Mechanical Properties of Orthodontic Thermoplastics PETG/PC2858 after Blending

Yan Song MA[1], Dong Yu FANG[1], Ning ZHANG[1], Xue Jia DING[2], Kun Ya ZHANG[3], Yu Xing BAI[1]

Objective: *To characterise and compare the tensile characteristics after multi-proportional blending, to determine the proper blending ratio for new thermoplastic material and to compare its mechanical performance with commercial thermoplastics.*

Methods: *PETG and PC2858 aggregates were blended in five different ratios. Standard specimens of each ratio were molded and tested to determine their mechanical performance. Then the new material with the proper blending ratio was chosen and compared against commercial thermoplastics.*

Results: *With the increase of PC2858 content, the tensile and impact strength increased but elongation at break decreased. When blending ratio (wt %) was 70/30, the PETG/PC2858 exhibited optimal mechanical properties, with a tensile strength of 63.42 ± 1.67 MPa, and a stress relaxation rate of 0.0080 ± 0.0005 N/s, which exceeded those of Erkodur and Biolon.*

Conclusion: *By blending PETG and PC2858 at the weight ratio 70/30, we obtained new thermoplastic material which outperformed commercial products.*

Key words: *blending modification, mechanical properties, thermoplastics*
Chin J Dent Res 2016;19(1):43–48; doi: 10.3290/j.cjdr.a35696

Invisible orthodontic treatment without braces, promoted by computer-aided design and computer-aided manufacturing (CAD/CAM) technology, has gradually become a popular orthodontic approach since the Invisalign System was launched by Align Technology in 1998[1]. Compared with traditional fixed appliances, invisible aligners are aesthetically appealing, and have been meeting the requirements demanded by the increased number of adult patients. In addition, given that they are easy to use, they are more comfortable and the predictability of the treatment goal is improved, this technique is more attractive. However, it is difficult for aligners to resolve complicated cases such as severe crowding, a deep bite and rotation of round teeth in practice. Orthodontists often need case refinement or even have to turn to brackets given that treatment efficacy of aligners is significantly lower than that of fixed appliances[2-5].

Thermoplastics for aligners are a sort of polymer material with different properties. Amongst all the inherent properties, mechanical performance plays a critical role in developing continuous orthodontic forces and obtaining an acceptable therapeutic effect. Invisible orthodontic force, derived from the deformation and resilience of aligners is radically determined by the autologous structures, the arrangement and entanglement of molecular chains. The desirable properties of orthodontic thermoplastics should include transparency, lower hardness, better elasticity and resilience, and resistance to aging. However, common thermoplastic products in the market are mostly used for retainers instead of aligners. Therefore, to improve the efficacy

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1 Department of Orthodontics, School of Stomatology, Capital Medical University, Beijing, P.R. China.
2 Key Laboratory of Beijing City on Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing, P.R. China.
3 School of Biomedical Engineering, Capital Medical University, Beijing, P.R. China.

Corresponding author: Dr Yu Xing BAI, Department of Orthodontics, School of Stomatology, Capital Medical University, Tian Tan Xi Li, #4, Dongcheng District, Beijing 100050, P.R.China. Fax: 86-10-57099220. Email: byuxing@263.net

This work was supported by the National Natural Science Foundation of China (NSFC Grant No. 81470779) and Beijing Municipal Commission of Health and Family Planning (Grant No. 2013-2-013).

of aligners, it is important to study the characteristics of thermoplastics and to develop a better material which exhibits more effective properties.

Based on the previous study, blending is an effective way to modify the present materials and to develop novel thermoplastics. Polyethylene Terephthalate Glycol (PETG), Polycarbonate (PC) and Thermoplastic Polyurethanes (TPU) are mostly used for bending modification[6]. PETG, non-crystalline co-polyester, which consists of 1, 4 - cyclohexane two methanol (CHDM) ,ethylene glycol (EG) and terephthalic acid (TPA), exhibits better transparency, good fluidity, and strong solvent resistance[7-10]. PC, which is compatible with PETG after blending, is another type of engineering plastic, which offers outstanding mechanical properties such as excellent strength, dimensional stability and a low water absorption rate. For orthodontic use, this material is transparent to visible light and has remarkable light transmission. In addition, sticky during melting makes PC display high impact strength and toughness[11-13].

TPU is a kind of universal elastic polymer with abrasion and oil resistance, which improves the viscoelasticity, solvent resistance and the ease of processing of the blend. However, the increased opacity after blending restricted its application in developing invisible orthodontic thermoplastics.

In view of the previous study, PC2858, a novel brand of PC, had superior mechanical properties compared to others, which made it possible to reform its performance consistently. The purpose of this study was to improve the mechanical properties of PETG by blending modification with PC2858 at different ratios, allowing calculation of the optimal blending ratio and comparison of the mechanical performance between the new and commercial materials.

Materials and methods

Raw pellet materials for the blending modification

The raw pellet materials for the blending modification included PC (2858, Bayer, Leverkusen, Germany), PETG (BR003, Eastman Chemical, Tennessee, USA), PC2858 granules, which were dried in blast air dryers for 8h at 110°C and PETG granules, which were put in a vacuum drying oven for 6h at 65°C. PETG and PC2858 granules were then blended under five different ratios (wt %): 10/90, 30/70, 50/50, 70/30, 90/10, at a temperature gradient of 230°C to 290°C. Type 1A tensile test specimens (80 mm × 20 mm; 4 mm thick), according to ISO standard 527-2, as well as the rectangular type A impact testing specimens (80 mm × 20 mm; 4 mm thick), with a charpy notch on each, in the middle of one 80 mm × 4 mm surface, according to ISO standard 179-1, were molded by the injection molding machine.

Mechanical properties tests for PETG/PC2858 blend

Tension test

Type 1A specimens of each blend ratio were prepared for uniaxial tensile testing. Each specimen was stretched along its long axis until it ruptured at room temperature under a rate of 5 mm/min by a universal testing machine (BOSE Electro-Force System, Massachusetts, USA). Tensile strength and elongation at break were recorded and the mean value and standard deviation of six test specimens of each ratio was calculated.

Impact test

Type A notched-specimens of each ratio were carefully aligned on the platform of a pendulum impact machine (RP/N 6957.000, CEAST, Pianezza, Italy) to make sure that the striking pendulum edge would perpendicularly hit the direct center of the surface which was opposed to the notched surface on each specimen, according to

Table 1 Mechanical properties of five PETG/PC2858 blending (wt%) ratios (n = 6, x ± s).

PETG/PC2858	Tensile strength (MPa)	Elongation at break (%)	Impact strength (KJ/m^2)
90/10	52.32 ± 1.98^a	150.52 ± 5.31^b	8.82 ± 0.12^b
70/30	60.27 ± 2.42	147.38 ± 3.49	9.03 ± 0.15
50/50	63.50 ± 2.13^b	135.08 ± 2.41^a	9.31 ± 0.16^b
30/70	65.83 ± 3.12	124.93 ± 4.02	9.53 ± 0.06
10/90	66.85 ± 1.72	109.36 ± 1.87	9.58 ± 0.11

[a] Significantly different from the blending ratio 70/30 by one-way ANOVA ($P < 0.05$).

[b] Not significantly different from the blending ratio 70/30 by one-way ANOVA ($P > 0.05$).

ISO standard 179-1. The pendulum was lifted to the prescribed height then released downwards to break each specimen. The impact energy absorbed by the specimens were recorded to calculate impact strength (acU). For each blending specimen ratio, the mean value and standard deviation of six test specimens of each ratio was calculated.

Molding the PETG/PC2858 membranes

Comparing tensile and impact properties of the blend under five ratios, as mentioned above, the correct ratio of PETG/PC2858 would be chosen based on the comprehensive mechanical performance. PETG/PC2858 thermoplastic membranes (1.0 mm thick with a 120 mm diameter) were injected and formed under a certain ratio with a specific round mold under a temperature gradient of 190°C to 230°C. The following tests relating to the PETG/PC2858 membranes' mechanical properties would be conducted using the proper PETG/PC2858 blending ratio.

Tensile properties of three kinds of membranes

Tension test

Type 5B dumbbell-shaped specimens of PETG/PC2858, Erkodur (Erkodent, Erich Kopp GmbH, Pfalzgrafenweiler, Germany) and Biolon (Dreve Dentamid GmbH, Erich Kopp GmbH, Unna, Germany) were formed for tensile tests from each kind of membrane (1.0 mm thick), according to ISO standard 527-2. Each specimen was stretched until ruptured at a rate of 5 mm/min by a universal testing machine according to guideline GB/T 1040.3-2006. The tensile stress-strain curve of each kind was traced and the tensile strength, elongation at break and Young's modulus were calculated automatically. For each blending specimen ratio, the mean value and standard deviation of six test specimens of each ratio was calculated.

Stress relaxation test

Type 5B specimen of each ratio was stretched to a 5% strain (within 30 s at a rate of 5 mm/min) of the initial length and the initial force N0 was recorded by the universal testing machine taken, according to ASTM guideline D624-00; the strain was then maintained allowing the force to recover within 1 h (i.e. 3600 s). The remaining force N1 was recorded after 1 h. The stress relaxation rate (N/s) was calculated under the formula: (N0 N1)/3600 and the tensile force-time scatter diagram within 1 h was described. For each blending specimen ratio, the mean value and standard deviation of six test specimens of each ratio was calculated.

Statistical analysis

Differences in respective mean values were analysed using one-way analysis of variance (ANOVA) testing. Statistical significance was accepted at the $P < 0.05$ level.

Results

Mechanical properties of different PETG/PC2858 blends (Table 1)

Tensile Strength

Along with the increase of PC2858, the tensile strength increased. When the content of PC2858 was at 30%, the tensile strength was 60.27 ± 2.42 MPa, significantly different from the strength when PETG/PC2858 was at 90/10 ($P < 0.05$). As the PC2858 was increased by more than 30%, tensile strength increased smoothly but did not show a significant difference between two adjacent ratios ($P > 0.05$).

Elongation at break

With the increase of PC2858, the elongation at break of the blend dropped. The elongation at break was 147.38 ± 3.49 as the ratio of PC2858 was at 30%. There was a statistically significant difference between the ratios 70/30 and 50/50 ($P < 0.05$), but no significance between 70/30 and 90/10 ($P > 0.05$).

Impact strength

The impact strength reflected the absorbed energy as the specimen was broken. The greater the content of PC2858, the higher the impact strength of the PETG/PC2858 blend. When PETG/PC2858 was at 70/30, the impact strength was 9.03 ± 0.15 KJ/m^2, which did not show a statistically significant difference compared to results obtained for 90/10 and 50/50 ($P > 0.05$).

Based on the test results of the different ratios of PETG/PC2858 blend, we found that when PETG/PC2858 was at 70/30, the material was of high strength and the toughness was preferable. We consequently formed PETG/PC2858 (70/30) membrane (1.0 mm thick), using a special mold at 230°C to 260°C temperature gradient (Fig 1), to carry out the following tests.

Tensile performance of three kinds of thermoplastic membranes

The tensile results of three kinds of thermoplastic membranes are presented in Table 2. The tensile strength and elastic modulus of PETG/PC2858 were 63.42 ± 1.67 MPa and 828.31 ± 10.12 MPa, respective-

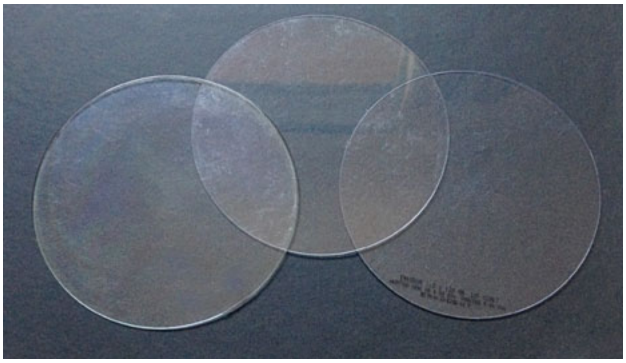

Fig 1 Thermoplastic membranes of three kinds of materials were shown on the figure. Among the three membranes, PETG/PC2858 (70/30) binary blending membrane was on the left, which had similar transparency and dimensions to the commonly used membranes (Biolon on the middle and Erkodur on the right).

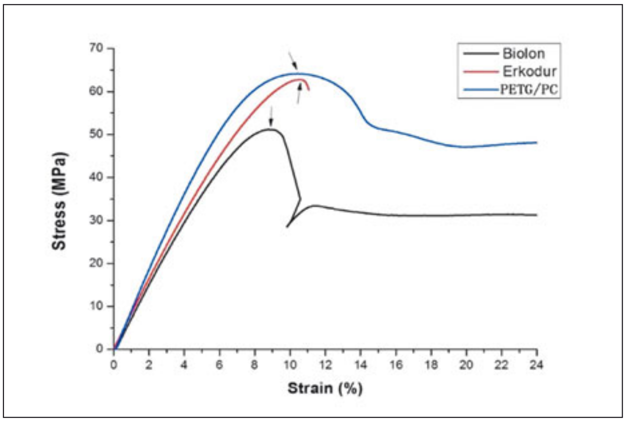

Fig 2 Stress-strain curves of three kinds of membranes under tension were shown. Arrows point to yield limits (tensile strength) of each kind of material. PETG/PC2858 and Biolon had significant plateaus before the specimens were broken while the Erkodur specimens showed stretch failures right after the yield limit.

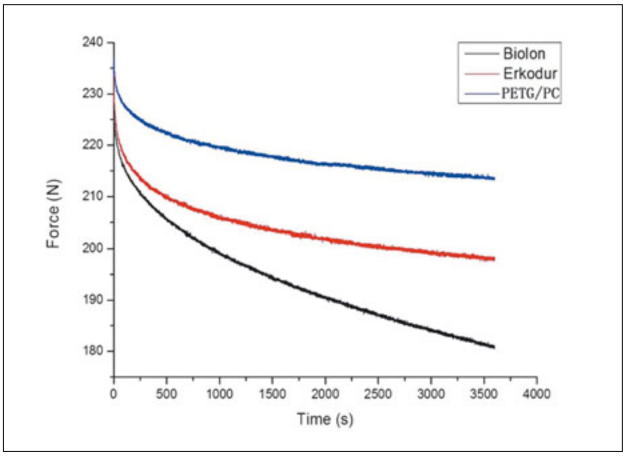

Fig 3 Stress relaxation trend of three kinds of materials were shown by scatter points of forces within 1 h. The force of PETG/PC2858 decreased conspicuously slower than Biolon.

ly, higher than Erkodur but with no statistical significance ($P > 0.05$). The corresponding results of Biolon were significantly different from the other two kinds ($P < 0.05$); Biolon had the lowest strength and modulus amongst the three kinds. The elongation at break of Biolon was significantly lower than PETG/PC2858 and Biolon, respectively ($P < 0.05$).

The stress-strain curves of three kinds of materials were revealed with different colours (Fig 2). The Erkodur specimen ruptured as soon as its curve passed the yield limit, which suggested the breakage pattern was close to brittle fracture. The curves of PETG/PC2858 and Biolon underwent a relatively longer plateau until it was interrupted by failure.

The long-term tensile performance of three kinds of materials were shown in Table 3. The tensile force of PETG/PC2858 fell from 239.8 ± 9.21 N to 211.7 ± 7.96 N within 1 h. The relaxation rate of PETG/PC2858 was 0.0080 ± 0.0005 N/s, slightly slower than Erkodur but without significant difference ($P > 0.05$), but evidently slower than 0.0128 ± 0.0008 N of Biolon ($P < 0.05$). In terms of the scatter patterns recorded, the force descending trend of Biolon material was more conspicuous than either PETG/PC2858 or Erkodur (Fig 3).

Discussion

Although thermoplastic appliances have been widely used in recent years, severe malocclusions have presented new challenges for aligners[14], which are different from traditional fixed appliances, especially in terms of material type and the force delivery mechanism. The mechanical properties of thermoplastics are influenced by molecule structures and environmental conditions[15]. The short-term and long-term mechanical properties are the primary reason for better treatment efficiency.

Thermoplastics are non-crystalline polymers made up of various polyesters which offer different results. Various material types and characteristics can be obtained through blending modification. Polyethylene terephthalate glycol (PETG) has very good transparency, fluidity and resilience. In our previous study, PETG was taken as the main ingredient, blended with polycarbonate (PC), thermoplastic polyurethane (TPU) and polybutylene terephthalate (PBT). Although PETG/PC/TPU ternary blend showed superior elasticity and resilience to other blends, TPU reduced its transparency and tensile strength. This may be derived from the imperfect compatibility of raw materials. Moreover, the processing condition of PETG/PC/TPU was very strict and the molding temperature range of the injection was too narrow to prevent blends from being oxidised.

Table 2 Short-term tensile properties of three kinds of thermoplastic membranes (n = 6, x ± s).

	Tensile strength (MPa)	Elongation at break (%)	Elastic Modulus (MPa)
PETG/PC2858	63.42 ± 1.67[a]	146.96 ± 3.71[b]	828.31 ± 10.12[a]
Erkodur	62.56 ± 1.52	112.63 ± 1.20	822.50 ± 11.10
Biolon	52.02 ± 0.99	144.73 ± 3.05	772.27 ± 13.75

[a] Significantly different from Biolon by one-way ANOVA ($P < 0.05$).
[b] Significantly different from Erkodur by one-way ANOVA ($P < 0.05$).

Table 3 Stress relaxation rate of three kinds of membranes within 1 h (n = 6, x ± s).

	Initial force (N0)	Remaining force (N1)	Stress relaxation rate (N/s)
PETG/PC2858	239.80 ± 9.21	211.70 ± 7.96	0.0080 ± 0.0005[a]
Erkodur	234.20 ± 8.95	204.30 ± 7.13	0.0083 ± 0.0005[a]
Biolon	226.70 ± 7.34	180.90 ± 8.83	0.0128 ± 0.0008

[a] Significantly different from Biolon by one-way ANOVA ($P < 0.05$).

Orthodontists could not cater to the patients who require a “clear and invisible” orthodontic process if aligners look obscure and tinted.

Polycarbonate (PC) had excellent tensile and bending resistance properties, as well as better compatibility than TPU when blended with PETG[16]. In the preliminary study, we chose three kinds of PC (APeC, PC2805 and PC2858) to blend with PETG. The results showed that PETG/PC2858 had better resilience than the other two kinds. The transparency of PETG/PC2858 was higher than 88%, which indicated PETG/PC2858 met the basic aesthetic requirement to produce aligners.

The results of different PETG/PC2858 blending ratios illustrated that when PC2858 was less than 10%, tensile strength was lower than 53 MPa, close to Biolon. As the PC2858 content came to 30%, tensile strength increased to 60.27 MPa. This strength might include a strong resistance to permanent deformation which was not desirable for a stable and continuous orthodontic force. PC2858 has higher tensile strength than PETG. Both PETG and PC2858 are polar polymer materials. They have the same ester bond and a mass of intermolecular hydrogen bonds. PETG/PC2858 has preferable compatibility after blending. On the other hand, PETG has a soft ethylene glycol base and a cyclohexane-1, 4-diyldimethanol (CHDM) base, both of which bind to each other and improve the resilience and toughness of the blend. This can be seen from the impact test. As the P2858 content increased by more than 30%, the elongation at break reduced. Hence, when the PETG/PC2858 ratio is at 70/30, the blend material has a better mechanical performance.

We found that among the three kinds of membranes, PETG/PC2858 had the highest tensile strength, which was much better than Biolon. PC2858 increased the mechanical strength of the blending membranes. Compared with Erkodur, PETG/PC2858 membrane had much higher elongation at break, which meant blend membranes exhibited ductile fracture, but not as brittle as Erkodur. Biolon had the lowest Young’s Modulus, which was 772.27 ± 13.75 MPa, slightly better than Erkodur and PETG/PC2858. Therefore, the elasticity of the new material requires enhancing for further research.

According to Proffit’s theory, the ideal orthodontic force ranges between 0.35 and 0.60 N[17]. Hahn et al measured the *in vitro* orthodontic force of Erkodur, which was three to 11 times more likely than the ideal force. The orthodontic force of Biolon was 1.5 times more than Erkodur[18,19], which was mainly because Biolon was rigid and produced a higher resilience force under deformation. Although the *in vitro* study showed that the invisible orthodontic force was much higher than the ideal force, it is hard to obtain the actual initial force without consideration for the buffering effect of periodontal ligaments.

In terms of long-term tensile properties, PETG/PC2858 showed the lowest stress relaxation 0.0080 ± 0.0005 N/s, which performed slightly better than Erkodur but not significantly. We could see from Figure 3 that the stress of three materials fell quickly during the first 500s. PETG/PC2858 had a slower falling tendency than Erkodur and Biolon. When the materials were tensed by 5% strain and molecule chains began to debond, the strong intermolecular force between PETG and PC2858 maintained the force for a longer duration. Amongst the three, Biolon had the best elasticity but quickest stress relaxation rate. Vardimon et al[20] carried out an *in vivo* test of Invisalign orthodontic force by sensors. The force attenuated quickly in the first 2 days, therefore it was important that the thermoplastic materials provided a relative everlasting force during the beginning of the given step.

Therefore in conclusion, PETG is compatible with PC2858 after blending and the suitable ratio (wt %) to process PETG/PC2858 blend membranes is 70/30. PETG/PC2858 membranes have integrated better short and long term tensile performance, in comparison to Erkodur and Biolon, and it still has space to improve elasticity. The actual orthodontic force of the new type of membranes still needs to be measured in subsequent studies.

Acknowledgment

This research was supported by The Key Laboratory of Beijing City, who were involved in the preparation and processing of Novel Polymer Materials, and the Biomechanical Laboratory of the Capital Medical University (Beijing).

Conflicts of interest

The authors reported no conflicts of interest related to this study.

Author contribution

Dr Yansong Ma for the literature research, experimental studies, data analysis and writing the manuscript; Dr Dongyu Fang for the data analysis and revising the manuscript ; Dr Ning Zhang for revising the manuscript; Dr Xuejia Ding for the study design; Dr Kunya Zhang for the data acquisition; Dr Yuxing Bai for ensuring the integrity of the entire study, for the study design and for approving the final version of the manuscript.

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