Electronic Supplementary Information (ESI)

Self-Adaptive Water Vapor Permeability and Its Hydrogen Bonding Switches Of Bio-inspired Polymer Thin Films

Jinlian Hu * [a], You Wu [a], Cuili Zhang [a], Ben Zhong Tang [b], Shaojun Chen [c]

a. Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Kowloon, Hong Kong 999077, China.

b. Department of Chemistry The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China

c. Department of Polymer Materials, Shenzhen University, Shenzhen, China Nanhai Ave 3688,Shenzhen,Guangdong,P.R.China,518060

*Correspondence to: tchujl@polyu.edu.hk

Experimental and modeling

Materials: 2,6-dihydroxymethyl pyridine (DHMP) were purchased from Acros, hexamethylene diisocyanate (HDI), methylene diphenyl diisocyanate (MDI), 1,4-butanediol (BDO), dimethylformamide (DMF, HPLC Grade) and poly(4-vinyl phenol) (PVP) were from Sigma Aldrich. All the chemicals were freshly used without further purification.

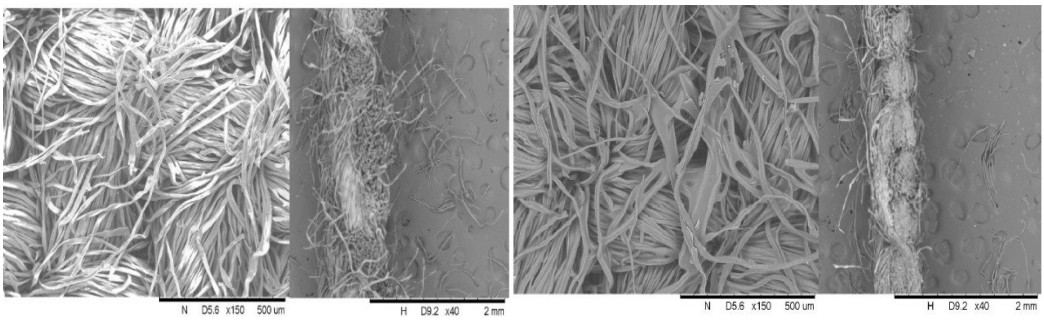
Synthesis of SMP: The SMPs were synthesized with hard segment contents of 25%. Specifically, DHMP (2.90g, 20.8mmol) were first solved in DMF (10mL) at 45^{o}C for 5 mins to get a transparent solution. Then HDI (3.34g, 19.8mmol) was added into the mixture dropwise with stirring. The solution was maintained at 45^{o}C for another 90mins. Then a solution with HDI (1.40g, 8.3mmol) and BDO (0.68g, 7.5mmol) in DMF (10mL) were poured into the reaction system and stirred at 45^{o}C for another 5 hours. The solution was casted into a pre-heated Teflon mold in a 60^{o}C oven for 24 hours, then transferred to vacuum oven at 50^{o}C for another 24 hours.(shown in Fig. 1(c))

SMP films, the polymer with specific weight (say, 0.20g) was first dissolved in DMF (10mL) and then transferred to a Teflon mold (8cm×8cm) which was preheated at 60^{o}C for 1 hour. The mold was put into oven of 60^{o}C overnight and vacuum later applied to remove residue solvent. The film was then put into open area with relative humidity around 70% for one hour. For SMP/PVP films, The synthesized SMP and different amount of PVP were solved in DMF to form a unified solution with solid content of 10%.

FTIR spectra were recorded using a Perkin-Elmer spectrum 100 FTIR spectrometer with a universal ATR sampling accessory. All samples were scanned 16 times in the range of 650–4000 cm^{-1} with the resolution of 2 cm^{-1}.

WVP was measured according to ASTM E96C, desiccant method. The polymer films were covered to a glass cup filled with preheated calcium chloride and sealed. The weight gained was recorded every fixed period at different RH after 15mins stabilization.

SEM (scanning electron microscopy) was used to examine the surface morphologies and cross section of uncoated fabric and self-adaptive shape memory polymer coated fabrics. Fig. S1(a) Shows the surface morphology of the uncoated fabric. The uncoated fabric surface contained many of protruding fibers. The surface was not flat. The cross-section view of the uncoated fabric was not compacted. Fig. S1(b) Shows the surface morphology SMPU coated sample. Coating concentration became flattener than that of uncoated fabric. The fibers were controlled by the polymer coating.



(a) **(b)**

Figure S1 Surface morphology (left) and cross section (right) of (a) uncoated (b) SMPU coated fabric.

Modeling of HBs in SMP: To understand the relationship between the strength and type of different hydrogen-bonding interactions in this kind of supra-molecular polymer, we performed quantum chemical calculations to obtain an insight into the strength of hydrogen-bonding interactions on the monomers in polymer structure with methyl as the end. The equilibrium geometries and binding energies were calculated by B3LYP method using the 6–31G* basis sets. The obtained binding energies of the complexes were corrected both for basis set superposition error (BSSE) by the Boys-Bernardi full counterpoise method [1], and for zero-point vibrational energy (ZPE) at 298.15 K. The calculated vibrational frequencies were scaled by 0.9603 for B3LYP/6–31G*. All calculations were performed with the Gaussian 03 program[2].

References

1. S. F. Boys and F. Bernardi, *Molecular Physics*, 1970, **19**, 553-&.
2. M. J. Frisch, G. W. Trucks, H. B. Schlegel, et,al. , *Gaussian 2003W*, Gaussian Inc, Pittsburgh PA, 2003.