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Supplementary Information for

Water-Responsive Actuators Based on the Solution Casted PVA/Epoxidized-SBS Two-way Shape Memory Bilayer Composite Film

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Contents List

placed in the air to dry (the second line) for different duration.

Figure S7. Photos of the wetting-drying process of the E-SBS film. The E-SBS film was immersed in water (the first line) as well as taken out of the water and placed in the air to dry (the second line) for different duration.

Figure S8. The peeling curves of the 180° peeling test for the PVA/E-SBS bilayer composite films before and after being immersed in water for 10 minutes in the first, third and fifth cycles of wetting-drying processes.

Table S2. The interfacial toughness values of the PVA/E-SBS bilayer composite films before and after being immersed in water for 10 minutes in the first, third and fifth cycles of wetting-drying processes.

Figure R9. OM photos of the cross-section of the PVA/E-SBS composite bilayer film during the first (a), third (b) and fifth (c) cycles of wetting-drying processes. The first and second lines were photos of the composite films in the dry state and immersed in water for 10 min, respectively.

Figure S10. Photos of water-responsive two-way shape memory process of the thinner PVA/E-SBS composite film (300 μm). The first line are photos of the composite film immersed in water for different duration. The second line are photos of the composite film taken out of the water and placed in the air to dry for different duration.

Figure S11. (a)The final curvature, (b) bending speed and (c) recovery speed of the PVA/E-SBS bilayer films with different thickness ratios (PVA layer/E-SBS layer). The thickness of E-SBS layer remains unchanged.

Movie S1. The shape changeing process of immersing the bilayer film in water.

Movie S2. The shape changing process of placing the bilayer film in the air to dry.

Movie S3. The shape changing process of immersing the bilayer film in water again.

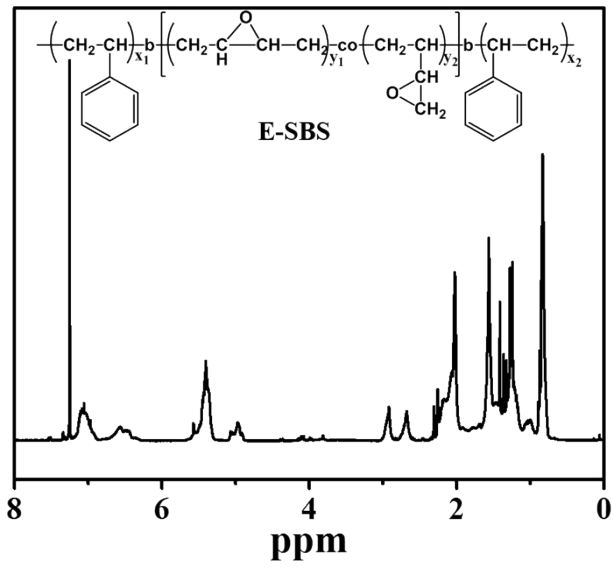


Figure S1. The ^{1}H NMR spectrum of the E-SBS.

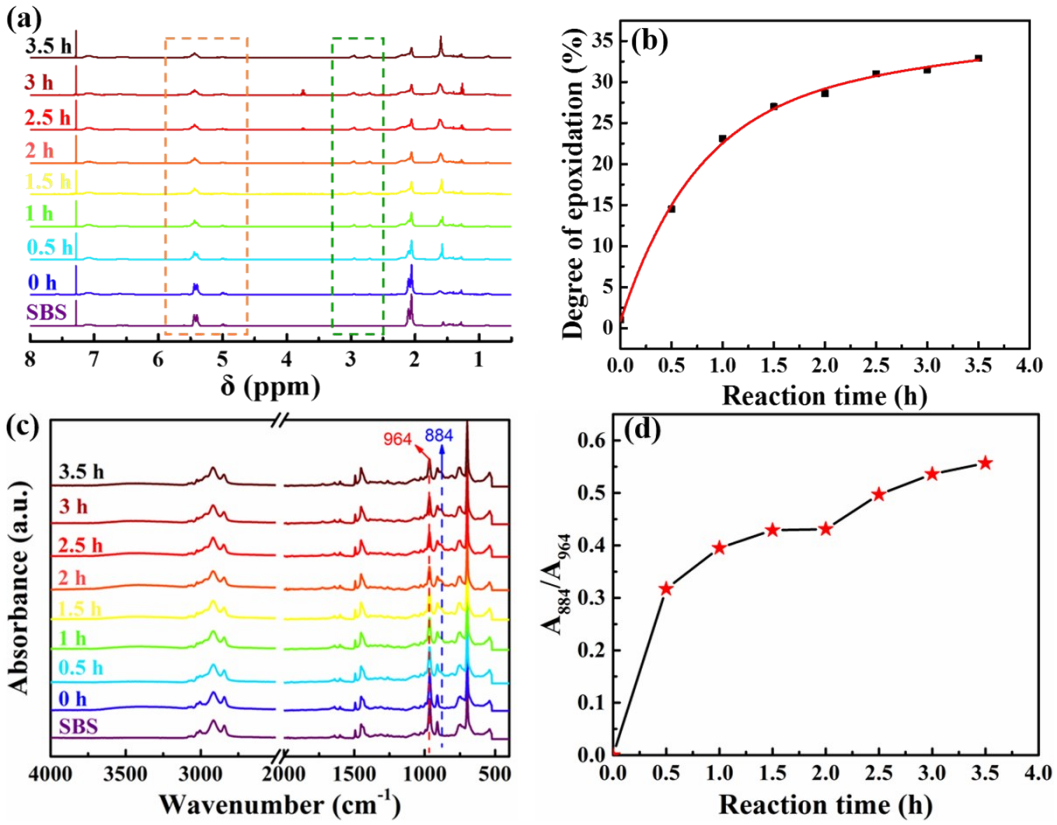


Figure S2. (a) The ^{1}H NMR spectrum, (b) epoxidation degree, (c) the FTIR spectrum and (d) relative absorption intensity A_{884}/A_{964} of SBS during epoxidation under different reaction time.

Considering that the reaction time has an important influence on the degree of epoxidation of SBS, we studied the change of epoxidation degree of SBS with reaction time by ^{1}H-NMR and FTIR and the results were shown in Figure S2. As can be seen in Figure S2a, two peaks appear at δ= 5.03 and 5.45 ppm, corresponding to the protons of the double bonds of 1,2- and 1,4-butadiene units in the polymer. Two peaks at δ= 2.70 and 2.96 ppm are derived from trans-epoxy groups and cis-epoxy groups. It was found that the peaks of the protons of the double bonds were getting smaller and the peaks of the epoxy groups were getting bigger. The degree of epoxidation of SBS with different reaction time was calculated according to the ^{1}H-NMR spectrum and recorded in Figure S2b. It was demonstrated that with increase of the reaction time, the degree of epoxidation of SBS increased while the rate of increase gradually decreased in the range of 0-3.5 h.

FTIR spectrum in Figure S2c showed the absorption intensity of the peaks at 964 cm^{-1} corresponding to double bonds is getting weaker, while 884 cm^{-1} corresponding to epoxy groups is getting stronger with the increase of the reaction time. Figure S2d shows the relative absorption intensity of epoxy groups obtained from the FTIR spectrum of A_{884}/A_{964} with reaction time. It was found that the relative absorption intensity of epoxy group has a positive correlation with the epoxy value. From the results of ^{1}H NMR and FTIR, it can be known prolonging the reaction time is an effective method to improve the degree of SBS epoxidation. According to Udipi's work (*K. Udipi, Epoxidation of styrene-butadiene block polymers. II. Journal of Applied Polymer Science, 1979, 23, 3311-3321*), the epoxidation reaction is accompanied by the side reaction like crosslinking, which increases with the increase of reaction time. It suggested that more side reactions would occur if the reaction was carried out for too long. Therefore, in order to ensure sufficient epoxidation degree and less side reactions, we conducted the reaction for 2 hours. The results showed that under this circumstance, the achieved epoxidation degree of SBS was sufficient to improve the adhesion between two layers and at the same time, few side reactions happened in this duration so that the final product could be well dissolved in THF, which enabled the subsequent casting process.

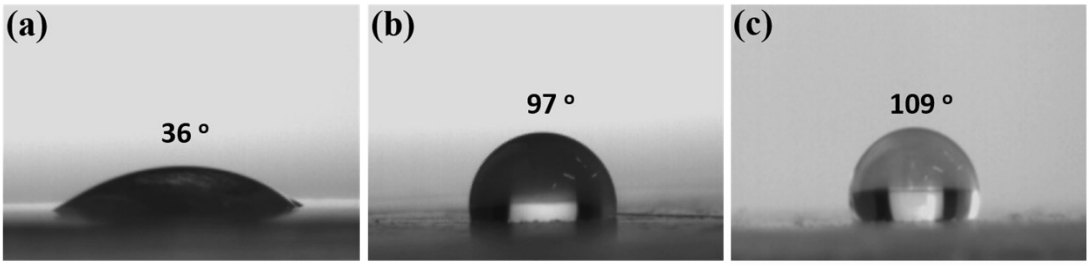


Figure S3. Water contact angle of (a) PVA (b) E-SBS (c) SBS.

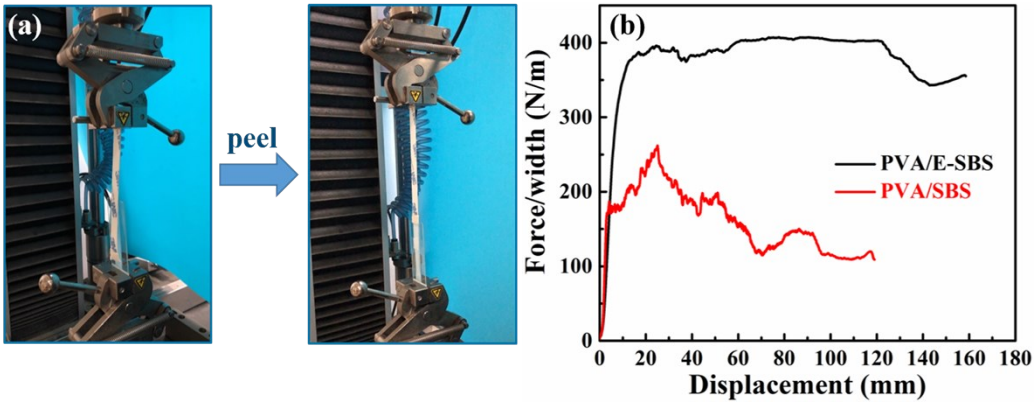


Figure S4. (a) Photos of the device for 180° peeling test. (b) The peeling curves of the 180° peeling test for the PVA/E-SBS and PVA/SBS bilayer composite films.

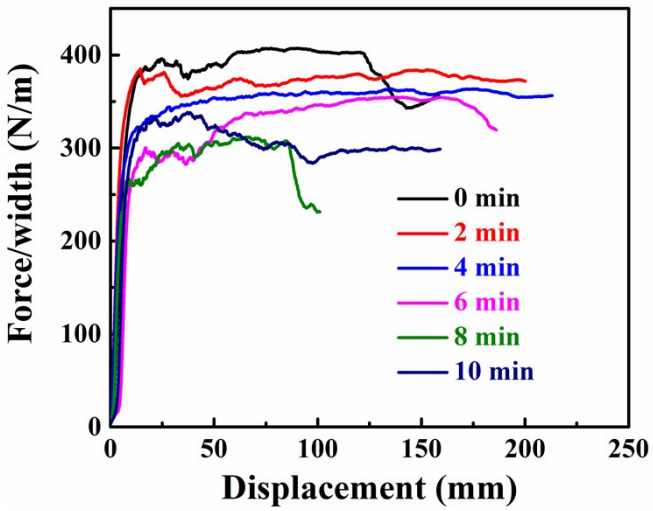


Figure S5. The peeling curves of the 180° peeling test for the PVA/E-SBS bilayer composite films immersed in water for different duration.

Table S1. The interfacial toughness values of PVA/E-SBS bilayer composite films immersed in water for different duration.

Immersion time	Interfacial toughness
0 min	379 J m^{-2}
2 min	367 J m^{-2}
4 min	348 J m^{-2}
6 min	320 J m^{-2}
8 min	279 J m^{-2}
10 min	297 J m^{-2}

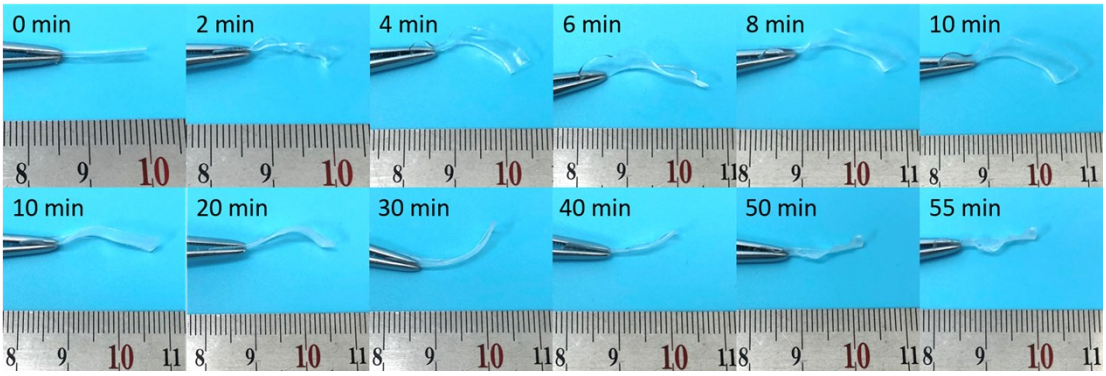


Figure S6. Photos of the wetting-drying process of the PVA film. The PVA film was immersed in water (the first line) as well as taken out of the water and placed in the air to dry (the second line) for different duration.

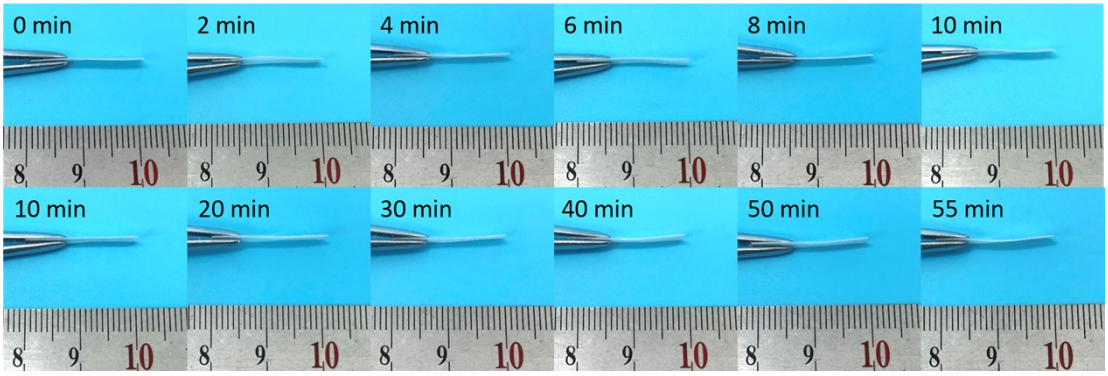


Figure S7. Photos of the wetting-drying process of the E-SBS film. The E-SBS film was immersed in water (the first line) as well as taken out of the water and placed in the air to dry (the second line) for different duration.

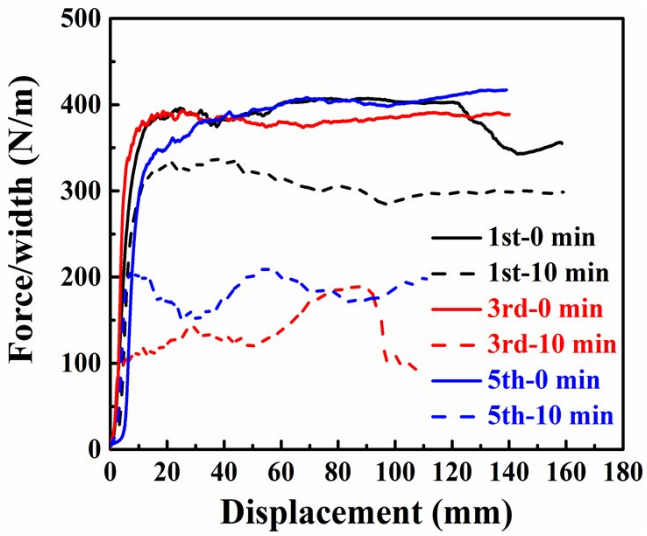
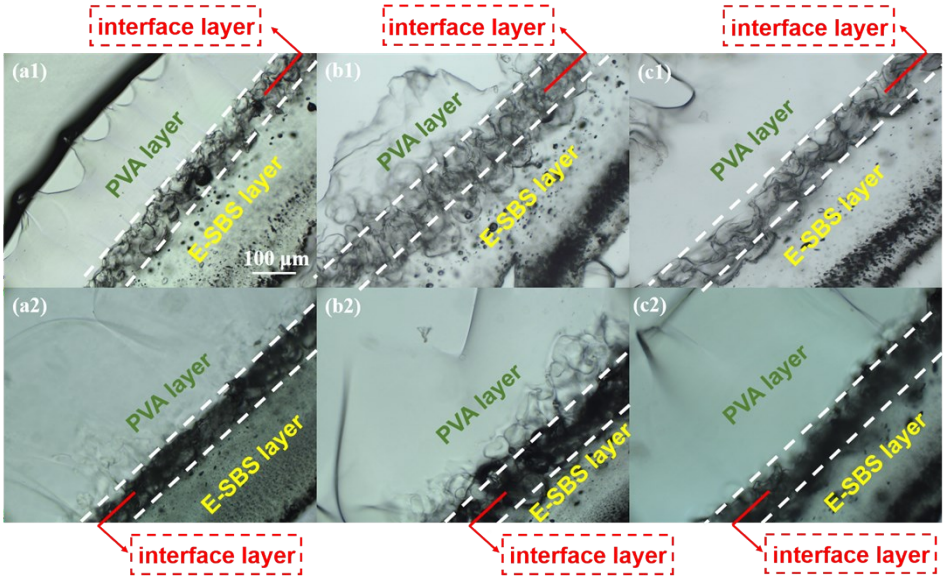


Figure S8. The peeling curves of the 180° peeling test for the PVA/E-SBS bilayer composite films before and after being immersed in water for 10 minutes in the first, third and fifth cycles of wetting-drying processes.

Table R2. The interfacial toughness values of the PVA/E-SBS bilayer composite films before and after being immersed in water for 10 minutes in the first, third and fifth cycles of wetting-drying processes.

Sample	Interfacial toughness
1st-0 min	379 J m^{-2}
1st-10 min	297 J m^{-2}
3rd-0 min	373 J m^{-2}
3rd-10 min	135 J m^{-2}
5th-0 min	372 J m^{-2}
5th-10 min	177 J m^{-2}



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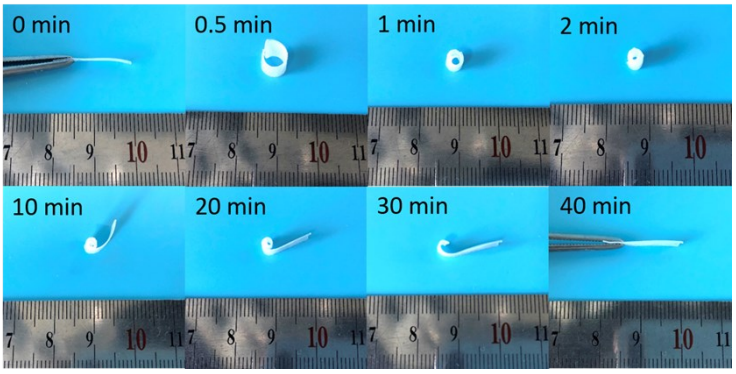

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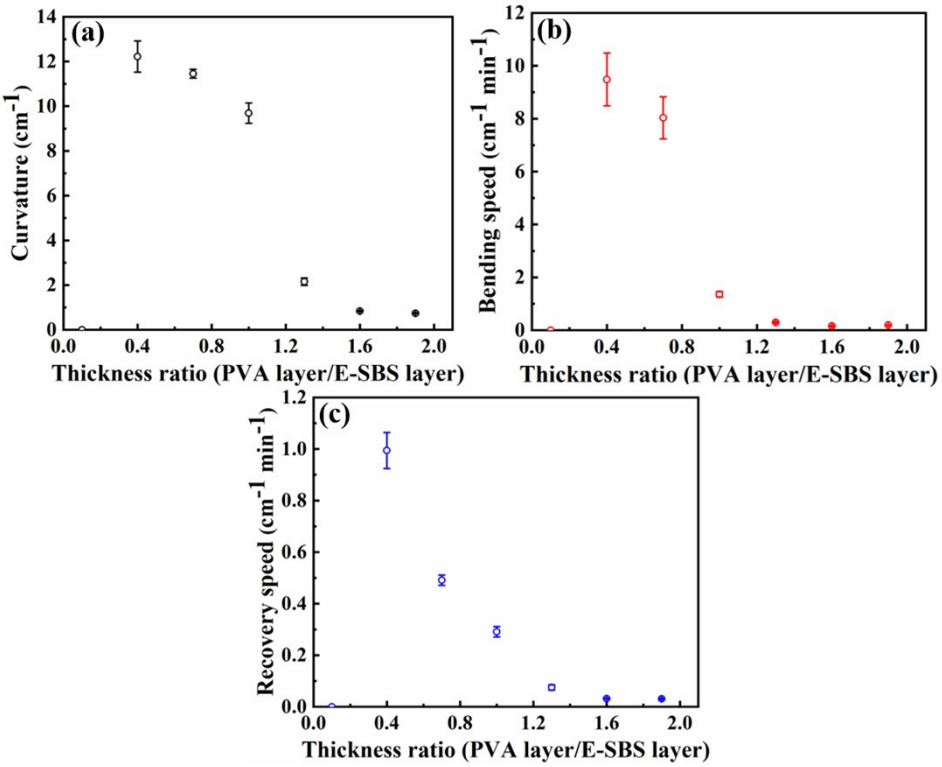

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