ACS APPLIED MATERIALS & INTERFACES

Letter

Cite This: ACS Appl. Mater. Interfaces XXXX, XXX, XXX−XXX

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Shape Memory Ankle−Foot Orthoses

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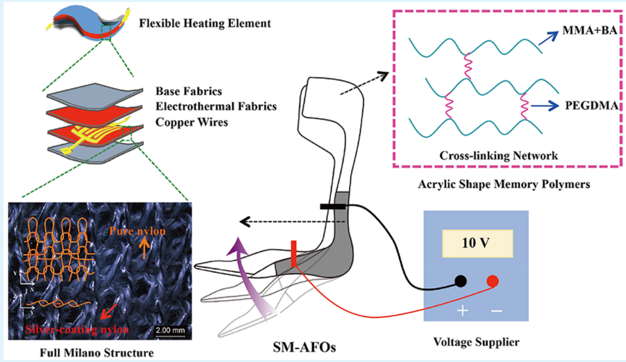
Supporting Information

ABSTRACT: Electrically actuated ankle−foot orthoses (AFOs) were designed and prototyped using shape memory textile composites. Acrylic copolymers were synthesized as the matrix to demonstrate shape memory effects, whereas electrothermal fabrics were embedded to generate uniform heat as a trigger. Superior to conventional polymeric orthoses, shape memory AFOs (SM-AFOs) could be repeatedly programmed at least 20 times with stable shape fixity and recovery. Evidenced by clinical practice, SM-AFOs were effectively actuated at 10 V, allowing the correction of ankle angles with 10° plantarflexion. Ultimately, we envision a smart orthopedic system that can advance progressive rehabilitation with manipulation under safe and convenient conditions.



KEYWORDS: *shape memory, ankle-foot orthoses, acrylic copolymers, electrothermal fabrics, drop foot*

Orthotic devices are externally applied apparatuses used to correct or support body parts in order to modify the structural and functional characteristics of the neuromuscular and skeletal system.[1] Patients who have body problems such as strained or stretched tendons[2] and ligaments,[3] conditions like cerebral palsy[4] and stroke,[5,6] and broken or displaced bones[7] could be prescribed with orthotic devices. Ankle−foot orthoses (AFOs) are normally made to assist drop-foot patients to walk better by supporting the ankle to maintain the normal gait.[8] Not only can AFOs control the deformation of ankles and prevent excessive plantarflexion, they also support normal alignment and mechanics.[9]

Conventional orthoses are mostly high-temperature thermoplastics[10] or thermoset plastics,[11] in which once the shape is set it would hardly be formed into another shape. The fabrication of a custom-made orthoses involves many procedures, which are time-consuming and produce considerable amount of chemical wastes. Specifically, these fabrication processes include taking body impression using plaster, forming a positive cast made from the plaster negative mold, and forming the polymeric plastic materials into the cast shape, followed by trimming and finishing procedures to obtain the final orthotic device.[12]

The problem of wastefulness is especially prominent in case the orthosis is designed for the purpose of progressive correction or the need for adjustment from time to time. For instance, a cerebral palsy patient who has spasticity in plantar flexor muscles, commonly known as drop-foot deformity, could be treated with serial casts or orthoses to provide stability and prolonged stretch to the spastic muscles, which are then immobilized in a lengthened position.[13] The orthosis is generally believed as a more cosmetic and effective approach. The orthosis is completed in series and is regularly replaced by another orthosis with adjustment of the plantarflexion/dorsiflexion angle at the ankle joint in a weekly basis.[14] Hence, a considerable amount of time and materials are consumed in the fabrication of these orthotic devices.

Shape memory polymers (SMPs) can simplify the shape-forming processes of AFOs. Orthoses made of SMPs can be softened and subsequently be molded into a new shape. These orthotic devices can return to their original shape if an incorrect shape is formed. It allows better fitting and reduces excessive waste of materials due to incorrect shape forming. The activation of the shape memory effect can be triggered by raising the temperature of the polymer, and is often achieved by putting the polymer in a hot water bath or under hot wind.[15] However, the shape forming process would be very dangerous if it is carried out with the patient's body part attached, such as in the case of serial casting to treat drop-foot deformity.[16]

Herein, we present a facile preparation of electrically actuated intelligent AFOs by using shape memory textile composites. Electroactive AFOs comprise acrylic SMPs and heating fabrics, which are knitted with full Milano structure using the combination of textile fibers and metallic fibers. Efforts have been spent on the study of structure and properties of shape memory AFOs (SM-AFOs) and their

Received: May 28, 2018
Accepted: September 17, 2018
Published: September 17, 2018

DOI: 10.1021/acsami.8b08851
ACS Appl. Mater. Interfaces XXXX, XXX, XXX−XXX

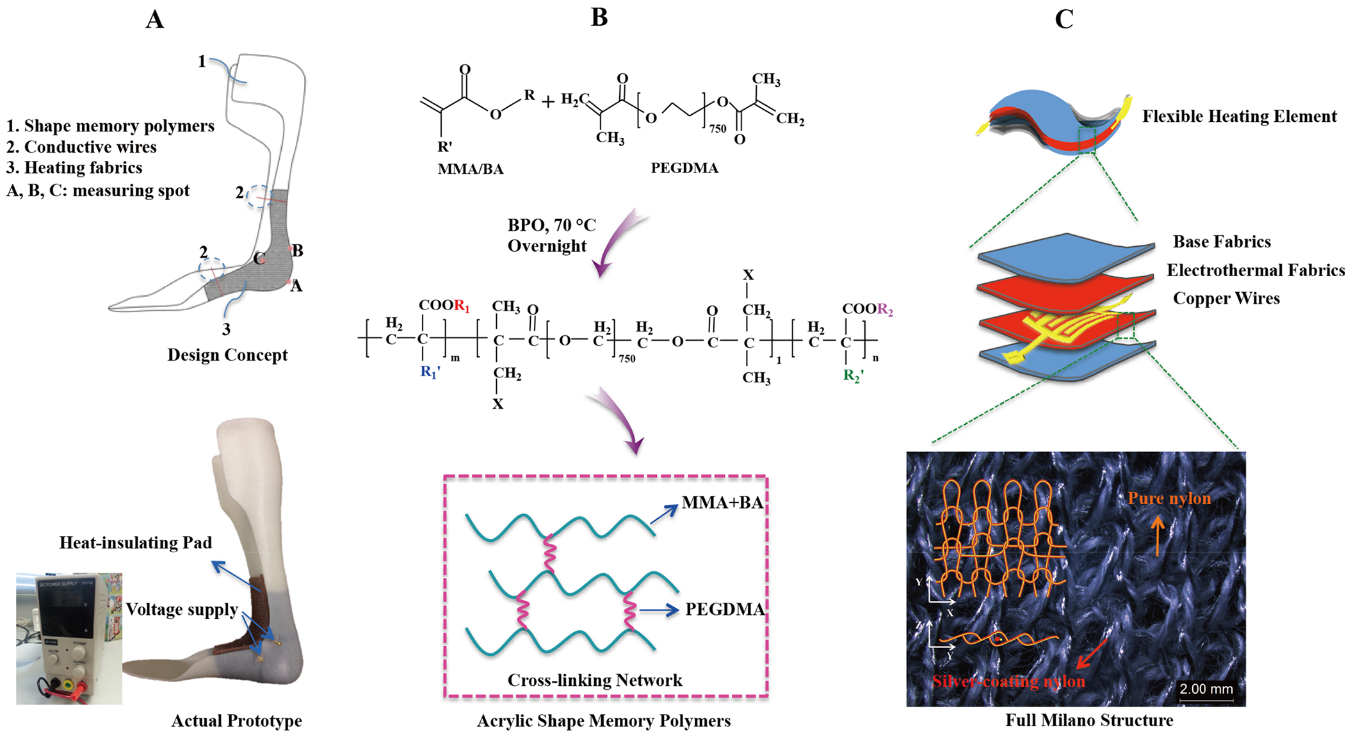


Figure 1. Schematic illustration of the fabrication of electroactive SM-AFOs. (A) Design and prototype of SM-AFOs; (B) synthesis of acrylic SMPs with a cross-linking network; (C) flexible heating element comprising copper wires, base fabrics, and electrothermal fabrics. The electrothermal fabrics were made by full Milano stitching with pure and silver-coating nylon yarns.

practical manipulation under a safe and convenient environment. Upon electrical stimulus, shape memory AFOs can flexibly change their shapes with sufficient recovery stress, allowing patients to repeatedly or progressively adjust the ankle angle. In comparison to traditional AFOs, it is much more cost-effective and time-saving to utilize SM-AFOs.

Of various approaches for treating ankle−foot pathologies, wearing rigid or semirigid ankle braces has been widely accepted in recent years.[8] These devices, such as AFOs, help improve the gait impairments by forcing the ankle joint angle to keep close to 90°. A critical obstacle and challenge of polymeric orthoses on the progressive correction of drop-foot/plantarflexion deformity concerns tedious adjustment of new orthosis from week to week. To address this problem, an intelligent SM-AFOs was designed and prototyped in Figure 1A. SMPs are a class of stimuli-responsive materials, which are capable of retaining the predefined shape by programming process and subsequently recovering to the original shape under a stimulus.[17−19] Therefore, SMPs have been investigated for various biomedical applications.[20−22] As previously reported by our group,[23] a wrist orthotic device was fabricated by using shape memory polyurethane. To date, most polymeric AFOs are made of polypropylene (PP) and acrylates. Compared with PP, acrylate is more flexible to design and the structure and properties of acrylic copolymers can be regulated with abundant active groups. Thus, in addition to polyurethane, acrylates (Ottobock) specifically used for orthotics, were studied in this work to prepare the acrylic SMPs for AFOs. Briefly, as shown in Figure 1B, SMPs were synthesized by bulk free-radical copolymerization of methyl methacrylate (MMA), butyl acrylate (BA) and poly(ethylene glycol) dimethacrylate (PEGDMA). Thereof, chemical cross-links as net-points are responsible for the permanent shape while the rest of polymers act like a switch to immobilize the temporary shape.[24]

Electricity, as a trigger,[25,26] was developed here for the shape memory effect by charging the conductive fabrics under a DC voltage. For generation of uniform heat, a unique conductive fabric composing of pure and silver-coating nylon yarns was made to form stable loop structure by full Milano stitching (see Figure S1). Plain and 1 × 1 rib are the most typical knitting structures; however, in this case, niether is suitable for the production of electrothermal fabrics. For the former, the distinct face and back structure results in different thermal resistance. For the latter, significant strain difference under deformation is observed in the longitudinal and transverse direction. To address these concerns, we selected full Milano with uniform surface structure and balanced stretching deformation due to the architecture of half plain and half rib (Figure 1C). Despite multiple laminations of copper wires, base, and conductive fabrics, this textile composite is so flexible to be integrated with SMPs by a vacuum forming approach (see Figure S2). It is worth noting that a series of factors such as mechanical properties, conductivity, flexibility, and knitting parameters are pivotal for optimization of heating composites. For better mechanical properties, we introduced carbon fibers to the polymeric orthoses.[27,28] Similarly, carbon fiber-reinforced SM-AFOs (see Figure S3) were prepared with improved toughness and stiffness. Nevertheless, their excellent conductivity usually led to overheating phenomenon as a consequence of short-circuit fault. Even AFOs could be directly damaged due to unstable conductivity. Eventually, stable conductive fabrics with full Milano structures were developed in place of carbon fibers. Toughened by these fabrics, Young's modulus and toughness of SM-AFOs (see Figure S4) were higher than these of PP-based AFOs.[12] It is of

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ACS Appl. Mater. Interfaces XXXX, XXX, XXX−XXX

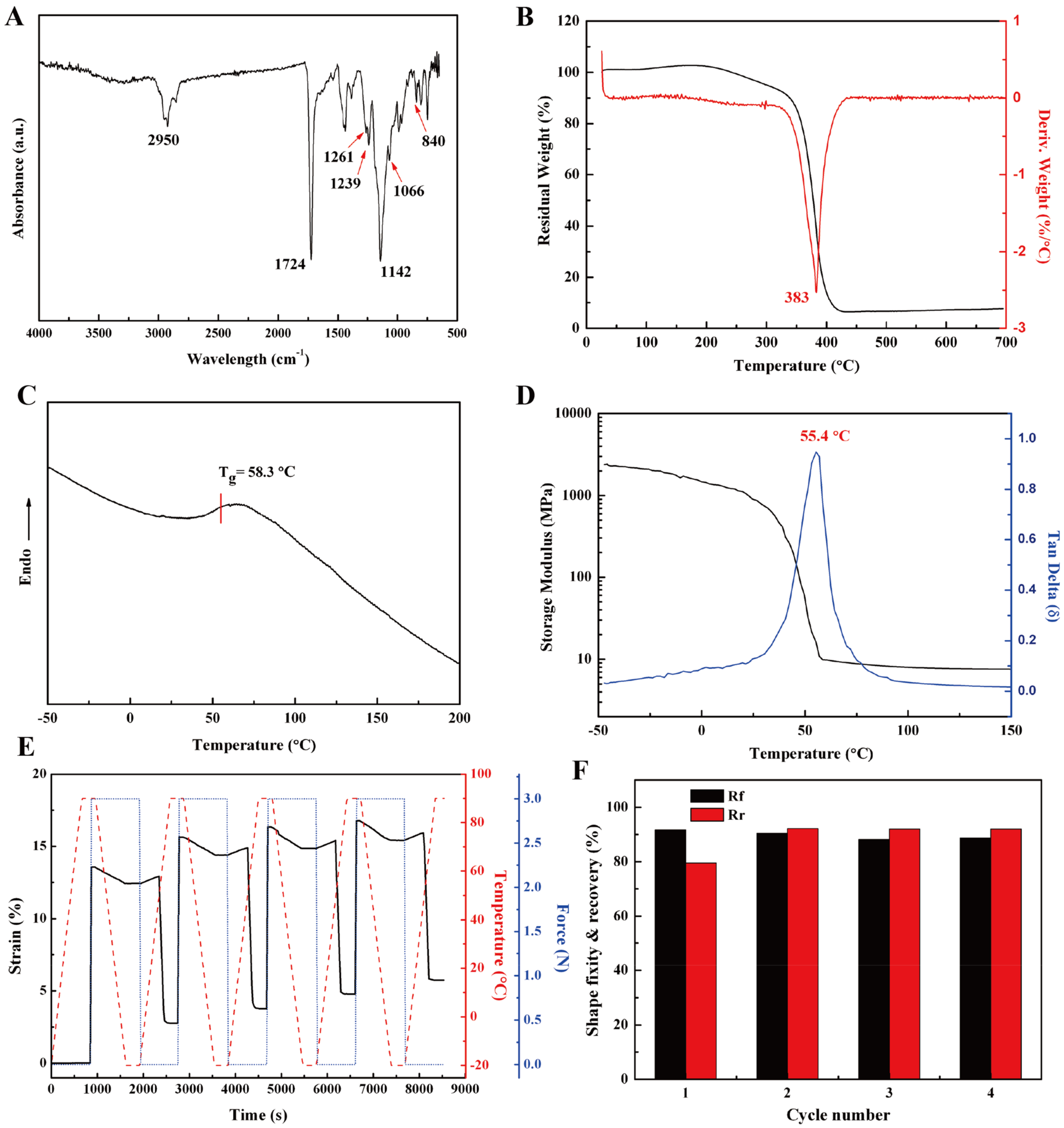

Figure 2. Structure and shape memory properties of acrylic SMPs by characterization of (A) FTIR, (B) TGA, (C) DSC, (D) DMA, (E) Thermomechanical cycles and (F) shape fixity and recovery ratios.

equal importance to manipulate AFOs in response to a safe voltage (<36 V) for heat generation, allowing the trigger of shape memory effect in a controlled manner.

FTIR was performed to confirm the chemical structure of SMPs. Figure 2A shows the characteristic peaks at 2922, 1724, 1437, and 1142 cm^{-1}, attributing to CH_2, C═O, CH_3, and C−O stretching vibrations in MMA, BA, and PEGDMA. As earlier studied,[29] PMMA and PBA had similar molecular backbones with slight differences found in FTIR spectra. A peak at 840 cm^{-1} was particularly assigned to the CH_2CH_2O vibration of PEGDMA. Thermogravimetric analysis (TGA) curve of SMPs is shown in Figure 2B. It can be seen that the degradation was approximately completed at 425 °C with the fastest weight-loss temperature of 383 °C, revealing the high stability of acrylic SMPs. Given that the feed ratio of MMA to BA was 5:1 and limited PEGDMA was added as cross-linker, the theoretical glass transition temperature (T_g) of copolymers can be calculated as 63.4 °C according to the Fox equation.[30] As depicted in Figure 2C, D, only one T_g was observed, indicating that the resultant product was homogeneous. Despite slight difference of T_g determined by DSC (58.3 °C) and DMA (55.4 °C), both of them closely obey the Fox equation with an

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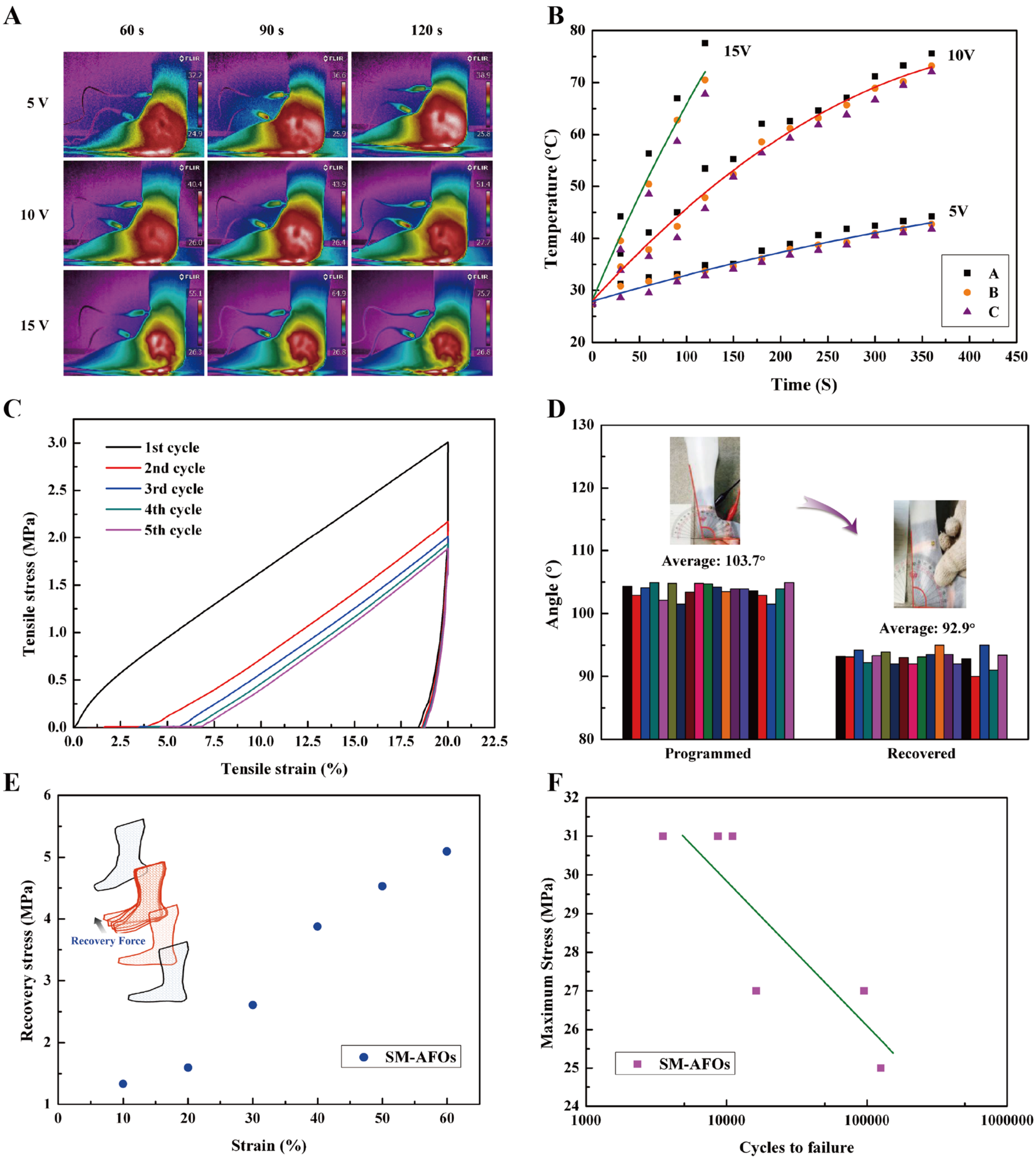

Figure 3. Thermomechanical and shape memory characterization of SM-AFOs. (A) Thermal infrared images of SM-AFOs at different voltages. (B) The temperature of SM-AFOs vs time under various voltage supplies. Different measuring spots of A, B, and C can be found in Figure 1. (C) Thermomechanical cycles of SM-AFOs. (D) 20-time recycle testing of SM-AFOs. (E) Recovery stress of SM-AFOs under various strains. The inset shows the ankle correction induced by recovery stress. (F) Fatigue performance of SM-AFOs.

averaged T_g of 56.9 °C. Generally, amorphous SMPs have broader transition temperature regions (∼30 °C) than semicrystalline ones.[31] This phenomenon was also reflected in DSC and DMA results. Thus, it was not surprising to find the permanent shape can be recovered at a temperature slightly lower than T_g. Figure 2E exhibits the shape memory cycle curve of SMPs. In a typical shape memory cycle, the sample is deformed at a programmed temperature and the temporary shape is fixed after cooling. Afterward, the permanent shape is recovered once the sample is reheated at a temperature above T_g.[32] SMPs show good thermomechanical properties with stable shape memory. Except for the first shape memory cycle, the average values of shape recovery (R_r) and shape fixity (R_f) were above 92 and 89%, respectively (Figure 2F).

Taken into consideration the safety and convenience, the voltage supply will be limited less than 36 V. The heat efficiency and diffusion are evaluated for SM-AFOs (Figure 3A, B). As expected, SM-AFOs obtained better heat efficiency with regard to the increase of applied voltage. In other words, it was faster to heat SM-AFOs to the required temperature at a higher

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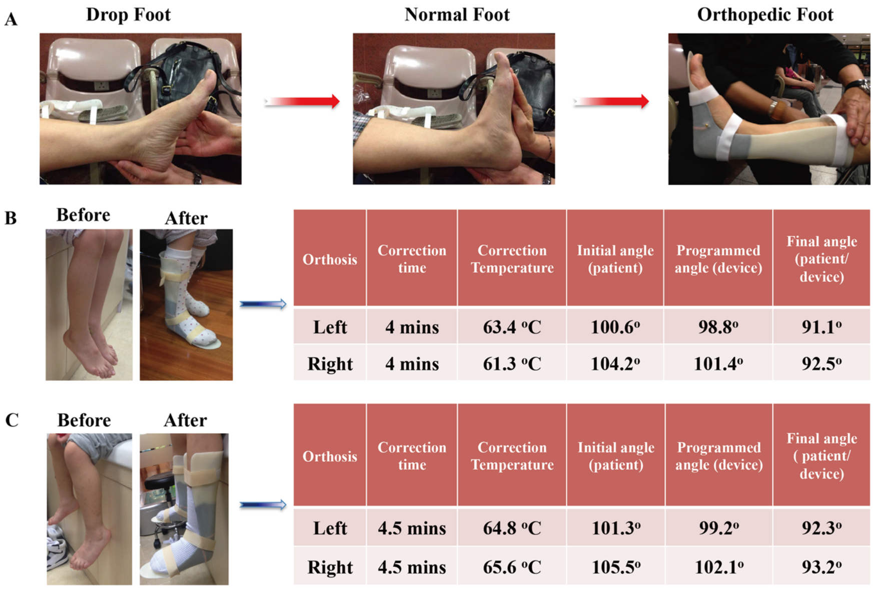

Figure 4. Clinical trials of SM-AFOs for the correction of drop-foot/plantarflexion deformity. (A) Feet of patients in different states; (B, C) Two cases for the correction of drop-foot deformity of children patients by using SM-AFOs.

voltage. However, worse heat diffusion was monitored with remarkable difference under an elevated voltage. In spite of the linear temperature−time relationship and uniform heat dispersion, 5 V voltage can hardly reach the transition temperature. For 15 V voltage, the heating rate was too rapid to induce significant temperature gradient throughout the ankle area, probably leading to adverse effects on the shape deformity and recovery of SM-AFOs. Eventually, the program and recovery of SM-AFOs was accomplished in several minutes using a medium voltage of 10 V (see Video S1).

Shape memory effects of acrylic SMPs were demonstrated by the DMA (Figure 2E), whereas shape memory behaviors of SM-AFOs were investigated by the tensile−strain cycles, as shown in Figure 3C. Similarly, the shape fixity and recovery ratios became stable since the second cycle. To further examine the thermomechanical properties of SM-AFOs, we performed twenty-time repeated programming (Figure 3D). To be specific, the ankle angle of SM-AFOs was programmed from 90 to 105° at 65 °C and then fixed at an average angle of 103.7° after cooling to the ambient temperature. Finally, the angle was recovered to an average angle of 92.9° at 65 °C. Therefore, it became feasible to employ SM-AFOs to generate an ankle angle correction within 10° plantarflexion. This value was comparable to other studies with correction of plantarflexion ranging from 10 to 20°.[33,34] In comparison to SMPs, the R_r and R_f of SM-AFOs were changed from 92 to 79% and from 89 to 91%, respectively. We attribute the difference to the integration of textile-based composites into SMPs.

SM-AFOs have already proved the ability in multiple programming and recovering, however it is of significance to evaluate their recovery stress for the purpose of clinical practice. Because of unavoidable stress relaxation at high temperature, the recovery stress was normally lower than the tensile stress at the same strain. This phenomenon was evidenced by 20% strain in Figure 3C, E. Not surprisingly, the recovery stress was increased with regard to the increase of strains. According to earlier research by our group,[35] the ankle joint resistive torque was measured with an average value of 4.6 and 8.4 N m under the slow and fast stretching condition, respectively. And the corresponding stress was calculated as 0.65 and 1.19 MPa (see Figure S5). Actually, the related stress would be even lower for the children patients in this study because of child−adult differences in the kinetics of torque.[36] Even though the stress would drop at the same strain during initial programming, it became more and more stable later on. Taken together, the recovery stress (1.33 MPa) at 10% strain was considered sufficient for ankle corrections, especially in a slow recovering condition. For long-term usage, fatigue performance of SM-AFOs (Figure 3F) was studied with good durability. This result is also favorable for progressive rehabilitation.

Drop-foot, a kind of gait inefficient diseases, is mainly due to the total or partial central paralysis of the muscles, including structural disorders, motor disorders and control disorders at the ankle joint.[37] One major aim in this study was to examine the effect of SM-AFOs on the angle correction in a common clinical situation. As demonstrated by Figure 4A, drop foot can be effectively corrected by the SM-AFOs to a normal ankle angle. The detailed correction results on two children patients with spastic cerebral palsy are described in Figure 4B, C. In both cases, it was moderate to have the correction time completed in 4−5 min. Additionally, it was feasible to fully trigger the SM-AFOs at a temperature ranging from 60 to 65 °C, which was considered safe for body skins particularly under protection of stockings and heat-insulating pads (see Figure S6). In agreement with the results in Figure 3D, the ankle angle of patients could be corrected to be close to 90° within 10° plantarflexion. Another target was focused on the evaluation of kinetics and kinematics by using SM-AFOs, and preliminary results suggested a gait improvement during walking (see Video S2).

In conclusion, electrically actuated intelligent AFOs were designed and facilely prepared by using shape memory acrylic copolymers and conductive textile composites. To the best of our knowledge, the functionality of shape memory is a unique feature rarely reported for the polymeric ankle-foot orthoses, enabling the recycle of AFOs with good shape fixity and

DOI: 10.1021/acsami.8b08851
ACS Appl. Mater. Interfaces XXXX, XXX, XXX−XXX

recovery. Thanks to the full Milano stitching, a stable structure of conductive fabrics was developed for uniform heat diffusion. Similar to acrylic SMPs, SM-AFOs showed remarkable thermomechanical behaviors with sufficient recovery stress and stable shape memory effects. Under a safe and convenient voltage of 10 V, SM-AFOs could be heated above T_g in 4−5 min during programming and recovering process. SM-AFOs demonstrated the capability of assisting ankle motions with actuation, providing a range of 10° plantarflexion correction in clinical practice. The gait analysis with/without SM-AFOs are ongoing to further investigate their potential on progressive rehabilitation for drop-foot patients. The subtle employ of shape memory characteristic and flexible conductive textiles in this work establishes a fascinating platform to facilitate the development of next-generation AFOs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b08851.

Experimental section, fabrication of heating fabrics and SM-AFOs, carbon fiber-reinforced AFOs, Stress−strain curve and recovery stress of SM-AFOs, operation of heat-insulating pads (PDF)

Video S1, SM-AFOs electrically actuated at 10 V (MPG)

Video S2, patient walking with SM-AFOs (MPG)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Innovation and Technology Commission (ITP/012/12TP), and Research Grants Council, University Grants Committee (PolyU 5158/13E). The authors are thankful to Dr. Lin Gu and Ms. Shanshan Zhu for guidance with DMA test, as well as Prof. Raymond Ng (Top Ten International Ltd.) for assistance with clinical trials.

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ACS Appl. Mater. Interfaces XXXX, XXX, XXX−XXX