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Application of shape memory polyurethane in orthodontic

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Abstract A shape memory polymer wire for orthodontic application was prepared by melt-spinning of polyurethane block copolymer (PU) which was synthesized in a two-step process from a reaction of 4,4′-methylene bis(phenylisocyanate), poly(ε-caprolactone)diol (PCL), and 1,4-butanediol. An orthodontic test using the PU wire was carried out in an orthodontic model with a metal bracket. High shape recovery force of 70 gf for PU wire at 40 wt% hard segment content could be preserved for even 1 month after a shape recovery force test at a constant temperature of 50°C. The shape recovery force decreased exponentially during the initial 2 h, but reached an equilibrium shape recovery force of 50 gf after about 20 days. It was found that this shape recovery force was sufficient to correct misaligned teeth in the orthodontic test. The shape memory PU wire possesses strong potential as a novel orthodontic appliance with esthetically appealing appearance.

1 Introduction

Orthodontics involve the application of corrective appliances, commonly called braces, to move teeth. A brace consists of an orthodontic bracket and an orthodontic archwire. Metals such as stainless steel and nickel-titanium alloy are often used as orthodontic materials owing to their superior properties, such as rigidity, flexibility, fatigue, durability, and operability [1]. Their metallic color, however, poses aesthetic problems. Recently, much effort has been exerted to enhance the aesthetic archwire and brackets by replacing metals with transparent, translucent, or tooth-colored polymers or ceramics [2–4].

A pioneering research on a clear polymer bracket using polycarbonate to make a labial appliance almost invisible was reported in the 1960s by Newman [5]. It was easily fractured, however, when force was applied in orthodontic treatment [6]. With respect to the use of ceramic brackets, which have a satisfactory aesthetic appearance, clinical difficulties have been encountered, such as brittleness, low fracture toughness, increased friction, and debonding problems, in addition to costliness. Recently, Teflon-coated stainless steel wire or fiber-reinforced polycarbonate brackets have also emerged as alternative aesthetic orthodontic materials [7–11].

As a novel orthodontic material, shape memory polymers may have high potential, from both functional and aesthetic viewpoints. In comparison to shape memory alloys, they possess many advantages, such as low density, high shape recovery, easy processing, transparency, and aesthetically satisfactory appearance. Together with their relatively transparent appearance, their application to orthodontic appliances can provide the latter with easy operability and considerable shape recovery force.

Among shape memory polymers, shape memory polyurethane (PU), composed of hard and soft segments, has received increasing attention from many researchers for both scientific interest and practical industrial and biomedical applications [12–16]. PU has phase-separated structures between the hard and soft segments due to its thermodynamic immiscibility. The hard segments play a role of physical crosslinks with high melting temperature via hydrogen bonding and crystallization, and soft segments supply reversible phase transformation, which is necessary for achieving a shape memory effect. The

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transition temperature of PU, which is near body temperature, can be controlled by the glass transition temperature or the melting temperature of amorphous soft segments. Therefore, shape recovery in PU can be applied to orthodontic appliances to correct misaligned teeth through thermal heating from body temperature.

In this paper, an orthodontic appliance utilizing shape memory PU with poly(ε-caprolactone) as a soft segment was prepared, and its applicability was investigated with characterization of PU materials.

2 Experimental

2.1 Sample preparation

4,4′-Methylene bis(phenylisocyanate) (MDI, Junsei Chemical) and poly(ε-caprolactone)diol (PCL) (MW = 3,000 g/mol) were dried in a vacuum oven prior to their use, and 1,4-butanediol (BD, Duksan Chemical) was stored in a 4 Å molecular sieve. Synthesis of PU was carried out via a two-step process as shown in Fig. 1. Calculated amounts of MDI and PCL in 100 ml of freshly distilled dimethylacetamide were stirred under nitrogen at 80°C for 3 h in a 500 ml four-neck cylindrical vessel equipped with a mechanical stirrer in order to make a prepolymer. In the second step, BD was added dropwise to the reaction mixture depending on the MDI/PCL ratios. When the polymerization was completed, PU was removed with the use of a solvent under vacuum, and was further solidified via baking in an oven at 100°C for 24 h. Three sets of PU samples with hard segments of 30%, 40%, and 50% by weight were obtained by controlling the amounts of PCL, MDI, and BD, as shown in Table 1. Synthesized PUs were dissolved uniformly in dimethylacetamide with a concentration of 10 wt%, and were stirred constantly to ensure homogeneity. The homogeneous solutions were transferred to a closed Petri-dish and were allowed to stand at 60°C for 24 h. The resulting samples were obtained in a film form with a thickness of 1.07 mm, and were then slowly dried at room temperature for several days in a vacuum oven.

Table 1 Compounding formulations and thermal properties of shape memory PU

Mole ratio			HS content (wt%)	M_w^a (g/mol)	T_m^b (°C)	ΔH_m^c (J/g)	T_d^d (°C)
MDI	PCL	BD					
4.0	1.0	3.0	30	28,096	36.6	7.6	287
6.0	1.0	5.0	40	31,159	39.5	13.2	301
9.0	1.0	8.0	50	39,547	43.5	13.1	313

[a] The average molecular weights were determined through gel permeation chromatography

[b] T_m denotes the melting temperature of soft segments. It was determined by DSC measurements

[c] ΔH_m denotes heat of fusion of soft segments

[d] T_d denotes degradation temperature by thermogravimetric measurement

After additional drying at 60°C for 24 h, the synthesized PU was used for preparing orthodontic PU wire by a twin screw extruder (Bautech model BA–19). The molding temperature was set between 150 and 210°C. The average diameter of the melt-spun PU wire was 0.387 mm.

2.2 Characterization

FT-IR spectroscopy (Jasco FT-IR 300E), equipped with attenuated total reflectance, was used to record the spectrum of the PU films. Differential scanning calorimeter (DSC) measurements were carried out at a heating rate of 10°C/min with a TA instrument 2010 DSC (Du Pont). A tensile test was performed at room temperature using a universal tensile tester (UTM, Lloyd LR50K). The gauge length and crosshead speed were determined to be 25 and 10 mm/min, respectively. To measure the shape memory behavior, a thermomechanical test was performed with the use of a UTM equipped with a controlled thermal chamber, and the relationship between stress and strain at various

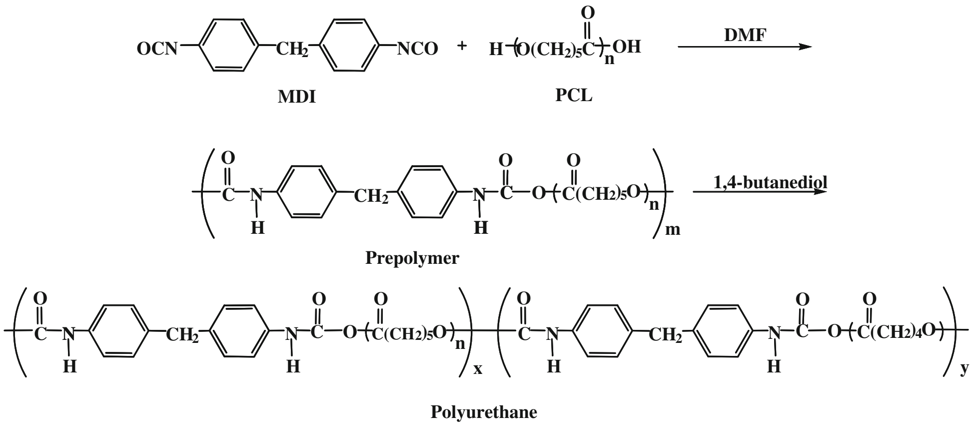


Fig. 1 Synthetic procedure of shape memory polyurethane used in this study

temperatures was analyzed. Specifically, deformation up to 100% of elongation was applied to the specimen with a constant crosshead speed of 10 mm/min at 20°C above the transition temperature of soft segments (T_r). The specimen was then quickly cooled to 20°C below T_r, with 100% elongation. After maintaining that temperature for 5 min with the load removed, the specimen was heated to 20°C above T_r to measure the recovery strain, and the shape recovery was calculated using Eq. 1 and 2, given below:

$$\text{Shape retention}\,(\%) = (\text{retention strain at } T_r - 20) \times 100/(\text{strain at } 100\%\text{ elongation}) \tag{1}$$

$$\text{Shape recovery}\,(\%) = \big(\text{strain at } 100\%\text{ elongation} - \text{recovery strain at} T_r + 20\big) \times 100\,/\,(\text{strain at } 100\%\text{ elongation}) \tag{2}$$

The shape recovery force was measured using the aforementioned equipment set-up in our laboratory. Before the measurement, the samples were elongated at 100% at 60°C and then cooled to RT. Using a load cell for tensile force measurement, the shape recovery force of each sample was recorded while maintaining a constant temperature of 50°C. The test temperature of 50°C was chosen for observation of a dominant shape recovery effect. Shape memory behavior was also observed by using a sample folded in ring form at 60°C followed by quenching in an ice-water bath. During heating of the samples, images of the shape recovery process were recorded using a video camera [17].

2.3 Fabrication of orthodontic appliance

A wire-type orthodontic appliance with a thickness of 0.387 mm and a length of 150 mm was prepared. Before using it in orthodontic treatment, the appliance was elongated to a desirable length at 60°C, and was then quenched to room temperature. The extent of elongation was controlled so as to be identical to the length required for the misaligned teeth to move. A dental study model (DNS3-TRM.223 CLASS I, Nissin Dental Production Inc., Japan) was used for the orthodontic treatment in this study. Before orthodontic treatment, the teeth were separated with a predetermined distance between them. 'Mini-Mono®-Brackets' (FORESTADENT Bernhard Farster GmbH, Germany), prescription stainless steel orthodontic brackets (0.018 in. slot), were then bonded using Transbond composite orthodontic cement (3M Unitek Corporation, 2724 South Peck Road, Monrovia, CA 91016-5097, USA), which was light cured according to the manufacturer's instructions. The prepared tooth surface was first thinly coated with the unfilled resin primer and the filled composite was placed on the bracket. The bracket was then firmly placed onto the middle of the buccal surface of the crown and orientated into the correct position. Any excess composite was removed and the cement was light cured for 40 s; 20 s from the mesial and 20 s from the distal sides of the bracket to ensure full curing.

3 Results and discussion

3.1 Thermal, mechanical, and shape memory properties of PU wire

The transition temperature was determined using DSC measurements. The DSC thermograms, which were obtained from the first heating scan at a rate of 10°C/min, are shown in Fig. 2. The endothermic peaks near 36–42°C are due to the melting temperature of PCL crystals in the soft segment domain of PU. This acts as a transition temperature for shape memory. The increase of the hard segment content yielded a higher transition temperature due to the formation of more perfect crystals which resulted from increased phase separation of the hard and soft segments. The heat of fusion, which can be measured from the area of the thermogram, also increased with an increase of the hard segment content as shown in Table 1. The endothermic peak near 200°C is due to the melting of the hard segment domain, and the peak becomes larger with an increase of hard segment content. The phase-separated hard segment domain led to the formation of physical crosslinks, which are necessary to achieve shape recovery of the sample [12].

The mechanical properties of PU samples with different hard segment content are shown in Table 2. As the hard

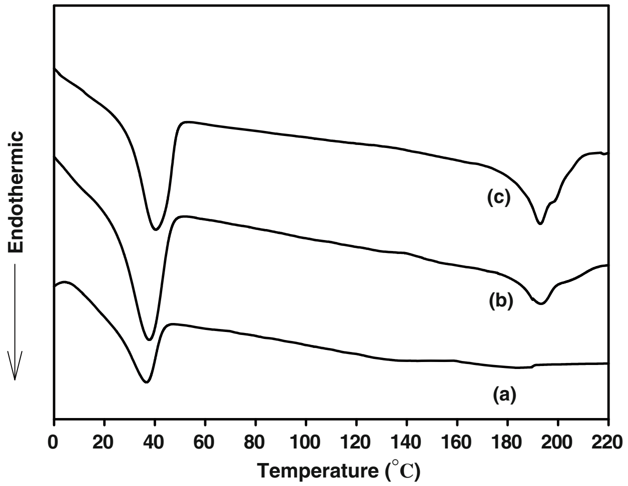


Fig. 2 DSC heating scans of orthodontic SMPU wires with different hard segment content: (**a**) 30 wt%, (**b**) 40 wt%, and (**c**) 50 wt%

Table 2 Tensile properties of shape memory PU

HS Content (%)	Breaking stress (MPa)	Elongation-at-break (%)	Modulus (MPa)
30	20.9	1,484	3.1
40	26.8	1,215	4.6
50	17.8	1,161	4.5

segment content in the PU is increased, the modulus exhibits an increase of up to 40% of the hard segment content. This is attributed to an increase of the hard domain, resulting from intermolecular hydrogen bonding between the hard segments. Tensile strength of 17.8–26.8 MPa was obtained for the PU samples of 30–50% hard segment content. However, the highest breaking stress was obtained at 50% hard segment content. The elongation-at-break of the PU samples decreased with an increase of hard segment content. At high hard segment content, the rigidity of the PU sample may restrict stretching, and the low degree of physical crosslinking at low hard segment content is responsible for PU breaking at less elongation.

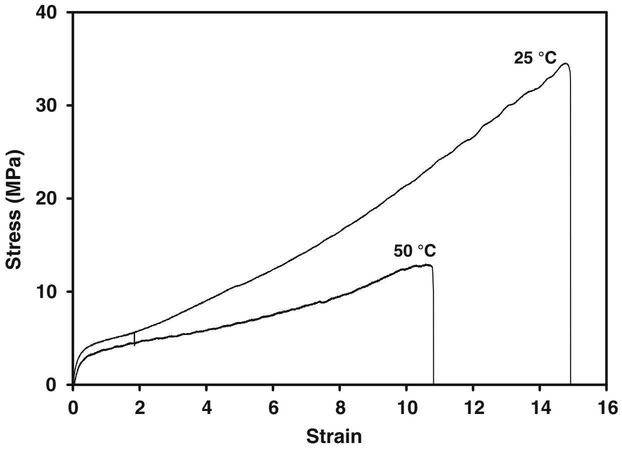
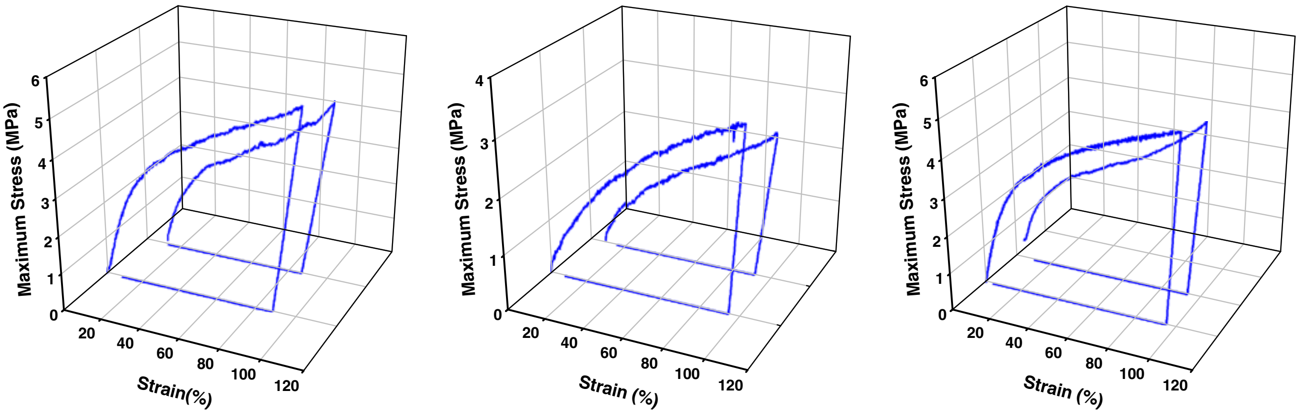


Fig. 3 Stress–strain curves obtained from the tensile test of SMPU (40 wt%) wire at temperatures higher and lower than the transition temperature of 40°C, respectively

The mechanical properties are also dependent on the temperature, in contrast with shape memory metals. Figure 3 shows two stress–strain curves, measured at 25 and 50°C, respectively, for samples at 40 wt% hard segment. The sample at 50°C showed lower stress values at the same elongation compared to that at 25°C. Nevertheless, the stress of the sample at 50°C is adequate to support teeth in a practical orthodontic application.

A shape memory test was carried out for the samples. Figure 4 shows the thermo-mechanical behavior of the samples. All of the PUs showed good shape retention of more than 90% at each hard segment content. An average shape recovery of 80–85% was obtained at 30–50 wt% hard segment content, and recovery slightly increased with an increase of hard segment content [18]. The original shape could almost be fully recovered at a temperature above the melting temperature of the PCL crystals in the PU wire. When stress is applied to the PU wire, the soft segment will be preferentially extended to the stress direction rather than the hard segment, because the hard segment is close to a glassy state and the soft segment is rubbery beyond the transition temperature. Stabilization of the hard segment is responsible for the high shape recovery above the transition temperature. As a result, it was found that the PU samples in a hard segment range from 30 to 50 wt% possessed good shape memory function. This finding was also supported by the shape recovery test using PU wire. The originally straight shape of the sample was deformed to a helical form at 60°C, followed by cooling of the sample to room temperature. The helical sample almost completely recovered its original straight shape in 30 s when heated to 50°C.



30 wt% 40 wt% 50 wt%

Fig. 4 Thermomechanical properties of PU block copolymer with different hard segment content

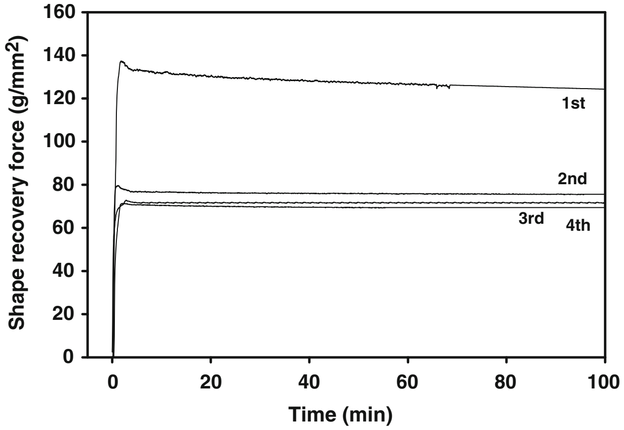


Fig. 5 Shape recovery force of SMPU (40 wt%) wire at 50°C

Figure 5 shows the shape recovery force of PU wire at 40 wt% hard segment content, which was tested at a constant temperature of 50°C using the shape recovery force measuring equipment set-up in our laboratory. Although the shape recovery test should be carried out near human body temperature, i.e., 37°C, for practical orthodontic application, a higher temperature of 50°C was chosen since it took too long time for the SMP wire to show shape recovery at body temperature. Nevertheless, the test result at 50°C is still meaningful with respect to investigating the orthodontic behavior of SMP wire, because the shape recovery effect can be analyzed in terms of temperature and time. As soon as the PU wire was heated to 50°C, the shape recovery force increased sharply up to almost 135 gf. When the temperature reached 50°C, the sample showed no further increase in shape recovery, and the shape recovery force decreased slowly with time. After 60 min, the shape recovery force was lowered to approximately 125 gf. On the other hand, the shape recovery force showed the highest value in the first cycle test and decreased with the number of test cycles. The result in the second cycle showed a particularly decreased value, and an equilibrium value was nearly reached in the final cycles. The decreased value results from incomplete recovery of molecular states in hard and soft segments after the previous cycle. Similar fatigue phenomena typically appear in relation to the mechanical properties of most materials. The long-term shape recovery force was also measured and is shown in Fig. 6. It is clearly seen that the sample preserves a shape recovery force of about 120 gf even after 3 months. Furthermore, the shape recovery curve after 2 months shows an almost constant value with time. This indicates that the SMPU possesses good shape recovery force for practical application as an orthodontic appliance for a period of 3 months and more.

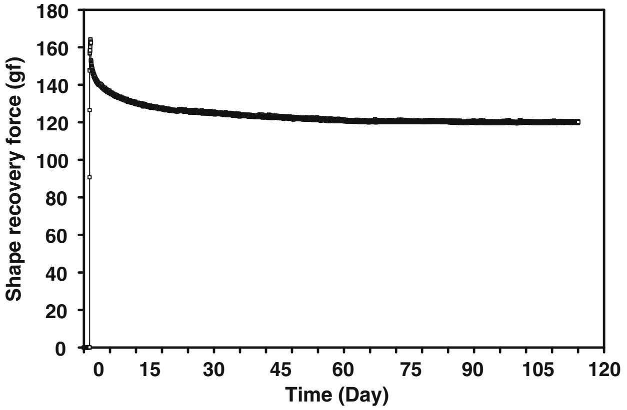


Fig. 6 Long-term shape recovery force of SMPU (40 wt%) wire at 50°C

3.2 Orthodontic behavior of shape memory PU wire

An orthodontic application was carried out using a dental model. The PU wire, which was prepared by melt-spinning, was used as an orthodontic appliance, and was attached to a multi-bracket system on the dental model. Prior to its attachment to the teeth, the wire-type appliance was used after elongation to 1.5 times its original length at 65°C for thermal stability of the wire. Adhesion of the appliance to teeth was carried out with the use of a rubber ring on the bracket instead of attaching a bracket, which is usually applied with a metal alloy appliance. In addition, this shape memory PU wire appliance is aesthetically more appealing than the bracket-equipped appliance, because the PU sample is transparent to some extent. Furthermore, the SMP wire itself is more aesthetically desirable for orthodontic treatment than shape memory alloys, and the overall aesthetic appearance of the orthodontic appliance can be further improved with the employment of a ceramic bracket.

The orthodontic test was performed using the PU wire. Movement of the teeth was clearly achieved when the appliance was heated above the transition temperature near 40°C. Upon heating the orthodontic appliance set in a measuring chamber kept at a constant temperature of 50°C, the initially misaligned teeth began to move slowly toward the wire-type appliance due to shape recovery of the wire between the brackets. In 1 h, the misaligned teeth were almost adjusted to the desired teeth alignment. This movement is too rapid for practical application to orthodontic treatment. However, it should be noted that the shape recovery force and resulting displacement can be controlled by adjusting the predetermined shape retention on basis of the magnitude of elongation of the wire when it is initially prepared. In the present system, the total displacement of the teeth moved during a 1 h period was 8.50 mm. This means that the displacement of teeth resulting from the shape recovery of PU wire upon heating can be controlled by using the predetermined shape retention of

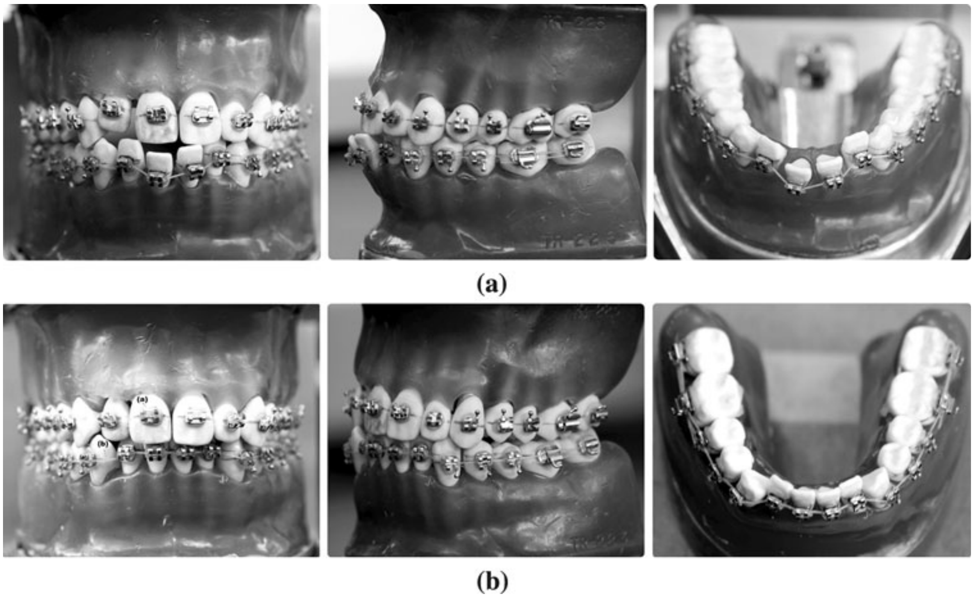


Fig. 7 Photographs of the appliance (**a**) before and (**b**) after orthodontic treatment. The movement of the misaligned teeth due to a lateral force originating from the shape recovery of the PU wire-type appliance is seen

the appliance. The position of the teeth before and after orthodontic treatment is seen in Fig. 7. The misaligned teeth could be adjusted to the desired position, where the degree of tooth movement is dependent on the relative position of the teeth. Consequently, it is verified that the shape memory PU wire has strong potential for orthodontic application, while providing aesthetically satisfactory appearance. In particular, this shape memory polymer appliance can provide a constant shape recovery force to teeth over a long period f time in contrast to the usual elastomers.

4 Conclusions

By using the shape memory PU wire as an orthodontic appliance, teeth alignment could be realized in orthodontic treatment. The PU wire prepared in this study showed high shape retention and shape recovery of 85% or more as well as good mechanical properties such as an elongation-at-break of 1215% and a breaking stress of 26.8 MPa at 40 wt% hard segment content. In the orthodontic test, the shape recovery force of the wire was sufficient to correct misaligned teeth when the appliance was heated above its transition temperature. The PU wire is a promising smart material for novel orthodontic appliances and provides satisfactory aesthetic appearance.

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