Shape memory clay flaps assisted body cooling fabrics

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Abstract. Mechanical responses of inorganic clay to external stimuli have been rarely implemented into devices that interact with the human body. We demonstrate that the hygroscopic and free swelling behaviours of Na-bentonite were engineered to design wearables, which give multifunctional responsiveness to human sweat. By printing bentonite nanoclay (BNC) composite on flaps of fabrics, they can reversibly change shape within a few seconds in response to environmental humidity gradients. Body's need for cooling is facilitated through controlled ventilation by opening and closing of these clay printed flaps. This study provides a background for developing new shape memory clay composite for many applications in garment industry.

Keywords: Bentonite nanoclay; Mechanical response; Moisture management; Polyester fabric; Clay swelling

1. Introduction

High swelling property of Na-bentonite clay is rarely used in applications, which lead to mechanical responses in relation to hydration. The moisture gradient is a stimulating factor, which can trigger shape transformation in clay due to mechanical amplification of moisture-induced strains in swellable clay. Similar observation can be found in nature in pine cone scales and wheat awns [1,2]. Moreover, it has been reported that shape changing polymers could be triggered by the moisture gradient in the environment [3,4]. However, a powder compound such as clay is an unsupervised material when it comes to shape changing material. Different types of clays are ubiquitous in nature. From those, bentonite nanoclay (BNC) exhibits high cation exchange capacity and high swelling capacity in relation to hydration [5]. The structure of bentonite is composed of a three-layer platelet with an octahedral aluminum hydroxyl sheet sandwiched between two layers of silicon-oxygen tetrahedral. The nano size space between adjacent platelets of BNC comprises of exchangeable cations such as Na^+, which draw water, and form a rigid network made up of water layers [6]. Hence, this nanospace is vital for BNC's incomparable hydrophilicity. In addition, Na-bentonite consists of negatively charged aluminosilicate layers, which are kept together by cations. Hence, their ability to absorb water between the layers, results in strong repulsive forces and clay expansion [7]. Further, the hydroxyl groups on edges of clay provide excellent sites for water adsorption [8]. Not only excellent hydrophilicity of bentonite clay, but also it inherents excellent health benefits in terms of skin related problems [9,10].

Here in, we report a moisture responsive Na-bentonite composite, which changes its shape and functions simultaneously with humidity change. Na-bentonite makes a perfect composite with silicone rubber, which assists to expand and contract when composite absorbs and removes water, respectively. Hence, this moisture responsive material can be used to improve moisture management property of sportswear. Moisture management is one of the key performance criteria in today's apparel industry [11]. However, highly demanded synthetic fabrics are lack in moisture management property due to its hydrophobic nature [12,13]. Na-bentonite composite is localised on ventilating flaps that can automatically adjust the moisture transfer of the fabric through change of skin exposure percentage by controlling the area of exposed skin via shape transformation. This will open up new avenues in using hygroscopic transforming materials to tackle problems related to moisture, such as in sports wearables and indoor humidity control.

2. Methodology

A dispersion of bentonite nanoclay was obtained by dissolving 4 g of nanoclay in 100 ml of deionized water. Particles of bentonite nanoclay, 100 nm in size, were obtained by ball milling (FRITSCH PULVERISETTE 7 premium line grinder). 4 g of bentonite clay (hydrophilic bentonite clay-Aldrich) in 100 ml of deionized water was activated with 2 g of NaCl (Aldrich). Then, reaction was kept stirring and boiling for one hour. After one hour, the dispersion was diluted with water. Dilution with water was repeated to make sure that all impurities soluble in water were removed. The dispersion was allowed to settle for 48 hours. The settled clay was centrifuged and allowed to dry in the oven at 105 °C. Then, powdered sample and unmodified clay were dispersed in silicon rubber solution, followed by adding curing agent to the reaction. Obtained Na-bentonite and unmodified clay composites were localised on one side of woven polyester fabrics and kept in the oven at 60 °C for 3 hours. The samples were characterized using Scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy (EDX-HITACHI SU6600 SEM coupled with EDX detector). X-ray powder diffraction (XRD) profiles were recorded on a Bruker PW 1050 diffractometer using Cu-Ka radiation (k = 0.154 nm), over a 2θ range of 3°–70°, step size of 0.01, and a step time of 2 s. The bending angles of rectangular samples (40 mm in length, 5 mm in width, and 0.2 mm in thickness) were measured to understand the mechanical performances of the samples at different time intervals. Bending angles were then calculated using a theoretical formula (Eq. 1) based on the classical Stoney formula [14]. The theoretical formula relates the bending angle, θ, to the expansion strain of the composite due to wetting (supplementary Fig. 1.).

$$\theta = 360\,\frac{L}{2\pi R} \tag{1}$$

where L is the length of the strip; R is the bending radius. The weight swelling ratio of the Na-betonite composite samples were calculated by measuring their weight before and after immersion in deionized water at different time intervals. The weight swelling ratio of absorbed water during immersion relative to the dry mass is given by;

$$\text{Weight swelling ratio} = \frac{\text{Mass (wet) - Mass (dry)}}{\text{Mass (dry)}}\ 100\% \tag{2}$$

where mass (wet) refers to the weight of the sample submersed in water at different time intervals; mass (dry) refers to the weight of the sample dried at 60 °C under vacuum for 36 hours. Clay composite was localised on prototype polyester fabric using a stencil (supplementary Fig. 2.). The fabric sample was kept in the oven at 60 °C for 3 hours. Stencil was removed from the fabric, and rectangular shape Na-bentonite composite was partially separated from the fabric to act as ventilating flaps. Finally, shape transformation of these ventilating flaps were observed.

3. Results and discussion

The SEM images in Fig. 1. (A) and (B) proved that Na-bentonite is uniformly distributed in silicon rubber composite, and intercalation of Na^+ is proved from EDX spectra in Fig. 1. (C) and (D). After intercalation, Na Wt% has risen from 3.4% to 5.3%. This results in enhancing water absorption in bentonite clay, and porous nature of clay promotes water travelling both inside the structure and outer surface. Consequently, Na-bentonite swelled rapidly by absorbing water. XRD spectrum (supplementary Fig. 3. A) shows the typical peak of (001) plane, which corresponds to the basal spacing of bentonite clay which exhibits a peak at $2\theta = 7.8°$, indicating the basal spacing of 1.4 nm. XRD spectrum of Na-bentonite (supplementary Fig. 3. B) shows a significant shift in corresponding peak of (001) plane, which has increased to 1.8 nm. Hence, above results confirm the successful intercalation of Na^+ in bentonite clay.

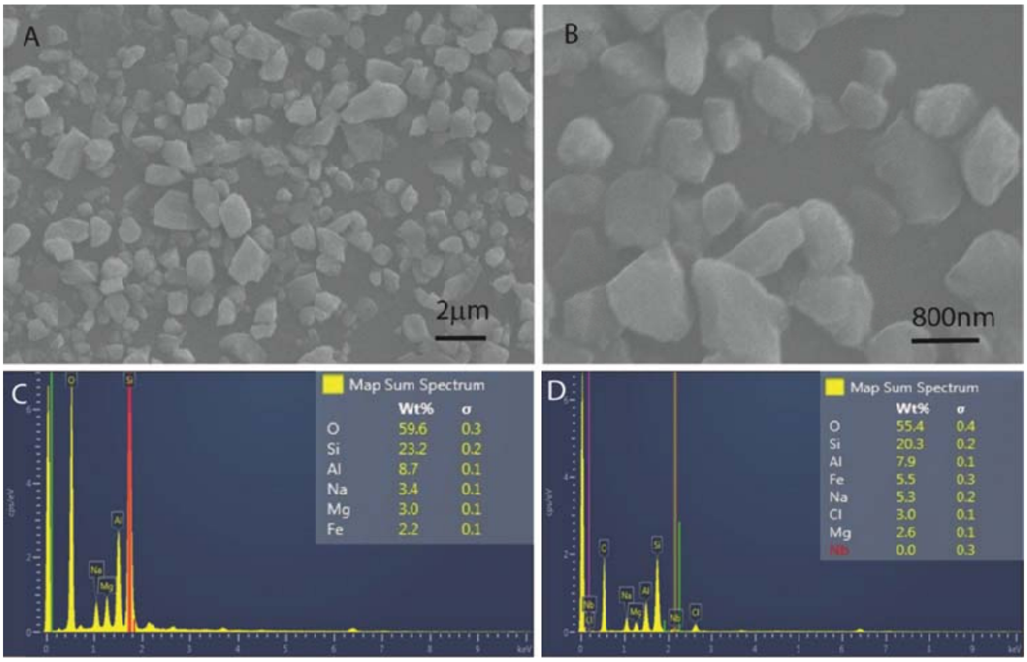

Figure 1. (A) and (B) SEM images of Na-bentonite composite. SEM-EDX spectra of unmodified bentonite clay (C) and Na-bentonite clay (D).

Fig. 2. shows the shape change of Na-bentonite composites upon exposing to water vapour. The original dimensions of the sample were 40 mm in length, 5 mm in width, and 0.2 mm in thickness. The non-stretching woven polyester fabric on top of the composite is restricted in expanding and as a result, the straight (original shape) specimens are bent upon absorbing moisture by Na-bentonite composite. The bent specimen fully regained its original shape quickly after being removed from the moisture environment. The weight swelling ratio of the samples were measured after immersed in water for 2 min, as a percentage with respect to the initial weight. Unmodified clay composite showed 10% increase in weight swelling ratio, while 23% increase in Na-bentonite composite. This clearly reveals that there is an obvious increase in weight, when the Na-bentonite composite is exposed to water compared to unmodified clay.

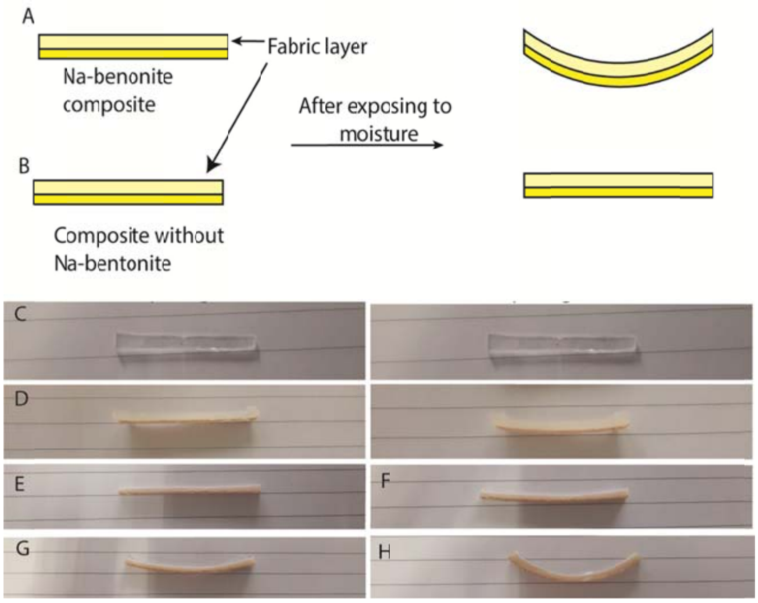

Figure 2. (A) Schematic diagram of shape transformation of Na-bentonite composite printed fabric when exposed to moisture. (B) Schematic diagram of inability in shape transformation of silicon rubber printed fabric when exposed to moisture. (C) and (D) Images of shape transformation of silicon rubber and Na-bentonite printed fabrics when exposed to moisture for 2 min, respectively. (E), (F), (G) and (H) Images of shape transformation of Na-bentonite composite printed fabrics after exposing to moisture for 0 s, 30 s, 1 min and 2 min, respectively.

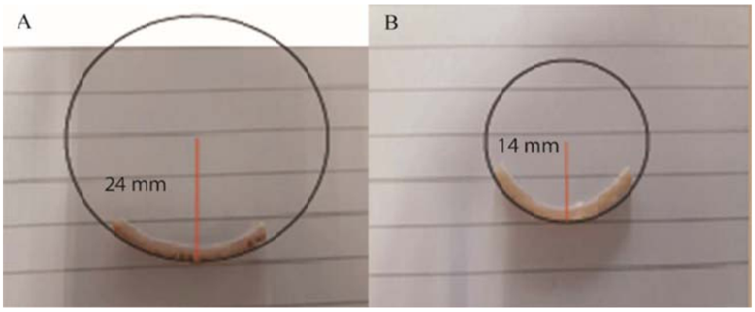

Figure 3. Images of radii of curvatures of (A) unmodified bentonite and (B) Na-bentonite composites.

The radius of curvature is the reciprocal of the curvature, and for a curve, it equals the radius of the circular arc which best approximates the curve at that point (Fig. 3.). Subsequently, completing the imaginary circle of the curve, the mean values of radii of the curvatures were measured as 24 mm for unmodified bentonite and 14 mm for Na-bentonite composite (Table 1.). Bending angles of unmodified and Na intercalated clay are 95.5° and 163.6°, respectively. This implies that Na-bentonite composite is more prone to absorb water compared to unmodified bentonite, as the lowest radius of curvature and the highest bending angle belongs to Na-bentonite composite. Considering this hydrophilic nature, Na-bentonite composite was used for localisation on prototype polyester fabric sample.

Table 1. Weight swelling ratios, bending radii and bending angles of unmodified bentonite and Na-bentonite composite at different time intervals.

Time (s)	Bentonite			Na Bentonite		
	Weight swelling ratio (%)	Bending radius (mm)	Bending angle (degrees)	Weight swelling ratio (%)	Bending radius (mm)	Bending angle (degrees)
30.0	5.0	60.0	38.2	8.5	48.0	47.7
60.0	7.5	40.0	57.3	15.5	38.0	60.3
90.0	9.0	28.0	81.8	20.0	24.0	95.5
120.0	10.0	24.0	95.5	23.0	14.0	163.6

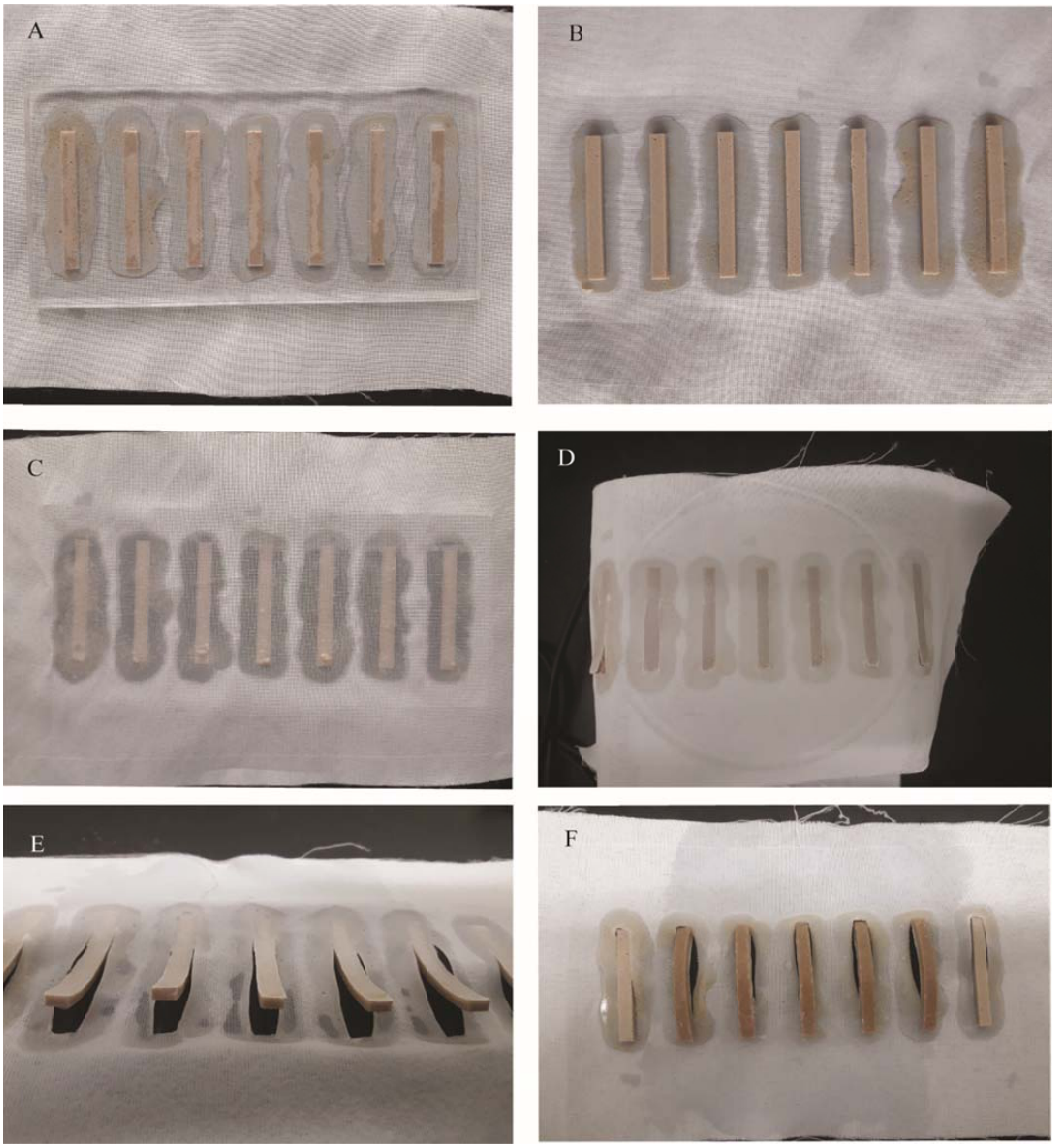

Figure 4. (A) Bottom view of fabric after fixing with Na-bentonite composite filled stencil. (B) and (C) Bottom and top views after removing the stencil, respectively. (D) Image when clay flaps were exposed to water vapour. (E) and (F) Top and bottom views of open clay flaps after exposed to water vapour, respectively.

Making sweat-responsive wearables modified with Na-bentonite composite was replicated in laboratory, by printing the clay composite on prototype fabric sample using a stencil. Fig. 4. clearly illustrates different stages from the printing of Na-bentonite composite on fabric to hydroscopic mechanical responsiveness of it. Shape transformation occurs in a flat clay composite layer when exposed to moisture. Fig. 4. (D) illustrates the flat ventilation flaps of prototype fabric sample before exposing to moisture, and Fig. 4. (E) and (F) illustrate the curved ventilation flaps after exposing to moisture. Owing to combination of non-stretching polyester and expansion of the composite, the ventilation flaps open on wetting. Na-bentonite composite printed flaps opened in 50 s when exposed to water vapour, then regained their original shape by closing the flaps in 65 s when removed from the moisture environment. This resembles the opening of flaps in the garment with increased human sweat, and closing of flaps with cooling of the human body.

Future works will focus on finding a more feasible printing method, which prints thin layers of Na-bentonite composite on fabrics in a range of designs. We predict that this scalable and adaptable technology can be used in industries beyond fabricating wearables, where moisture gradient is a key factor, such as hydration enhancement in skin care products, humidity control in smart homes, and moisture removal in biomedical textiles.

4. Conclusions

The designed novel Na-bentonite composite mechanically responds to moisture. SEM proved uniform distribution of Na-bentonite in the composite. Intercalation of Na^+ into bentonite was proved by EDX and XRD spectra. Weight swelling ratio and bending angle proved its expanding ability over unmodified bentonite composite. Na-bentonite printed flaps opened when absorbing the moisture and closed when it is dried. We harnessed the swelling behaviour of Na-bentonite clay, which provides us with a new perspective in using clay minerals for making moisture-responsive wearables. Our work will make it feasible to utilize Na-bentonite composite in many fields, with shape-changing interfaces in moisture changing environment.

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Supplementary Material

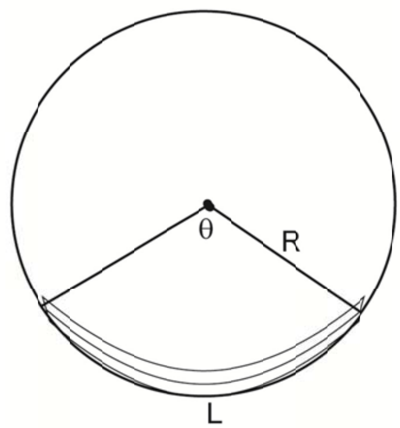

Fig. 1. Sketch of bending angle of Na-bentonite composite printed fabric sample.

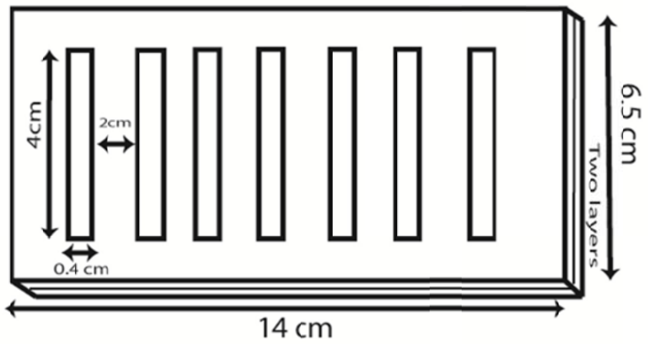

Fig. 2. Sketch of the stencil used in printing the clay composite on prototype fabric sample.

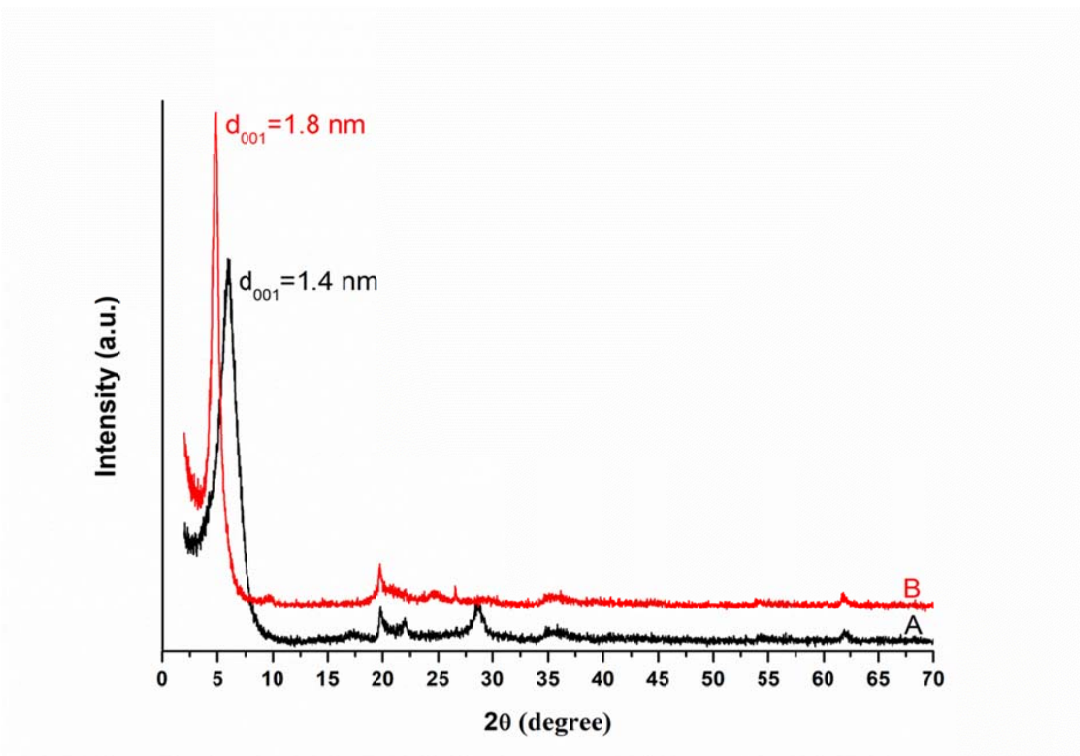

Fig. 3. XRD diffraction patterns of (A) unmodified bentonite clay and (B) Na-bentonite clay.

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