compared with EX30: Greater consistency of application of orthodontic forces, greater elasticity and an even more precise aligner fit.

FTIR and micro-Raman analyses reveal that both materials are polyurethane-based, but LD30 also contains another polymer, thus explaining its superior properties. For the used samples, FTIR and Raman analyses did not show the presence of biological material absorbed by or embedded in the aligners. Micro-Raman results confirm the data collected by FTIR, the absence of the second profile in the FTIR analysis can be explained with a surface distribution of this second material that cannot be appreciated in the FTIR transmittance mode.

From a structural point of view, the crystalline domains act as a reinforcing grid, thus improving the performance of the material over a wide range of temperatures[11]. From the XRD analysis of EX30N and LD30N aligners, two broad peaks were detected, a typical pattern for materials containing semi-crystalline or amorphous structure, not defined by a crystalline model. Therefore, the degree of translucency or opacity of the polymer can be directly affected by its crystallinity. Low crystallinity creates benefits in flexibility, resilience and fit, but not in strength, chemical resistance and stability. This means that both polymer mixtures are transparent, elastic and well-adaptable to tooth morphology, even if LD30 seems to possess a greater translucency and flexibility while maintaining better levels of resilience than EX30. LD30 showed a lower θ_C and a higher elasticity than EX30. From a clinical perspective, this results in maximum manageability in the insertion and removal of the aligner, and increased comfort for and compliance of the patient. Furthermore, from the mechanical point of view, the higher degree of elasticity allows for better adaptation to the complexity of dental morphology, adhering perfectly to any surface and providing safety in terms of continuity of force expressed during the treatment as compared with that of an aligner built in a more rigid material. The structural modifications of both materials were similar after use, in agreement with the results of the study by Bradley et al.[35].

The differences in mechanical properties, obtained from the tensile and indentation tests, between LD30 and EX30 could be evidenced in a greater breaking strength of the LD30 material, more rigid than the EX30, which presented a pronounced plastic behavior. The LD30 material had a greater elastic limit, which indicated a trend toward brittle failure in indentation. The observed differences indicated that LD30 was less susceptible to wear than was EX30. Furthermore, both materials became harder and more hyperplastic, causing discomfort for the patients with usage.

The structural modifications of both materials were similar after use. The main differences between EX30 and S<t lay in their original structures, with the latter being more amorphous and thus less rigid. Making purely mechanical considerations, we must also evaluate whether the effectiveness of tooth movement with thermoplastic appliances is less than that expressed by fixed appliances[36]. Therefore, the use of thermoplastic materials in orthodontics requires a sufficient understanding of the characteristics of the materials themselves if an appropriate choice of material is to be made according to its properties. Essentially, unlike the traditional orthodontic techniques, the quality of the orthodontic force exerted by a thermoplastic appliance depends on the mechanical properties in the manufacturing process of the material itself[37]. From a clinical point of view, it must also be considered that, in the oral cavity, the orthodontic devices are subjected to both short- and long-term load forces. For example, a short-term load occurs during the insertion and removal of the aligner, while a long-term load occurs due to forces of mastication exerted during the night[38]. Though subjected to a long-term load in the oral cavity, a thermoplastic orthodontic device must, however, exercise continuous and controlled orthodontic forces, such as those designed to cause tooth movement. In this regard, it is necessary to consider that a thermoplastic material is viscoelastic in nature, which means that the force generated by the planned movement decreases with time[37]. Finally, we look for a thermoplastic material with significant linear elastic behavior and a high point of return. Therefore, of the two polymer blends examined, the "new generation" or LD30, seems abler to meet these demands than EX30, and appears to be less rigid than EX30.

CONCLUSIONS

Smart Track, the last generation of Invisalign® showed a common constituent based on polyurethane, and an additional element that justifies the difference in mechanical properties. In particular, LD30 exhibited a more amorphous structure and a greater elastic recovery than that with Exceed30 with smaller residual deformation.

The XRD analysis confirmed the reduced crystallinity of LD30 with respect to Exceed30, thus explaining the higher translucency even after use.

All tests and measurements demonstrated that Smart Track orthodontic aligners have greater

translucency, higher flexibility, better adaptability to the dental arch and greater consistency of application of orthodontic forces than those produced with the previous polymer blend Exceed30.

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