

**PRINTABLE SHAPE MEMORY POLYMER COMPOSITION AND PRINTED
DENTAL ALIGNER FABRICATED FROM THE SAME**

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority to the Singapore patent application no. 10202303047Y filed on 27 October 2023, the contents of which are hereby incorporated by reference in its entirety for all purposes.

TECHNICAL FIELD

[0002] This application relates to a printable shape memory polymer composition and a printed dental aligner fabricated from the same. In particular, the application relates to a printable shape memory polymer composition and a 4D printed dental aligner fabricated from the printable shape memory polymer composition.

BACKGROUND

[0003] Shape memory polymer (SMP) is a stimuli-responsive elastomer that retains a temporary deformed shape when subjected to external forces and can be triggered to return to its original shape, typically through heat. This ability to maintain a deformed state and recover makes SMPs promising for applications in robotics and medical devices. In orthodontics, for example, dental aligners can leverage the shape-changing capabilities of SMPs to facilitate multiple stages of alignment.

[0004] There are very few SMP dental aligner technologies available in the market. Existing SMP dental aligner products, whether thermoformed or 4D printed, must be carefully programmed by manufacturers in order for it to exhibit multiple shapes. Users or patients are required to purchase a proprietary water heater to activate the shape recovery of the SMP dental aligner, changing it to shapes pre-set by the manufacturer. If the SMP dental aligners are accidentally exposed to heat, this can trigger premature shape recovery, resulting in irreversible

shape changes and poor fitting of the dental aligner on patient's teeth. This poses a challenge in maintaining the shape at appropriate temperatures throughout the supply chain and during storage by patients.

[0005] SMPs possess very unique thermomechanical properties that are not well-studied to date. The formulation of resin, the manufacturing process employed (whether conventional or 3D printed), the post-curing process, and the programming of SMP shapes all have significant effects on the force recovery behaviour. Currently, the unique properties of SMPs are not fully utilized in the application of dental aligners.

[0006] It is therefore desirable to provide a shape memory polymer (SMP) and a dental aligner that seek to address at least one of the problems described hereinabove, or at least to provide an alternative.

SUMMARY

[0007] According to a first aspect of the present disclosure, a printable shape memory polymer composition for use in fabricating a 4D printed dental aligner is provided. The composition comprises a first (meth)acrylate monomer containing one (meth)acrylate functional group, and a second (meth)acrylate monomer containing one (meth)acrylate functional group and one or more second functional groups selected from the group consisting of hydroxyl, isobornyl and benzyl, which provides transient crosslinks to the printable shape memory polymer composition. The printable shape memory polymer composition further includes one or more crosslinkers, containing two or more (meth)acrylate functional groups, and a photoinitiator, wherein the printable shape memory polymer composition is responsive to change in temperature at temperature T_g to become flexible, allowing the printable shape memory polymer composition to be shaped and reshaped at temperature T_g .

[0008] According to a second aspect of the present disclosure, a 4D printed dental aligner is provided. The 4D printed dental aligner comprises a printable shape memory polymer composition that includes a first (meth)acrylate monomer containing one (meth)acrylate

functional group, and a second (meth)acrylate monomer containing one (meth)acrylate functional group, and one or more second functional groups selected from the group consisting of hydroxyl, isobornyl and benzyl, which provides transient crosslinks to the printable shape memory polymer composition. The printable shape memory polymer composition further includes one or more crosslinkers, containing two or more (meth)acrylate functional groups, and a photoinitiator, wherein the printable shape memory polymer composition is responsive to change in temperature at temperature T_g to become flexible, allowing the 4D printed dental aligner comprising the printable shape memory polymer composition to be shaped and reshaped at temperature T_g .

[0009] In some embodiments, the temperature T_g ranges from 35 °C to less than 100 °C.

[0010] In some embodiments, the 4D printed dental aligner comprising the printable shape memory polymer composition is programmed to have a first preparation temperature ranging from 35 °C to the T_g of the printable shape memory polymer composition.

[0011] In some embodiments, the 4D printed dental aligner comprising the printable shape memory polymer composition is programmed to have a second preparation temperature ranging from 35 °C to the T_g of the printable shape memory polymer composition, but lower than the first preparation temperature, for teeth alignment.

[0012] In some embodiments, the 4D printed dental aligner can be shaped and reshaped multiple times by a patient.

[0013] In some embodiments, the 4D printed dental aligner is configured to accommodate at least 0.5 mm of teeth displacement when in use during first cycle of teeth alignment.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] Various embodiments of the present disclosure are described hereinbelow in the detailed description with reference to the following drawings:

FIG. 1 illustrates the shape recovery of a 4D printed aligner. (a) shows a 4D printed aligner in its original end-of-treatment shape, and (b) shows the 4D printed aligner after reshaping into a

transient shape. The reshaped aligner (b) can recover back to its original shape (a) (shown by the bottom arrow) upon thermal stimulation.

FIG. 2 illustrates the fitting of a single 4D printed aligner onto 3 different teeth moulds with different states of alignment. The fitting was done in an order that reflects teeth relapse: from (A) the least aligned, to (B) the partially aligned, and to (C) the most aligned teeth moulds.

FIG. 3A shows reshaping cycle of the 4D printed dental aligner. The temperature, displacement and force of the 4D printed dental aligner were measured when being reshaped by 0.5mm. The 4D printed dental aligner reset its shape via exposure to high temperature at 100 °C before being reshaped to fit the relapsed teeth arrangement.

FIG. 3B shows multiple reshaping of the 4D printed dental aligner, simulating different states of teeth alignment (displacement). The 4D printed dental aligner was reshaped twice, at 0.5 mm and 0.25 mm displacements. The force exerted by the 4D printed dental aligner was maintained constant within the optimal force magnitude (OFM), regardless of the reshaping displacement.

FIG. 4 shows the experimental results of the shape recovery force exhibited by the 4D printed dental aligner comprising the SMP composition in accordance with an embodiment of the present disclosure. (a) shows the temperature profile the dental aligner experienced, (b) shows the displacement on the dental aligner experienced, (c) shows the resultant force versus time, and (d) shows the resultant modulus versus time.

FIG. 5 shows the comparison of resultant force between the 4D printed SMP composition and thermoformed polymer displaced at 0.50 mm and 0.25 mm at 35 °C within the first hour.

DETAILED DESCRIPTION

[0015] The following detailed description is made with reference to the accompanying drawings, showing details and embodiments of the present disclosure for the purposes of illustration. Features that are described in the context of an embodiment may correspondingly be applicable to the same or similar features in the other embodiments, even if not explicitly described in these other embodiments. Additions and/or combinations and/or alternatives as

described for a feature in the context of an embodiment may correspondingly be applicable to the same or similar feature in the other embodiments.

[0016] In the context of various embodiments, the articles “a”, “an” and “the” as used with regard to a feature or element include a reference to one or more of the features or elements.

[0017] In the context of various embodiments, the term “about” or “approximately” as applied to a numeric value encompasses the exact value and a reasonable variance as generally understood in the relevant technical field, e.g., within 10% of the specified value.

[0018] As used herein, the term “and/or” includes any, and all combinations of one or more of the associated listed items.

[0019] As used herein, “comprising” means including, but not limited to, whatever follows the word “comprising”. Thus, use of the term “comprising” indicates that the listed elements are required or mandatory, but that other elements are optional and may or may not be present.

[0020] As used herein, “consisting of” means including, and limited to, whatever follows the phrase “consisting of”. Thus, use of the phrase “consisting of” indicates that the listed elements are required or mandatory, and that no other elements may be present.

[0021] A detailed description of various embodiments will be described below with reference to the drawings.

[0022] In the present disclosure, a printable shape memory polymer (SMP) composition for use in fabricating a 4D printed dental aligner is provided.

[0023] The term “shape memory polymer” as used herein refers to polymeric materials that are stimuli-responsive. Upon application of external stimuli, these materials can change their shape in response to the external stimuli. The SMP composition of the present disclosure is responsive to heat. The polymers within the SMP composition undergo a change in their molecular structure when subjected to heat, allowing the SMP composition to become flexible to be shaped, reshaped and revert to its original shape upon cooling.

[0024] The SMP composition of the present disclosure is printable. The SMP composition can be employed for use in suitable printing methods including, but are not limited to, vat photopolymerization, digital light processing, stereolithography, xolography and polyjet. The SMP composition provides a new and feasible mechanism that can extend the lifespan of a 4D printed dental aligner and enable shape recovery of the 4D printed dental aligner, making it suitable for teeth alignment. More importantly, the 4D printed dental aligner comprising the SMP composition can exert multiple stages of force on a patient's teeth, which can consistently provide sufficient effective force throughout the treatment period for aligning the teeth.

[0025] The 4D printed dental aligner can be easily reshaped by the patient, which is repeatable to fit different teeth alignments. This can be easily accomplished by a simple water soaking method, making the reshaping of the 4D printed dental aligner completely manageable for the patient. This method will be further elaborated upon later in the specification. The reshaped dental aligner can provide a force equivalent to the optimal force magnitude (OFM) required to align the teeth effectively.

[0026] According to a first aspect, a printable SMP composition for use in fabricating a 4D printed dental aligner is provided. The composition comprises a first (meth)acrylate monomer containing one (meth)acrylate functional group; a second (meth)acrylate monomer containing one (meth)acrylate functional group, and one or more second functional groups selected from the group consisting of hydroxyl, isobornyl and benzyl, which provides transient crosslinks to the SMP composition; one or more crosslinkers containing two or more (meth)acrylate functional groups; and a photoinitiator, wherein the printable SMP composition is responsive to change in temperature at temperature T_g to become flexible, allowing the printable SMP composition to be shaped and reshaped at temperature T_g .

[0027] As used herein, the term " T_g " refers to glass transition temperature at which the SMP composition transitions from a hard, glassy state to a more flexible state. At this temperature or above this temperature, the SMP composition becomes flexible, allowing it to be shaped and

reshaped into desired form. In various embodiments, the temperature T_g ranges from 35 °C to less than 100 °C. In some embodiments, the temperature T_g is 65 °C.

[0028] In various embodiments, the first (meth)acrylate monomer is selected from the group consisting of benzyl methacrylate, 2-phenoxyethyl acrylate, 2-phenoxyethyl methacrylate and 2-hydroxyethyl acrylate. The first (meth)acrylate monomer is present in an amount ranging from 10 to 50 mol% of the SMP composition. In some embodiments, the first (meth)acrylate monomer is less bulky than the second (meth)acrylate monomer. This is to ensure the flexibility and deformability of the SMP composition when the SMP composition is programmed to be flexible at or above temperature T_g . The first (meth)acrylate monomer is provided to supplement the function of the second (meth)acrylate monomer, as both the first (meth)acrylate monomer and the second (meth)acrylate monomer contain similar side functional groups but different distance from backbone polymer. The first (meth)acrylate monomer also helps to lower the T_g of the SMP composition to below 100 °C.

[0029] In various embodiments, the second (meth)acrylate monomer is selected from the group consisting of isobornyl acrylate, isobornyl methacrylate and 2-hydroxyethyl methacrylate. The second (meth)acrylate monomer is present in an amount ranging from 10 to 50 mol% of the SMP composition. The side functional groups of the second (meth)acrylate monomer provides temporary or transient crosslinks, such as van der Waals, hydrogen bonding, and physical entanglement to the SMP composition at a temperature below T_g for providing transient shape recovery. Being transient crosslinks, the second (meth)acrylate monomer provides greater stiffness and modulus to the SMP composition when the SMP composition is programmed to be rigid below T_g , and yet the transient crosslinks are able to be removed when the SMP composition is heated to or above T_g to allow deformation.

[0030] In various embodiments, the one or more crosslinkers are selected from the group consisting of polyethylene glycol diacrylate, trimethylolpropane ethoxylate triacrylate and polyethylene glycol dimetacrylate. The total amount of the one or more crosslinkers present in

the SMP composition ranges from 20 to 60 mol% of the SMP composition. The crosslinker(s) is provided to permanently crosslink the SMP composition during the printing process. It is employed to raise the temperature T_g of the SMP composition to above 50 °C. This is to allow full shape recovery back to the original shape when the SMP composition is heated to or above T_g .

[0031] In various embodiments, the photoinitiator is selected from the group consisting of diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide and phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide. The photoinitiator is present in an amount ranging from 0.05 to 1.0 mol% of the SMP composition. The photoinitiator is provided to initiate photopolymerization of the polymers within the SMP composition during the printing process.

[0032] In some embodiments, the SMP composition comprises 10 to 50 mol% of the first (meth)acrylate monomer; 10 to 50 mol% of the second (meth)acrylate monomer; 20 to 60 mol% of the crosslinker(s); and 0.05 to 1.0 mol% of the photoinitiator, based on the total number of moles of the SMP composition.

[0033] In some embodiments, the first (meth)acrylate monomer is benzyl methacrylate, the second (meth)acrylate monomer is 2-hydroxyethyl methacrylate. In some embodiments, the crosslinkers are polyethylene glycol diacrylate and polyethylene glycol dimetacrylate. In some embodiments, the photoinitiator is diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide.

[0034] In an exemplary embodiment, the SMP composition comprises 19.8 mol% of benzyl methacrylate; 19.8 mol% of 2-hydroxyethyl methacrylate, 59.4 mol% of crosslinkers comprising 29.7 mol% of polyethylene glycol diacrylate and 29.7 mol% of polyethylene glycol dimetacrylate; and 1 mol% of diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide, based on the total number of moles of the SMP composition.

[0035] In various embodiments, the SMP composition is prepared by mixing the first (meth)acrylate monomer, the second (meth)acrylate monomer, the crosslinker(s) and the photoinitiator together and magnetically stirred for 24 hours.

[0036] The SMP composition can be used to print clear dental aligners with accurate and precise teeth features, which increases the contact area between the dental aligner and the teeth, thereby enhancing the teeth alignment process.

[0037] According to a second aspect, a 4D printed dental aligner comprising the printable SMP composition of the present disclosure is provided. The 4D printed dental aligner comprises a printable SMP composition comprising a first (meth)acrylate monomer containing one (meth)acrylate functional group; a second (meth)acrylate monomer containing one (meth)acrylate functional group and one or more second functional groups selected from the group consisting of hydroxyl, isobornyl and benzyl, which provides transient crosslinks to the printable SMP composition; one or more crosslinkers, containing two or more (meth)acrylate functional groups; and a photoinitiator, wherein the printable SMP composition is responsive to change in temperature at temperature T_g to become flexible, allowing the 4D printed dental aligner comprising the printable SMP composition to be shaped and reshaped at temperature T_g .

[0038] In various embodiments, the temperature T_g ranges from 35 °C to less than 100 °C. In some embodiments, the temperature T_g is 65 °C.

[0039] In some embodiments, the 4D printed dental aligner comprising the printable shape memory polymer composition is programmed to have a first preparation temperature ranging from 35 °C to the T_g of the printable shape memory polymer composition.

[0040] In some embodiments, the 4D printed dental aligner comprising the printable shape memory polymer composition is programmed to have a second preparation temperature ranging from 35 °C to the T_g of the printable shape memory polymer composition, but lower than the first preparation temperature.

[0041] At the first preparation temperature, or above, the 4D printed dental aligner becomes flexible, allowing the 4D printed dental aligner to be shaped or reshaped into the desired form. Below the first preparation temperature but above the second preparation temperature, the 4D

printed dental aligner becomes less flexible but still allows minor adjustments of the 4D printed dental aligner to be made for teeth alignment when the 4D printed dental aligner is fitted over the patient's teeth. In some exemplary embodiments, the first preparation temperature is set at 65 °C, while the second preparation temperature is set at 35 °C.

[0042] The 4D printed dental aligner has a wearing temperature range of 25 °C to 65 °C. The term "wearing temperature" as used herein refers to temperature that the 4D printed dental aligner can be safely worn without losing its structural integrity or effectiveness. At a temperature above 65 °C, the 4D printed dental aligner will become flexible and deformed. The typical maximum wearing temperature for dental aligners is around 40 °C to 50 °C. By changing the wearing temperature to 25 °C to 65 °C, the 4D printed dental aligner can achieve a suitable modulus, thus achieving the required force within the OFM at any stages of the teeth alignment, and yet able to maintain its structural integrity and effectiveness at temperature between 51 °C and 64 °C.

[0043] In some embodiments, the 4D printed dental aligner has a shape reset temperature of around 100 °C. In other embodiments, the 4D printed dental aligner has a shape reset temperature above the T_g of the SMP composition but below 100 °C. This is the temperature at which the 4D printed dental aligner can be fully reset to form other shapes.

[0044] The 4D printed dental aligner can be shaped and reshaped multiple times. After it is shaped according to the teeth, it can be reshaped as desired. This can be accomplished by soaking the 4D printed dental aligner in hot water at the T_g or above T_g of the printable SMP composition for the dental aligner to become flexible. Once the dental aligner becomes flexible, it can be reshaped into desired shape. This step can easily be performed by the patients themselves, without the need to visit a dental professional or undergo complex procedures. This convenience allows for quick adjustments to enhance comfort and effectiveness in teeth alignment.

[0045] FIG. 1(a) shows a 4D printed dental aligner having an original shape **101** in its original end-of-treatment shape. When the dental aligner is stimulated with hot water at the T_g of the printable SMP composition, for example, at 65 °C, the dental aligner becomes flexible, capable of reshaping. The dental aligner is reshaped and maintained in its new shape after cooling down.

[0046] FIG. 1(b) shows the dental aligner after reshaping into a transient shape. The reshaped dental aligner **102** can recover back to its original shape **101** (shown by the bottom arrow) upon thermal stimulation, by reintroducing the dental aligner in hot water at the T_g of the printable SMP composition, for example, at 65 °C. The dental aligner resets itself to its original shape and the shape changing process can be repeated to reshape the dental aligner. With the ability to reshape and recover back to its original shape, the single 4D printed dental aligner is capable of fitting into various stages of teeth alignments (FIG. 2), and as and when desired.

[0047] FIG. 2 illustrates the fitting of a single 4D printed dental aligner onto various teeth moulds in different states of alignment. The first row (i) shows the front teeth with no dental aligner. The second row (ii), third row (iii), and fourth row (iv) show three different teeth moulds in different states of alignment. The second row (ii) shows the front teeth with dental aligner, the third row (iii) shows the side teeth with dental aligner, and the fourth row (iv) shows the back teeth with dental aligner. The fitting was done in an order to reflect teeth relapse: from (A) the least aligned, to (B) the partially aligned, and to (C) the fully aligned teeth moulds. The dental aligner was prepared at an elevated temperature of 65 °C. This gains temporary flexibility to fit the dental aligner over teeth that have a displacement of 0.8 mm, thereby allowing the alignment process to proceed.

[0048] The alignment of the teeth greatly depends on the force exerted by the dental aligner on the teeth. For the teeth to align optimally, the force has to be kept within the OFM, and this can be achieved by the 4D printed dental aligner of the present disclosure. In some

embodiments, the 4D printed dental aligner can apply the same amount of force magnitude when worn onto teeth of different displacements. This is done by immersing the 4D printed dental aligner in water at a specific temperature, for example, at the T_g of the printable SMP composition or between 35 °C and the T_g of the printable SMP composition right before being worn.

[0049] Referring to FIG. 3A, a 4D printed 3-point bending sample was tested to simulate the reshaping process of the dental aligner. The sample underwent a 4-stage process:

[0050] Stage 1: The sample was heated to 100 °C (301) to reset the shape (302) of the sample.

[0051] Stage 2: This is the preparation stage (303) where the sample was allowed to cool from 100 °C to 65 °C (304).

[0052] Stage 3: This is the stage where the sample was reshaped (305). At 65 °C (306), the sample was fitted over the teeth (307) and reshaped at 0.5 mm displacement (308), while the temperature gradually decreased to reach 35 °C.

[0053] Stage 4: After reshaping, force was applied by the sample on the teeth for teeth alignment (309) at 35 °C (mouth temperature) (310). The resulting force was maintained between 0.5N to 0.7N (311), which is the OFM for lateral teeth displacement.

[0054] This dedicated force can be maintained within the OFM regardless of the degree of teeth relapse (i.e., the displacement of teeth from the ideal aligned position). This is made possible by changing the effective modulus of the 4D printed sample through temperature changes at the preparation stage (303).

[0055] In some embodiments, the 4D printed dental aligner can undergo several cycles of teeth alignment due to its ability to reshape and recover back to its original form. This is made possible by the crosslinker(s) and the second (meth)acrylate monomer contained in the SMP composition. The crosslinker(s) helps to generate sufficient recovery force during first cycle of teeth alignment, that is, when the 4D printed dental aligner is worn at the T_g of the SMP

composition, for example, at 65 °C, which has a higher displacement. The second (meth)acrylate monomer helps to generate sufficient recovery force during second and subsequent cycles of teeth alignment, that is, when the 4D printed dental aligner is worn at 35 °C, which has a lower displacement.

[0056] In some embodiments, the 4D printed dental aligner can accommodate at least 0.5 mm of teeth displacement during the first cycle of teeth alignment and at least 0.25 mm of teeth displacement during the second cycle of teeth alignment.

[0057] In FIG. 3B, the 4D printed dental aligner underwent two cycles of reshaping, with two different preparation temperatures, at 65 °C (311) and 35 °C (312), respectively, and two different displacements, at 0.5 mm and 0.25 mm, respectively, to simulate the teeth getting more aligned (313). By changing the preparation temperatures to 65 °C and 35 °C, the effective modulus of the 4D printed dental aligner can be adjusted, resulting in the force applied by the 4D printed dental aligner maintaining within the OFM (314) at any stages of the teeth alignment, regardless of the displacement. The resetting stage, which can take place at a temperature above the T_g of the SMP composition but below 100 °C, also helps by allowing the 4D printed dental aligner to recover back to its original shape before being deformed for the next reshaping cycle.

[0058] In the present disclosure, the mechanism of the resulting forces exerted on the teeth by the 4D printed dental aligner is controllable by a simple process of manipulating the programmed temperature T_g . Unlike conventional dental aligners which are limited to 0.2 to 0.3 mm of teeth displacement, the 4D printed dental aligner of the present disclosure can accommodate at least 0.5 mm of teeth displacement while ensuring that the force remains within the OFM regardless of the displacement. This allows the 4D printed dental aligner to be worn for a longer period of treatment, reducing the total number of dental aligners needed to complete the treatment by half. The 4D printed dental aligner of the present disclosure can eliminate storage issues as the dental aligner is printed on-demand based on a patient's specific treatment

plan. This reduces the need for storing large inventories of pre-made dental aligners. The 4D printed dental aligner can also reduce wastage as lesser dental aligners will be needed to complete the treatment. The 4D printed dental aligner also allows patients to optimize their teeth alignment with ease and at reduced cost, as the shaping and reshaping of the 4D printed dental aligner can be easily performed by the patients themselves and there is no need to purchase proprietary water heaters or return to orthodontists for reshaping of the dental aligner.

[0059] The 4D printed dental aligners of the present disclosure can be prepared by the patients as the resetting mechanism for reshaping the dental aligners is easy to manage. The patients can reshape the dental aligner themselves if the dental aligner loses its aligning force due to external factors or due to a teeth relapse. The patients can have the assurance that their teeth will be guided back to the intended alignment, even when they reshape the dental aligners themselves. This is possible due to the combination of shape memory and the tuneable modulus of the printable SMP composition - features which are not found in other 4D materials.

[0060] The 4D printed dental aligner can also act as a retainer during the end of the alignment process, to safeguard the patients from teeth relapse and preventing them from having to go through the alignment treatment again.

[0061] To facilitate a better understanding of the invention, the following examples of specific embodiments are given. In no way should the following examples be read to limit or define the entire scope of the invention. One skilled in the art will recognize that the examples set out hereinbelow are not an exhaustive list of the embodiments of this invention.

EXAMPLES

Example 1

[0062] This example illustrates how the modulus of the dental aligner may be adjusted.

[0063] Firstly, a dental aligner was 4D printed to the desired end-shape teeth alignment using the printable SMP composition of the present disclosure. The 4D printed dental aligner then underwent a soft programming.

[0064] In the soft programming, the 4D printed dental aligner was heated to an elevated temperature of 65 °C to soften dental aligner. Once it was softened, it was immediately worn onto the teeth of the patient to align the dental aligner onto the teeth. The dental aligner in the patient's mouth adjusted to the mouth's temperature, exerting an optimal orthodontic force for a given teeth displacement. The teeth displacement may range between 0.25 and 0.50 mm.

[0065] Over a period of usage, the dental aligner may stop providing orthodontic force due to stress relaxation and reduced teeth displacement. At this time, resetting of the dental aligner may be required. This can be done by immersing the dental aligner in water at a temperature above the T_g of the SMP composition to allow free shape recovery back to its original shape for reuse. In this example, the dental aligner was immersed in water at 85 °C. After the dental aligner was recovered back to its original shape, it was allowed to cool to room temperature. The dental aligner may be heated again to an elevated temperature of 65 °C to soften the dental aligner again. The entire process was repeated to reshape and align the dental aligner onto the teeth again.

[0066] In some embodiments, after the 4D printed dental aligner was recovered back to its original shape and was allowed to cool to room temperature, the 4D printed dental aligner underwent a hard programming. In the hard programming, the 4D printed dental aligner was worn onto the teeth of the patient at room temperature, just like normal dental aligners. The dental aligner in the patient's mouth was adjusted to the mouth's temperature, exerting an optimal orthodontic force for a given teeth displacement. The teeth displacement in this case fell within 0.00 to 0.25 mm. Over a period of use, the dental aligner may stop providing orthodontic force due to stress relaxation and reduced teeth displacement, as described in the earlier embodiment. The dental aligner can then be reset in the same manner outlined above, allowing the entire process to repeat, reshaping and realigning the dental aligner onto the teeth again.

[0067] FIG. 4 shows the experimental results of the shape recovery force exhibited by the 4D printed dental aligner comprising the SMP composition of the present disclosure.

[0068] FIG. 4(a) shows the temperature profile the dental aligner experienced, (b) shows the displacement on the dental aligner experienced, (c) shows the resultant force versus time, and (d) shows the resultant modulus versus time.

[0069] The results shown in FIG. 4 were obtained during 14 continuous cycles of the experiment when programmed at 85 °C, 75 °C, 65 °C, 55 °C, 45 °C, 35 °C and 25 °C, with displacements of 0.25 mm and 0.50 mm.

[0070] FIG. 5 shows the comparison of resultant force between 4D printed SMP and thermoformed polymer displaced at 0.50 mm and 0.25 mm at 35 °C within the first hour. All tests, except the 4D printed SMP with 0.50 mm displacement, were displaced at 25 °C and heated to 35 °C immediately. Only the 4D printed SMP with 0.50 mm displacement was initially heated to 70 °C before displacement, and thereafter cooled to 35 °C immediately. This allows the 4D printed SMP to lower its modulus to match the resultant force.

[0071] Although embodiments of the invention have been shown and described, the invention is not limited to the described embodiments. Instead, it would be appreciated by those skilled in the art that various modifications and variations can be made to the embodiments of the invention without departing from the scope of the invention, the scope of which is set forth in the following claims.

CLAIMS

1. A printable shape memory polymer composition for use in fabricating a 4D printed dental aligner, the composition comprising:
 - a first (meth)acrylate monomer containing one (meth)acrylate functional group;
 - a second (meth)acrylate monomer containing one (meth)acrylate functional group, and one or more second functional groups selected from the group consisting of hydroxyl, isobornyl and benzyl, which provides transient crosslinks to the printable shape memory polymer composition;
 - one or more crosslinkers, containing two or more (meth)acrylate functional groups; and
 - a photoinitiator,wherein the printable shape memory polymer composition is responsive to change in temperature at T_g to become flexible, allowing the printable shape memory polymer composition to be shaped and reshaped at temperature T_g .
2. The composition of claim 1, wherein the first (meth)acrylate monomer is selected from the group consisting of benzyl methacrylate, 2-phenoxyethyl acrylate, 2-phenoxyethyl methacrylate and 2-hydroxyethyl acrylate.
3. The composition of claim 1, wherein the second (meth)acrylate monomer is selected from the group consisting of isobornyl acrylate, isobornyl methacrylate and 2-hydroxyethyl methacrylate.
4. The composition of claim 1, wherein the one or more crosslinkers are selected from the group consisting of polyethylene glycol diacrylate, trimethylolpropane ethoxylate triacrylate and polyethylene glycol dimetacrylate.
5. The composition of claim 1, wherein the photoinitiator is selected from the group consisting of diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide and phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide.

6. The composition of claim 1, wherein the composition comprises:
 - 10 to 50 mol% of the first (meth)acrylate monomer;
 - 10 to 50 mol% of the second (meth)acrylate monomer;
 - 20 to 60 mol% of the one or more crosslinkers; and
 - 0.05 to 1.0 mol% of the photoinitiator, based on the total number of moles of the printable shape memory polymer composition.
7. The composition of claim 1, wherein the first (meth)acrylate monomer is benzyl methacrylate, and the second (meth)acrylate monomer is 2-hydroxyethyl methacrylate.
8. The composition of claim 7, wherein the crosslinkers are polyethylene glycol diacrylate and polyethylene glycol dimethacrylate.
9. The composition of claim 8, wherein the photoinitiator is diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide.
10. The composition of claim 1, wherein the temperature T_g ranges from 35 °C to less than 100 °C.
11. The composition of claim 1, wherein the temperature T_g is 65 °C.
12. A 4D printed dental aligner comprising:
 - a printable shape memory polymer composition comprising:
 - a first (meth)acrylate monomer containing one (meth)acrylate functional group;
 - a second (meth)acrylate monomer containing one (meth)acrylate functional group, and one or more second functional groups selected from the group consisting of hydroxyl, isobornyl and benzyl, which provides transient crosslinks to the printable shape memory polymer composition;

one or more crosslinkers, containing two or more (meth)acrylate functional groups; and

a photoinitiator,

wherein the printable shape memory polymer composition is responsive to change in temperature at T_g to become flexible, allowing the 4D printed dental aligner comprising the printable shape memory polymer composition to be shaped and reshaped at temperature T_g .

13. The 4D printed dental aligner of claim 12, wherein the first (meth)acrylate monomer is selected from the group consisting of benzyl methacrylate, 2-phenoxyethyl acrylate, 2-phenoxyethyl methacrylate and 2-hydroxyethyl acrylate.

14. The 4D printed dental aligner of claim 12, wherein the second (meth)acrylate monomer is selected from the group consisting of isobornyl acrylate, isobornyl methacrylate and 2-hydroxyethyl methacrylate.

15. The 4D printed dental aligner of claim 12, wherein the one or more crosslinkers are selected from the group consisting of polyethylene glycol diacrylate, trimethylolpropane ethoxylate triacrylate and polyethylene glycol dimetacrylate.

16. The 4D printed dental aligner of claim 12, wherein the photoinitiator is selected from the group consisting of diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide and phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide.

17. The 4D printed dental aligner of claim 12, wherein the printable shape memory polymer composition comprises:

10 to 50 mol% of the first (meth)acrylate monomer;

10 to 50 mol% of the second (meth)acrylate monomer;

20 to 60 mol% of the crosslinker; and

0.05 to 1.0 mol% of the photoinitiator, based on the total number of moles of the printable shape memory polymer composition.

18. The 4D printed dental aligner of claim 12, wherein the first (meth)acrylate monomer is benzyl methacrylate, and the second (meth)acrylate monomer is 2-hydroxyethyl methacrylate, the crosslinkers are polyethylene glycol diacrylate and polyethylene glycol dimetacrylate, and the photoinitiator is diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide.

19. The 4D printed dental aligner of claim 18, wherein the printable shape memory polymer composition comprises:

19.8 mol% of benzyl methacrylate;

19.8 mol% of 2-hydroxyethyl methacrylate;

59.4 mol% of crosslinkers comprising 29.7 mol% of polyethylene glycol diacrylate, and 29.7 mol% of polyethylene glycol dimetacrylate; and

1 mol% of diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide.

20. The 4D printed dental aligner of claim 12, wherein the temperature T_g ranges from 35 °C to less than 100 °C.

21. The 4D printed dental aligner of claim 12, wherein the 4D printed dental aligner comprising the printable shape memory polymer composition is programmed to have a first preparation temperature ranging from 35 °C to the T_g of the printable shape memory polymer composition.

22. The 4D printed dental aligner of claim 12, wherein the 4D printed dental aligner comprising the printable shape memory polymer composition is programmed to have a second preparation temperature ranging from 35 °C to the T_g of the printable shape memory polymer composition, but lower than the first preparation temperature, for teeth alignment.

23. The 4D printed dental aligner of claim 12, wherein the 4D printed dental aligner has a shape reset temperature above the T_g of the printable shape memory polymer composition but below 100 °C.

24. The 4D printed dental aligner of claim 12, wherein the 4D printed dental aligner can be shaped and reshaped multiple times by a patient.
25. The 4D printed dental aligner of claim 12, wherein the 4D printed dental aligner is configured to accommodate at least 0.5 mm of teeth displacement when in use during first cycle of teeth alignment.
26. The 4D printed dental aligner of claim 12, wherein the 4D printed dental aligner has a wearing temperature range of 25 °C to 65 °C.