The thermal, structural and morphological characterization of dental polymers for clinical applications

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1. Introduction

Recently, thermoplastic polymers have attracted increasing interest in dentistry for several applications due to their interesting properties [1-5]. The development of polymers has led to critical biotechnological progress in the fields of biomaterials, drug delivery, medical device development, and tissue engineering [6]. Along with their use by dental clinicians, polymers are now produced in great quantity for a wide variety of dental applications, such as splinting materials, mouth guards, denture liners, denture teeth, denture base materials, maxillofacial prosthetic products, orthodontic appliances, filling materials, core build-up materials, obturation materials (endodontic treatment), dentin bonding agents, cementing and relining materials, fiber-reinforced resin materials, temporary restorative materials, and veneers with satisfactory clinical results related to an improvement of the quality of life [7-12].

Polymers such as polymethyl methacrylate (PA), polyetheretherketone (PK), and polycarbonate (PC) are often utilized in stress-containing dental applications. For example, if these polymers have enough mechanical strength and biocompatibility, as proven by PK, they can also be used as implant material instead of traditional metal ones [13]. Thus, before using these materials in applications that involve load-bearing type stress, it is important to determine the effect of such stress on their structure. As dental polymers are expected to withstand the occlusal forces during oral functions, these materials must display enough mechanical strength to prevent the crack formation, plastic deformation or failure [14].

Polymerization and mechanical properties of the polymers are
directly affected by surface hardness and crystallinity. The crystallization degree of the polymer that is related to kinetic conditions especially in the molding process can also change the glass transition temperature (TG) of the material [15]. TG is an inherent property that has physicochemical effects, functions as a key index to evaluate the properties of polymers and helps to determine the temperature range of material for application [16,17]. Temperature plays an important role in the maintenance of the polymers, as these materials may be exposed to various degrees of temperature in the mouth during cleaning, food intake, or in particular during adjustment, polishing and smoothing processes at the manufacturing stage [18-20]. Additionally, excessive peaks of orally achievable temperatures due to hot and cold food and drink intake may range from -1.2°C to 66.9°C [21]. Along with the increase of the temperature in the oral cavity, the restorative polymer material will come closer to the TG, leading to deformation at lower stress levels [22,23].

In previous studies, the effects of temperature on the fit, stability, internal stress, thickness and impact absorption parameters of some dental polymers have been reported, and it has therefore been proposed that polymers should have similar thermal properties with the dental structure in order to avoid damage to the dental tissues, loss of adhesion, and marginal infiltration [24-26]. Furthermore, the knowledge of the thermal properties of dental polymers is essential for predicting performance during materials lifetime, developing the best processing methods, monitoring effects of aging, or troubleshooting when the polymer does not perform as expected [27]. Therefore, it is necessary to understand dental polymer behavior when subjected to different levels of heat and to choose the appropriate temperature spectrum for clinical applications.

Composition and chemical structure properties have an impact on the mechanical characterization by directly affecting the performance of the polymeric dental products, like enabling the material to better absorb forces, which is important for the clinical success of the restoration [15,24,28]. For this purpose, some reinforcing agents may be used in polymer matrices to transfer occlusal forces from the weak polymeric matrix to the stronger filling material [14]. Therefore, this change in materials composition should be followed by elemental and compound analysis techniques such as Energy Dispersive Spectroscopy (EDS) and X-ray Diffraction (XRD) respectively. To support the data obtained from these two methods, thermal gravimetric analysis (TGA) is actively conducted to assess chemical composition by evaluating the material’s mass loss. The parameter measured in this test, onset thermal degradation, is used as an indicator of the chemical cross-linking degree of the polymer [15]. Although the chemical structure has been shown to affect elastic properties, Young’s modulus, tensile modulus, yield stress, stiffness, stress-strain curve, and lateral strain of dental polymers, the role of chemical properties on thermal, mechanical and morphological properties of dental polymers remains poorly understood, and much remains to be studied [29,30].

To date, it is unclear whether the guidelines of manufacturers, including mentioned materials’ temperatures and characteristics, are adapted to the thermal and mechanical properties of the commonly used materials from which the dental polymers are designed. To the best of our knowledge, no previous attempts have been made to test dental polymers in a comprehensive manner to compare the mechanical, thermal and structural properties. Therefore, a compelling scientific effort was conducted focusing on the investigation of the structure, morphology, and properties of the most common dental polymers (PG, PA, E, PC, PK) to determine their limits and indications. In this study, we aimed to compare the physicochemical characteristics of the above-mentioned dental polymers in an attempt to determine the most ideal biomaterial for dental restoration.

2. Materials and methods

2.1. est groups and materials

The summary of the material groups tested in the present study was depicted in Table 1. In this study, 5 commonly used commercially available thermoplastic dental polymer materials were evaluated including:

Group PG: Polyethylene terephthalate - glycol modified (PG) (ERKODENT Erich Kopp GmbH, Pfalzgrafenweiler, Germany)
Group PA: Poly(methyl methacrylate) (PA) (Amann Girrbach AG, Koblach, Austria)
Group E: Ethylene vinyl acetate (E) (Bioplast®. ScheurTM-Dental, Iserlohn, Germany)
Group PC: Polycarbonate (PC) (ERNST HINRICHS GmbH, Germany)
Group PK: Polyetheretherketone (PK) (Amann Girrbach AG, Koblach, Austria)

Study samples were produced by a CAD/CAM (Computer-Aided design- Computer-Aided Manufacturing) system (Amann Girrbach AG, Koblach, Austria). Virtual images of a disc with a diameter of 5 mm and a thickness of 4 mm were obtained with the laboratory scanner of the selected digital system (Ceramill® map 200+, Amann Girrbach AG, Koblach, Austria) by scanning a previously fabricated metal disc. After developing a milling plan, all samples were milled from related ready-made, polymer dental blocks or discs (stated above) in the milling unit (Ceramill® mikro 5X; Amann Girrbach AG, Koblach, Austria). Milled samples were polished to obtain a standard surface under abundant water for 60 s using silicon carbide papers from P400 up to P2000 in an automatic polishing device (SAPHIR 550; ATM GmbH, Mammelzen, Germany). After polishing, samples were cleaned in an ultrasonic bath (5 min-50°C), washed with distilled water and air-dried. The flow chart of the experimental route for the study materials tested via chemical and physical processes was shown in Figure 1.

For each group, 90 samples were analyzed. The sample size was determined based on an initial power analysis (PS software; Dupont and Plummer, 1997) conducted according to similar previous studies (mean gamma count with 80% power and 5% significance level). Each study group was further divided into 6 subgroups according to the conducted analysis (n=15 per subgroup). Therefore, a total of 450 samples was considered by performing all measurements 3 times and the results were recorded as mean and standard deviation.

2.2. Analyzes

2.2.1. SEM observations

To evaluate qualitatively the surface morphology and topography of the selected polymers, samples were observed with SEM (Zeiss EVO LS 10; Carl Zeiss NTS, Germany) using the acceleration voltage of 25kV. To prevent charging during irradiation, samples were sputter-coated with gold-palladium (Au-Pd) (80%-20%) prior to analysis, and at least three images were taken for each sample.

2.2.2. Identification of elements using EDS

Coupling with SEM, the microstructural analysis was further conducted by using EDS. The elemental weight percentages of samples were determined by EDS (Oxford AZtec Energy, Oxford Instruments, Abingdon, UK). For clear measurements, EDS was conducted on particles greater than 10 μm. Reading was performed from three areas per sample.

2.2.3. Hardness tests

The surface hardness of the samples was measured by using a Shore-D durometer (DIN 53 505, CASA) according to the ASTM standard D2240-00 (ASTM Standard D, 2240, 2010). At least five measurements were taken from each sample and all the data were processed using FIE software.
Table 1. Structural characteristics of mineralized human tissues and tested polymeric families and their potential dental applications.

| Material | Structure | Young’s modulus (GPa) | Advantages | Disadvantages | Dental applications | References |
|----------|-----------|------------------------|------------|---------------|---------------------|------------|
| PG       | 2.2       | High hardness Low water absorption Thermal shock resistance | Thermal expansion Low tensile strength | Bite and base plates Oclusal splints Casting objects/copings Functional trays | 73,74 |
| E        | 0.015-0.080 | Good mechanical behavior | Low tensile strength High flammability | Mouth guard Interocclusal splint Thermoplastic dental filling Denture liners | 34,75-79 |
| PC       | 2.0–2.4   | High toughness High mechanical retention Good abrasion resistance Heat resistance Dimensional stability | Low fatigue resistance Degradation Yellowing tendency Need of drying | Orthodontic brackets Pediatric crowns Temporary crown and bridges Oclusal splint | 80-83 |
| PK       | 3–4       | Stable Biocompatible Reduced degree of discoloration Good toughness High stiffness | High cost High processing temperatures | Fixed restorations Dental implants Individual abutments | 84-91 |
| Biocompatible | | | | Removable dentures and components Maxillary obturator prostheses | |
| PA       | 3–5       | Abrasion resistance High hardness and stiffness Low water absorption Favorable polishing ability | Low fractural strength Poor solvent resistance Notch sensitive | Artificial teeth Denture base Temporary crown and bridges Dental adhesive Impression tray Temporary crowns Implant drilling guide Night guard | 35,92-98 |

Dentin - 15 - - - - 99
Enamel - 40–83 - - - - 99
Cortical bone - 14 - - - - 100

PG, Polyethylenterephthalat – glycol; E, Ethylene Vinyl Acetate; PC, Polycarbonate; PK, Polyetheretherketone; PA, Polymethylmethacrylate.

Fig. 1. Flow chart of the experimental route for the study materials teste via chemical and physical properties.
2.2.4. Chemical characterization with FTIR analysis

The structural characteristics of the tested materials were evaluated by FTIR spectroscopy (FT-IR Spectrum100, Perkin Elmer, Waltham, MA) with an accessory of attenuated total reflectance (ATR) (Elmas/ZnSe ATR). The absorption spectra were noted with wave numbers 600 to 4000 cm\(^{-1}\) in the transmittance mode using a resolution of 2 cm\(^{-1}\) and 16 scans. To identify the percentage of reacted double bonds, the absorbance intensity ratios of the C = C(aliphatic) absorbance peak at 1638 cm\(^{-1}\) and the internal C = O(carbonyl) standard peaks at 1720 cm\(^{-1}\) were determined.

2.2.5. DSC analysis

DSC measurements of the specimens (8±1 mg, n=15) were performed by Perkin Elmer Diamond DSC 8230 (Perkin-Elmer, Waltham, MA) equipped with a cooling system (RCS 90, Refrigerated Cooling System). The specimens were tested with the heating rate of 10°C/min under nitrogen atmosphere (flow rate: 50 mL/min) in three heating steps. In step 1, the specimens were heated from -50°C to 150°C to erase the thermal past. In step 2, the specimens were cooled down from 150°C to -50°C. Finally, in step 3, the specimens were heated from -50°C to 200°C. With this method, TG of the specimens was determined. The obtained data was analyzed using NETZSCH-TA4_5 Proteus Software (NETZSCH Proteus, thermal Analysis, Netzsch, Selb, Germany).

2.2.6. TGA and thermal stability

Thermal stability of samples was evaluated by thermogravimetric analysis using EXSTAR TG/DTA 6300 (Seiko, Tokyo, Japan). Samples (8±1 mg, n=15) were placed in a ceramic crucible and tested with a heating rate of 10°C/min, from room temperature to 900°C under the nitrogen atmosphere (flow rate of 50mL/min). The thermal stability of the samples was determined by calculating the mass(weight) loss with the increase in temperature. TGA curves for each group were generated by using Pyris software (Pyris - Instrument Managing Software, Version 11, Perkin-Elmer,Waltham, MA).

2.2.7. XRD analysis

Wide-angle X-ray scattering measurements (the analysis for the particle size distribution and tap density) using synchrotron radiation were performed with an X-ray diffractometer Panalytical X’PERT PRO (Malvern Panalytical, Malvern, UK). In normal reflection mode, Ni-filtered Cu Kα radiation procedure (45 kV, 40 mA) was followed at room temperature with the alignment of samples (λ = Cu Ka 1 = 1.5418 Å). The samples were analyzed between the scanning range of 5-90° (2θ).

2.3. Statistical analyses

Statistical analyses were carried out using statistical software (SPSS V23; IBM Corp. Armonk, NY). All data were submitted to the Shapiro-Wilk test to verify the normality of data, and one-way ANOVA was used to compare normal distribution data between groups. Homogeneity of variance was examined by Levene’s test, and the differences between the groups were determined by using a Tukey’s HSD from multiple comparison tests. Analysis results were shown as means and standard deviation. The significance level was considered for p < 0.05.

3. Results and Discussion

In this study, the thermal and structural properties of commonly used dental polymers were characterized by using SEM, FTIR spectroscopy, TGA, XRD analysis methods, and hardness measurements. In addition to the information provided by manufacturers on the composition of the materials tested, EDS and XRD analyses were required to reveal their chemical and structural characteristics. To our knowledge, this is the first study that conducted a chemical, morphological and structural comprehensive evaluation of widely used dental polymers in an attempt to guide clinicians on their use and limitations.

3.1. Structural analysis

The structural analysis of the surfaces of the samples was carried out by SEM, and EDS was performed to analyze the chemical structure. The surface property of the samples was also evaluated with the hardness test. FTIR Spectroscopy relies on infrared light to scan samples and observe the bond properties of the material tested. This highly reliable method can identify the general type of material and its composition [31]. Therefore, this FTIR method was used to acquire detailed information about the structural contents of the samples.

3.1.1. Elemental Analysis and SEM

Five representative EDS images for each group with respective percent composition of identified chemicals are shown in Figure 2. While a significant amount of carbon (C) was determined in the structure of all groups, silica (Si) was detected secondly in the PK, PA, and E groups. The Si percentages of the materials tested were given in Table 2 by weight. Other elements such as sodium (Na), magnesium (Mg), oxygen (O), iron (Fe), sulfur (S), titanium (Ti), and calcium (Ca) were also detected.

The mechanical and physical properties of the polymers were reported to depend on the volume and types of additives [32]. To better characterize the chemical structure of the tested polymers, EDS was performed before the XRD analysis. EDS analysis showed the C as a major phase since it is a major element in the polymer structure. The reason for the presence of Si in the groups can be explained by the fact that Si is one of the ceramic samples and the materials are modified by manufacturers due to patient needs [33,34]. XRD analysis which was conducted in order to determine the ceramic-based materials in a detailed manner revealed SiO2 and the other ceramic-based compounds. SiO2 which is widely used as a filler in engineering polymers is added to the matrix in various contents in order to improve the properties of the material and to increase the bond strength to resin cement [33, 35,36]. All the Au and Pd content in the samples was determined because of the thin conductive layer which was coated on the samples prior to SEM analysis in order to prevent the charging effect. The other elements like Mg, Na and Ca are considered being due to the ceramic content in the structure to strengthen the material. Chemical analysis results show that the groups with high percentages of SiO2 may be used in applications performed with a silane coupling agent and resin cement or inorganic fillers [37].

SEM images of the study groups are shown in Figure 2 with inset images of corresponding samples. Regarding morphological observations of surfaces, visual cues for inhomogeneities such as bulges, valleys, ruptures, residues and partial spallation areas. The arrows indicate these defects and surface characteristics. Group E displayed the most irregular surface among all groups, while Group PK revealed the smoothest surface only with tiny residues.

3.1.2. Hardness test

In order to evaluate the mechanical performance of these materials, the hardness values of the samples were measured with a Shore D hardness tester. At least 3 measurements were conducted by each

| Group | Weight (%) |
|-------|------------|
| PG    | 0.26       |
| E     | 2.62       |
| PC    | 0.11       |
| PA    | 0.38       |
| PK    | 0.28       |

Table 2. Si percentages (mean weight%) measured by EDS in test materials.
sample, and the mean values of hardness were plotted (Fig. 4). The obtained shore ‘D’ values were ~65, ~75, ~82.4, ~37.4, and ~87.2 corresponding to PG, PC, PA, E, and PK, respectively. Among them, group PK and PA showed the highest hardness values as compared to groups PG, E, and PC. Therefore, the higher hardness was obtained due to dense skeleton that may be correlated with the SEM images (Fig. 2). Additionally, it was found that while the Shore D hardness values of the samples decreased, the mass loss of the samples increased (Table 3). Thus, the order of hardness values was PK>PA>PC>PG>E. These results were consistent with the Archard equation commonly used to model wear, and the increased hardness of a material can in most cases reduce the wear rate [38]. In addition to material performance, wear or mass loss is also important in terms of causing systemic effects (toxicological and/or biological) of inhaled or ingested worn particles that derive from dental materials with lower hardness values [39]. Therefore, high Shore D hardness
Table 3. Thermal properties of commercial dental polymers measured by DSC and TGA (mean ± standard deviation).

| Group | Mass loss (%) | Residues (%) | TD, onset (°C) | TG (°C) |
|-------|---------------|--------------|----------------|---------|
| PG    | 91.40 ± 1.40d | 8.60 ± 1.40a | 344.60 ± 2.66a | 80.00 ± 2.35c |
| E     | 79.80 ± 1.13c | 20.20 ± 1.13b| 289.50 ± 2.23b | 50.00 ± 2.12d |
| PC    | 75.90 ± 1.77b | 24.10 ± 1.77c| 401.10 ± 1.74c | 145.00 ± 2.00a |
| PK    | 44.60 ± 1.44a | 55.40 ± 1.44d| 520.70 ± 4.90 | 143.00 ± 1.87a |
| PA    | 73.70 ± 1.13b | 26.30 ± 1.13c| 167.60 ± 5.06e | 120.00 ± 2.00b |

p* <0.001 <0.001 <0.001 <0.001

Means in a given column with the same letters (a-e) are not statistically different (p>0.05). * One-Way ANOVA, TD,onset: Thermal decomposition onset temperature, TG: Glass transition temperature.

Fig. 3 (a-e). FTIR spectra of (a)PG, (b) E, (c) PC, (d) PK, (e) PA.

Table 4. Absorption peaks and bonds of the study groups according to FTIR spectra.

| Group | Peaks (cm⁻¹) | Bonds |
|-------|--------------|-------|
| PG    | 1713.64, 1240.23, 2917.25 and 2849.81 | -C=O stretching (ester group) | C-O-C stretching (ester group) |
| E     | 1200 and 1019.56, 1465.92 and 1371.16, 1736.32, 2949.71 and 2849.81 | C-O-C stretching (ester group) | Aliphatic –C-H bending |
| PC    | 1157.48 and 1218.88, 1504, 1601.92, 1769.60 | C-O-C stretching (ester group) | C-C stretching (phenyl group) |
| PK    | 1050 and 1305.01, 1486 and 1594.11, 1648.51 | C-O-C stretching (ester group) | C-C stretching (phenyl group) |
| PA    | 986.84, 1239, 1455.19, 1723.14, 2950.93 and 2993.21 | O–CH₃ bending | C-O-C stretching (ester group) |
|       |              | Aliphatic –C-H bending | C=O stretching (ester group) |

groups can be used in clinical applications that contain more stress like a mouth guard, substructure, oral appliances, denture base, filling or build-up, however additional studies are required. Here, it would also be worth mentioning that group E may be more prone to wear since there is a significant difference compared to the other groups. Therefore, the use of this material at long-term or high-level-stress-containing treatment modalities is not recommended. This result was expected since E has reduced hardness values when compared to the others but since the full composition of the materials is unknown, there is still a gap between the hardness values between materials tested. According to Donoso et al., higher hardness values result in lower porosity and smooth surface effect [40]. In this study, the lowest hardness belonged to group E which displayed the most irregular surface, while the opposite was valid for the group PK. This negative correlation between hardness and surface roughness is important due to the volume loss of the material during function or parafunction as surface roughness is directly proportional to the wear rate [41]. The surface roughness values of the study groups may also be explained by
the effect of specimen preparation (milling) or polishing procedures. Additionally, clinical adjustments such as polishing affect the surface roughness of the material [42]. Therefore, polishing is recommended to obtain optimal clinical performance of dental polymers and to extend the longevity of the restoration. Besides, increasing hardness can decrease the toughness of the material that characterizes a material’s resistance to fracture, and lower fracture resistance is undesirable for successful material performance [43,44].

3.1.3. FTIR analysis

The chemical bonding of dental polymers was characterized by FTIR spectroscopy. As shown in Figure 3, the FTIR spectrum showed the transmittance spectra of the characteristic peaks from PG, E, PC, PK, and PA. The lowest peak occurred at 1019.56 cm\(^{-1}\) in the group E, and the highest peak value, 1648.51 cm\(^{-1}\), was detected in the group PK (Table 4).

Mechanical properties of polymers are affected by the spatial distribution and structural arrangement of the polymer chains and detailed chemical characterization of the samples has been performed by FTIR analysis [45]. The FTIR spectrum of PG showed that the band at 1713.64 cm\(^{-1}\) belonged to the C=O group and the peak occurred at 1240.23 cm\(^{-1}\) indicated the C-O-C vibration of the ester group. The strong peaks at 2917.25 and 2849.81 cm\(^{-1}\) belonged to aliphatic C-H stretching vibrations for this material. The strong peaks at 2917.25 and 2849.81 cm\(^{-1}\) in Figure 3 belonged to aliphatic C-H stretching vibrations of E and strong C=O stretching vibration was observed at 1736.32 cm\(^{-1}\). The aliphatic C-H bending vibrations were seen at 1465.92 and 1371.16 cm\(^{-1}\) and the strong peak at 1200 cm\(^{-1}\) and the peak at 1019.56 cm\(^{-1}\) showed C-O-C stretching of ester groups in the E.

The main characteristic peak of PC was the C=O stretching vibration and it was observed at 1769.60 cm\(^{-1}\) in the FTIR spectrum. The stretching of the C-C bond of the phenyl group and the C=C bond vibration occurred at 1601.92 cm\(^{-1}\) and at 1504 cm\(^{-1}\), respectively. The O=C=O stretching of the ester group was seen between 1157.48 and 1218.88 cm\(^{-1}\). As shown in Figure 3, the peak observed at 1486.03 cm\(^{-1}\) was the aromatic C=C bond for PK. This group showed strong characteristic peaks at 1648.51, 1594.11, 925.56 cm\(^{-1}\) due to the C=C=O stretching, skeletal in-plane vibration of the aromatic ring and aromatic out-of-plane bending vibrations, respectively. The peaks between 1305.01 and 1050 cm\(^{-1}\) were C–O–C rotation and stretching vibrations of the diphenyl ether group. The bands at 986.84 and 1435.19 cm\(^{-1}\) belonged to O–CH\(_3\) bending and stretching deformation of PA, respectively. C=O stretching vibration peak was observed at 1723.14 cm\(^{-1}\). The peak at 1239 cm\(^{-1}\) was due to C–O=C stretching with bands at 2950.93 and 2993.21 cm\(^{-1}\) belonged to C–H stretching vibrations. It can be deduced from these data that all the groups showed consistent results with the current literature [46-50].

3.2. Thermal analysis

Thermal test results with TGA, DSC, and XRD for the structural evaluation of samples are as follows:

3.2.1. TGA and DSC

DSC analyses were performed to measure the thermal properties of the tested materials. The determination of TG (softening temperature) was calculated by using DSC curves (Table 3). The mean values of TG differed by groups (p<0.001), and the highest values were obtained in the PC (145.00±2.00°C) and PK (143.00±1.87°C) groups. The lowest mean value was obtained in group E (50.00±2.12°C).

The normal temperature in the oral cavity is between 32-37°C and can rise to various temperatures closer to the TG, thus can lead to irreversible material deformations [22,23]. Therefore, TG is an important parameter that needs to be taken into consideration and the polymers used to produce a dental restoration should have a TG high enough to prevent distortion and softening during usage [20]. Correlated with DC, our results displayed TG values between 50.00±2.12°C and 145.00±2.00°C for all groups, suggesting clinical implication under impact forces for group E due to the intake of hot contents. Since the oral temperature can rise to 67°C during food or beverage intake and E can be distorted by temperature easily, this material is not safe for permanent restorations or whole-day usage [21]. It was deduced from the results that the structure of the polymer chains was not significantly affected, and the other groups exhibited higher TG values suitable for daily use and dental applications in a high-temperature environment [51]. The samples of the groups PG, PC, and PK exhibited compatible TG values with the literature, while the groups PA and E displayed slightly higher values [51-55]. This
situations may be due to differences between brands, cross-linked structures, additives, and production methods of materials used in the present study and the literature. Additionally, the differences between the onset degradation of the materials indicate that the products have different cross-link densities. One of the most important parameters that can limit the applications of the polymer materials is thermal stability. Therefore, thermal stability is an area in need of improvement. For this purpose, the thermal properties of these polymer materials used in the dental area were investigated. The thermal stabilities of the materials were evaluated by means of TGA analyses. The degradation data and mass loss were obtained from the TGA thermograms (Fig. 5, Table 3). Figure 5 shows the thermogravimetric plots for the PK in the temperature range of 25-900°C with two-step decomposition, while PC exhibited a degradation step behavior in the range of 400-650°C. E also showed two degradation steps due to the removal of acetaldehyde and the degradation of the copolymer. Similarly, PETG showed a broad peak at 2θ = 5-90°. It was clear from the results that the samples exhibited different thermal degradation behaviors, as the mean values of mass loss differed according to the groups (p < 0.001). The highest mass loss was obtained in PG (91.41%±1.00%) group, while the lowest mean value was obtained in PK (44.60%±1.44%) group.

The X-ray diffraction patterns of selected dental polymers scanned over the range 2θ = 5-90° were shown in Figure 6. The XRD patterns of the PETG showed a broad peak because the polymer was amorphous and the pattern obtained was compatible with the literature, thus the polymer was indicated as PETG [60]. It was clearly noticed in the diffraction pattern of PMMA that three broad peaks at 14.3°, 30.64°, and 42.34° were present for PMMA which showed the amorphous nature of PMMA [61-63]. In the XRD pattern of PK, two sharp XRD peaks were 2θ = 19.6° (110 plane) and 23.72° 2θ (200 plane) were observed (ICCD card No. 06-062-1287) [64]. Accordingly, the XRD pattern of PK showed an intense peak at approximately 21° 2θ, which corresponded to the crystalline regions [64-66]. In Figure 6, the XRD pattern of a semi-crystalline PEEK polymer displayed peaks 18.8°, 20.99°, 22.9°, and 28.9° were indexed 110, 113, 200, and 213, respectively. These values obtained for PEEK with an orthorhombic crystal with Pbcn space group symmetry indexed 110, 113, 200, and 213, respectively. These values obtained for PEEK with an orthorhombic crystal with Pbcn space group symmetry were ranged from 55.40±1.44% (group PK) to 86.00±1.40% (group PG), indicating the highest mass loss in the PG group. Measurements showed two typical E weight losses, one corresponding to acetic acid and the second resulting from fragments from the polymer backbone. Least thermal loss and highest thermal degradation onset temperatures were observed at group PK because of the high thermal performance of PK. The findings of the present study confirmed the outcomes of the existing literature [57-59].

3.2.2. XRD

X-ray diffraction patterns of selected dental polymers scanned over the range 2θ = 5-90° were shown in Figure 6. The XRD patterns of the PETG showed a broad peak because the polymer was amorphous and the pattern obtained was compatible with the literature, thus the polymer was indicated as PETG [60]. It was clear from the results that the samples exhibited different thermal degradation behaviors, as the mean values of mass loss differed according to the groups (p < 0.001). The highest mass loss was obtained in PG (91.41%±1.00%) group, while the lowest mean value was obtained in PK (44.60%±1.44%) group.

The TGA scans for materials tested revealed that little or no mass loss occurred up to a temperature degree of 167.60±5.06°C and demonstrated that all the groups were thermally stable up to this degree under inert conditions. Consistent results were obtained with the study by Chen et al. and mass loss was observed almost completely in the group PG [56]. The final weight percent of the residue particles were ranged from 55.40±1.44% (group PK) to 86.00±1.40% (group PG), indicating the highest mass loss in the PG group. Measurements showed two typical E weight losses, one corresponding to acetic acid and the second resulting from fragments from the polymer backbone. Least thermal loss and highest thermal degradation onset temperatures were observed at group PK because of the high thermal performance of PK. The findings of the present study confirmed the outcomes of the existing literature [57-59].

4. Conclusion

This study evaluated the physicochemical and thermal properties of commonly used dental polymers. Further studies should be conducted to analyze other thermo-mechanical properties such as thermal expansion and shock absorbance, as well as hardness parameter was evaluated in this study, and detailed dynamic mechanical tests are needed. One limitation of this research was the in-vitro design with dry samples. These parameters should also be investigated in-vivo, as results may vary depending on the oral environment and the presence of water due to absorption.

Thermal degradation of the tested materials has been observed to start at the degree of 167.60±5.06°C and did not show any risk for the range of clinical applications, like adjustment or polishing. The TG of all polymers was between 50-145°C, and only E should be used with caution in terms of the hot content consumption or heat-generating clinical procedures. PK and PA showed the highest hardness values and lowest mass loss percentages among all tested polymers. Therefore, these two materials can be used safely in stress-containing treatments such as a denture base, provisional restorations, mouth guards, or build up. Correlating with SEM images, PK has been found to have the smoothest surface and E displayed the most irregular surfaces, indicating which material should be preferred to increase cleanliness or reduce plaque accumulation. Finally, the presence of SiO2 is important for the use of PK, PA, and E in applications performed with a silane coupling agent, and inorganic fillers or resin cement.

Conflict of Interest

The authors declare that they have no conflict of interest.

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