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Supporting Information

Povidone-iodine Enhanced Underwater Tape

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Content

1.Experimental Section

1.1 Raw Materials

4-Hydroxybutyl acrylate(4-HBA,97%), N-Isopropylacrylamide (98%), Isobornyl Acrylate (90%), Dioxane (99%) and Ethanol (99.5%) were all purchased from Aladdin (Shanghai, China) and used without any repurification. N-butyl acrylate (nBA, TCI, 99.0%) was filtered through a plug of basic alumina oxide before use.

1.2 Preparation of tapes

The process of the synthesis of underwater anti-bacterial pressure-sensitive tapes are divided into two steps. Firstly, polymer matrix was synthesized by one-pot free-radical copolymerization at 70℃ for 8 h between 4-Hydroxybutyl acrylate (4-HBA), Isobornyl Acrylate (IBOA) and N-Isopropylacrylamide (NIPAM). 2,2'-Azobis (isobutyronitrile) was used as initiator. The ratio of comonomer was shown in Table S1. Secondly, the polymer matrix and PVP-I_2 dissolved in Ethanol and mix them evenly. The mixture was maintained at 40 °C in vacuum oven for 24 h to remove the solvent. The dried mixture was then cut into pieces and made into tape by hot-pressing (Figure S1).

Table S1. Monomer feed ratio and nomenclature method

	Feed Ratio $n_{HBA}:n_{IBOA\ (BA)}:n_{NIPAM}$		**Feed Ratio** $n_{HBA}:n_{IBOA\ (BA)}:n_{NIPAM}$
HIN_{613}	0.06:0.01:0.03	HN_{73}	0.07:0.03
HIN_{715}	0.07:0.005:0.0025	HN_{82}	0.08:0.02
HBN_{715}	0.07:0.005:0.0025	HN_{91}	0.09:0.01

2.Methods and characterization

2.1 Nuclear Magnetic Resonance (NMR)

The ^1H NMR spectra were measured on a Bruker AV III HD spectrometer operating at 400 MHz in CD_3OD (δ (^1H) = 3.31 ppm) with TMS as reference.

2.2 Gel Permeation Chromatography (GPC)

The molecular weight and polydispersity index (PDI) were measured on the Tosoh HIC-8320GPC at room temperature. N, N-Dimethylformamide (DMF) as the eluent with the flow rate of 0.5 ml/min, where monodispersed polystyrene (PS) standard served to generate the calibration curves.

2.3 Rheology

Oscillatory frequency sweep tests were performed in the range of 0.01-100 rad/s with 0.1% strain. The sample was a disk with diameter 8 mm and thickness 0.3 - 0.5 mm, and the tests were performed in the torsion mode. The test method of wetting rheology is soaking the tape in water for 30s, and then recording the change of elastic and loss modulus according to the previous procedure.

2.4 Atomic Force Microscope (AFM)

AFM height diagrams were gotten by AIST-NT SPM smartSPMTM-1000 in the tapping (AC) mode with the spring constant of 70 N/m and the resonance frequency of 289 kHz. Sample preparation: HIN_{715} was dissolved in THF with the concentration of 0.1 mg/ml. Spin coated the solution on the silicon slice using the spin coater (KW-4A). Afterwards the silicon slice was placed in the vacuum oven at 60 ℃ for 30 mins.

2.5 Tensile Test

Tensile experiments of HIN_{715} tapes were performed on an Instron 5967 tensile tester with 100 mm/min tensile rate at room temperature by the standard tension test (ASTM D412). The samples for tensile tests were cut into the dumbbell shape by a normalized cutter with the gauge length of 15 mm, the width of 2 mm and the thickness of 0.3 - 0.6 mm. The fracture strength and breaking elongation can be calculated from the stress-strain curves. For each type of material, five samples were measured and averaged.

2.6 Differential Scanning Calorimeter (DSC)

The phase transition of tapes was investigated by differential scanning calorimetry using a DSC Q200 from TA instrument. Simple at preparation state, equilibrated with a reference filled with the same quantity of pure water, were submitted to temperature cycles between 0 and 110°C under nitrogen atmosphere. The heating and cooling rates were fixed at 2°C min^{-1}.

2.7 Lap-Shear Test

To measure adhesion strength and debonding energy, an Instron machine (model 5967 with load cell of maximum 450N) was used to apply unidirectional tension, according to the standard lap-shear test (ASTM F2255), and meanwhile the force and the extension were recorded. The free ends of the substrates were attached to flexible copper wire, to which the machine grips were attached.

The bonding objects used in this work were designed as plates, the size is 100 mm × 25 mm × 2 mm, and the area of the lap part is 25 mm × 12.5 mm. Shear strength was acquired on an Instron 5967 tensile tester at room temperature and the tensile rate is 30 mm/min.

2.8 Antibacterial effort of the tape

E. coli (Gram-negative bacteria) and S. aureus (Gram-positive bacteria) were used to investigate the antibacterial activities of the tapes.1ml bacterial suspension was inoculated on an ager plate, and use glass bar to make sure the bacterial suspension was spread evenly.

Then, our tapes were attached to the ager plate. After the bacterial was incubated at 37℃ for 24h,we photographed the ring formed around the tape directly which shows the antibacterial activity.

2.9 Cytotoxicity experiments

CCK-8(Cell Counting Kit 8, KeyGEN BioTECH, Nanjing, China) assay was utilized to measure the cytotoxicity of the tapes. We made L929 cells (mouse fibroblast cells) directly contacting a leaching solution of the tapes. The leaching solution of tapes was acquired by soaking the sterilized tape in DMEM at a concentration of 200mg mL-1 for 24h at 37℃. And then the supernatant was collected by centrifugation, followed by dilution to 5 mg mL^{-1} and supplementing with 10% (v/v) fetal bovine serum (FBS, Sijiqing, Hangzhou, China). 100 μL L929 cell suspension (1×104 cells mL-1) was inoculated in a 96-well plate. After incubation in 5% CO2, a t 37℃ for 24 h, the original cell culture medium was refreshed with the leaching solution. At the present time of 1 day, CCK-8 was added to each well, and subsequently cultured in the dark at 37℃ for 2 h. Then, the absorbance of the medium was measured with a microplate reader at 450 nm. The relative cell viability was calculated as Absexperiment/Abscontrol×100%, where Absexperiment and Abscontrol represent the absorbance of the tapes and blank control groups, respectively. The cell cultured with original medium served as the blank control.

2.10 Hemocompatibility test in vitro

We also acquired the leaching solution of the tapes by the method we mentioned in the past part of experiment, with the slightly modification. We soaking the tapes in the normal saline for 24h at 37℃ at a concentration of 10mg mL-1. The whole blood from rabbit was citrated and centrifuged at the speed of 1200rpm for 10 min. After finishing the centrifuged, the erythrocytes were washed 3 times and diluted to a concentration of 5%(v/v).On the one hand, 500μL erythrocytes and 500μL leaching solution were blending evenly and incubated at 37℃ for an hour. On the other hand,500μL erythrocytes were blended with 500μL 0.1% Trion x-100 and 500μL normal saline for positive and

negative control groups. Finally,100μL supernatant was added into a 96-well plate, then measured the absorbance of all wells with a microplate reader at 540nm. The hemolysis ratio was calculated as (Absexperiment - Abscontrol)/(AbsTriton – Abscontrol)×100%, Absexperiment, Abscontrol and AbsTriton represent the absorbance of the tapes(experiment groups), normal saline(negative groups) and Triton x-100(positive groups), respectively.

2.11 in vivo antibacterial ability

PVP-I_2 had showed its strong capacity of antibacterial in vitro. In order to discuss the in vivo performance, a mouse models were employed to define the tapes' ability to accelerate the wound healing. Incisions were made in the backs of mouse which diameter were about 10mm. To simulate an infected wound, all of the incisions were injected 1ml S. aureus suspension (10^9 CFU mL^{-1}), Sterile dressing (Tegaderm film,3M) was used to cover the wounds in blank group. In the experimental group, HIN_{715} sample was used to cover the wounds. Wounds were assessed daily for healing and signs of infection by visual inspection. The end point of the experiment was chosen to be day 10 after wound formation. Biopsies of the wounds were also taken on day 1,3, and 10.

2.12 Measurement of PVP-I_2 release from HIN_{715}

HIN_{715} samples were placed at the bottom of UV cuvettes. Then we position the UV cuvettes in a CARY 300 Scan UV–visible spectrophotometer from Varian. The cuvettes were filled with 2.5 ml distilled water and the release of PVPI was monitored in time by following the increase of the PVP-I2 characteristic UV–vis absorption peaks.

2.13 Statistical analysis

Statistical analysis was performed using the student's t-test to determine the statistical differences between the two groups. The results were expressed as the mean ± standard deviation (SD), where $p<0.05$ demonstrated a statistically significant difference.

3.Theory and Calculation

3.1 Definition of Adhesive Parameters

3.1.1 Bonding Strength (Shear Strength)

Adhesive strength is defined as the ratio of the maximum force of the adhesive joint in lap shear test and the overlap area, and calculated by Formula (1).

$$Bonding\ strength = {}^{Fmax}/_{S} \quad \text{..... (1)}$$

where Fmax is the maximum force in the lap shear process till failure, N; WL is the area of the

initial overlap of two objects, mm^2 .

3.1.2 Debonding Energy

Debonding energy is defined by Formula (2):

$$Debonding\ energy = \int F\,dx \Big/ A \quad \text{..... (2)}$$

where ∫ F dx is defined as the integral of the force vs. displacement graph, or energy of adhesion (J). WL is the measured overlap area of the adhesive joint (mm^2). All integration is performed using the integrate feature Origin (Pro), Version 2019b, OriginLap Corparation, Northampton, MA, USA

3.1.3 Swelling Rate

Swelling rate is defined by Formula (3)

$$Swelling\ rate = \frac{(W_2 - W_1)}{W_1} \times 100\% \quad \text{..... (3)}$$

where W_1 is the initial weight of the simple before swelling and the W_2 is the weight after being swelled.

Graphic

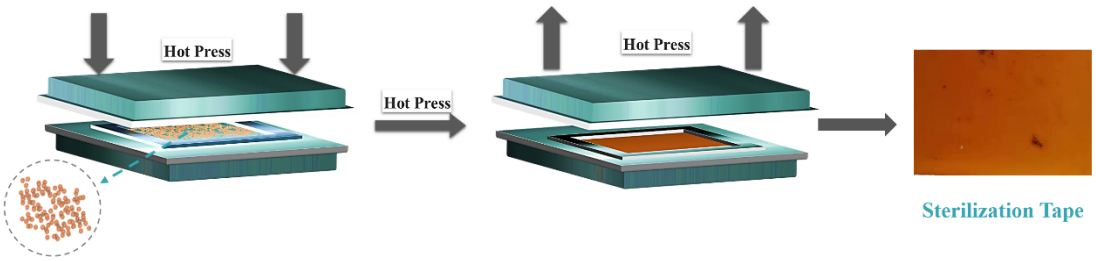

Figure S1. Schematic diagram of hot-pressing molding

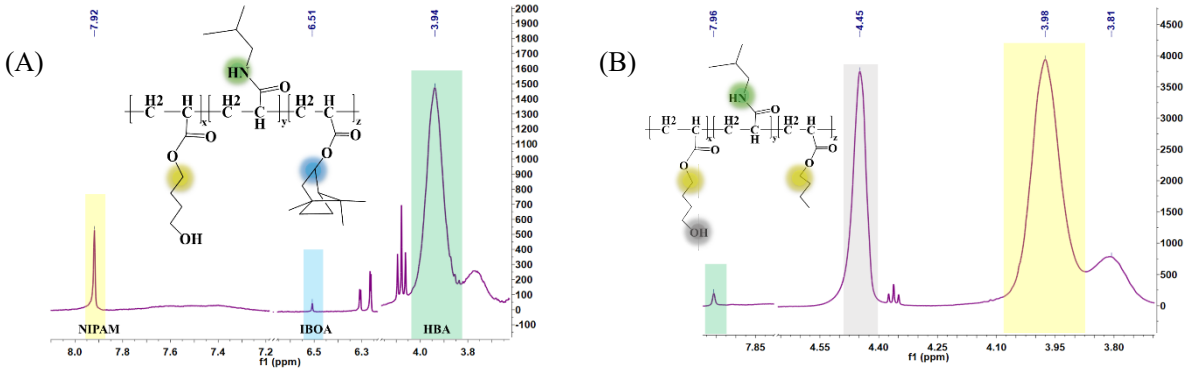

Figure S2. ^{1}H NMR spectra. ^{1}H NMR of HIN (A) and HBN (B), solvent is CD_3OD.

Comments: As shown in Figure S2A the signal presented at 7.92 ppm is attributed to the protons in the secondary amines group on NIPAM. The signal presented at 6.51 ppm is attributed to the protons on the carbon which bonded to an ether bond on isoborneol ring, and the signal at 3.94 ppm is attributed to the proton on the carbon bonded by HBA and ether. These signals prove that HIN is successfully synthesized. As shown in Figure S2B the signal presented at 7.96 ppm is attributed to the protons in the secondary amines group. The signal presented at 4.45 ppm is attributed to the proton on HBA hydroxyl groups, and the signal at 3.98 ppm is attributed to the proton on the carbon bonded by HBA and ether bond. These signals prove that HBN is successfully synthesized.

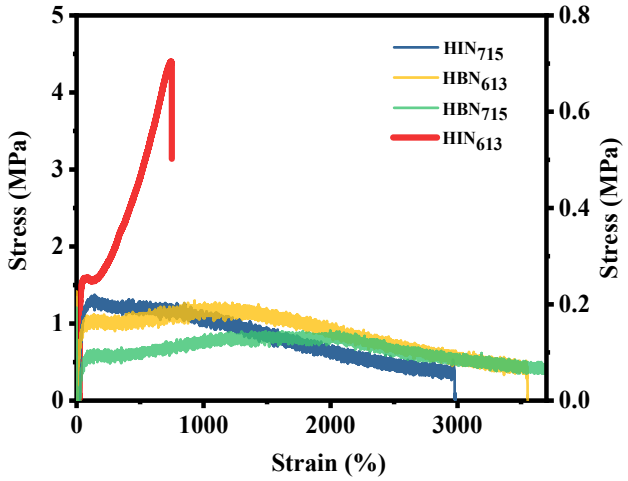

Figure S3. Stress-strain curves of polymer matrix by replacing IBOA with BA

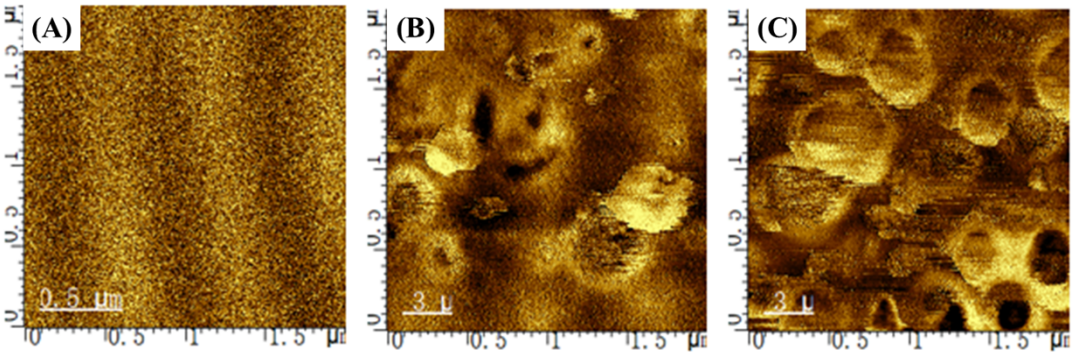

Figure S4. Atomic force microscopy image of HIN (A), HIN with 0.1g PVP-I_2 (B), HIN with 0.2g PVP-I_2 (C).

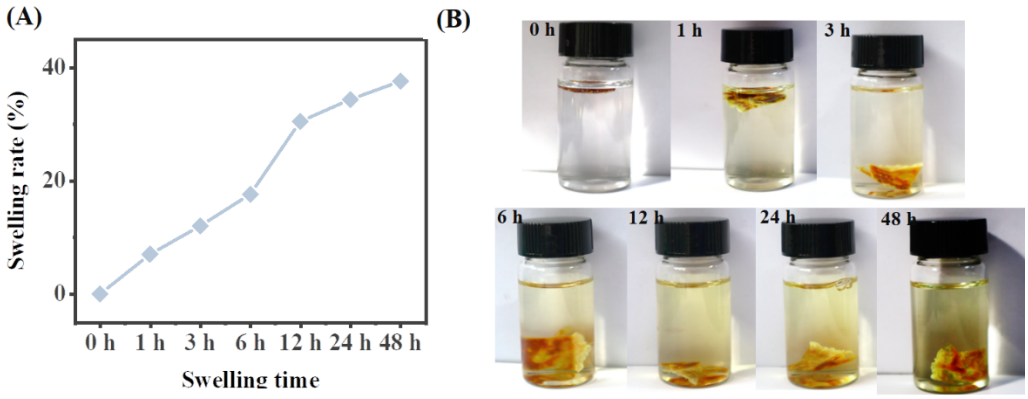

Figure S5 Swelling rate and photos of HIN_{715} with different underwater time at room-temperature

Comments: By detecting the weight of tape under water after different times, the swelling property of the tape have been evaluated and calculated on the basis of Formula (3). Due to the test temperature is room temperature, the lower temperature at present slows down the swelling rate. The results show that the swelling rate of the tape increases with underwater treatment time and presents the trend of "fast followed by slow". Undoubtedly, long-time swelling is the reason for the deterioration of adhesive strength of the tape. Besides, it is shown obvious color change, which is due to the release of anti-bacteria factor povidone iodine.

$$Swelling\ rate = \frac{(W_2 - W_1)}{W_1} \times 100\% \quad \text{.....(3)}$$

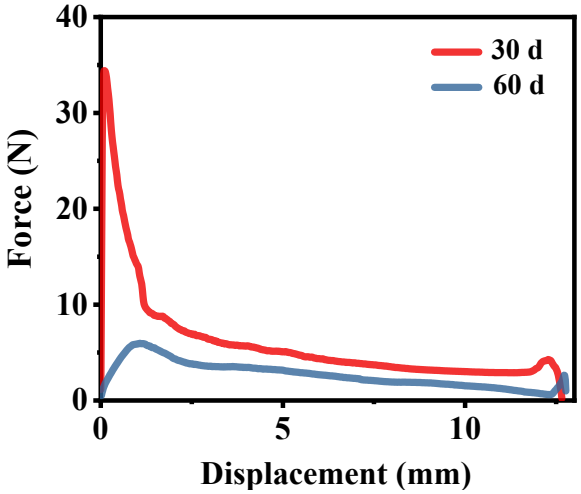

Figure S6. Long-term bonding performance, 30 days and 60 days

Comments：Figure S6 shows the long-term bonding performance of the tapes. After exposure to water for a long time, the adhesive strength of the tape has a significant decrease. After 60 days, even less than 10 N of force is needed to de-stick it, showing the characteristics of easy stripping and recycling of the tapes.

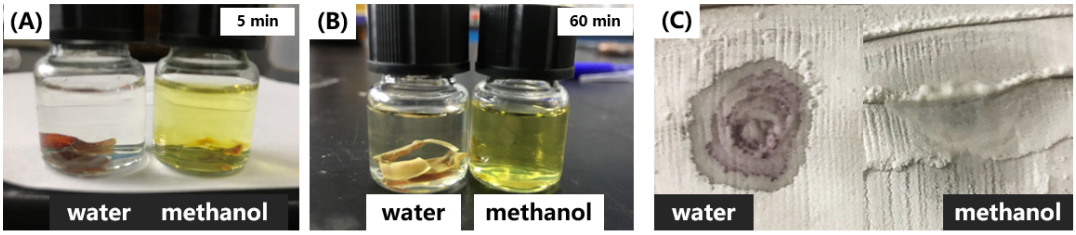

Figure S7. After exposure to methanol for 5min, most of the tape was dissolved (A). After 60min, the tape was in water and methanol (B). The aqueous solution touching the tape turned the starch blue (C)

Comments: Figure S7A S6B shows that the tapes can be quickly dissolved in solvents such as ethanol and methanol, so the tapes have the properties of easy removal and recycling. Figure S7C shows the properties of the tapes that can effectively release iodine when it meets water.

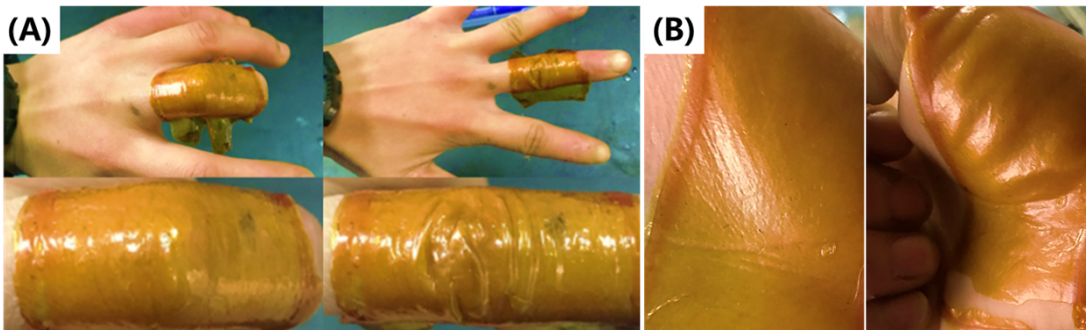

Figure S8. The fitting performance of the tape to human skin. (A) Adhesion on the knuckles, bent (left), straight (right); (B) Adhesion on the palm, open the hand (left), and clench the fist (right)

Comments: Tapes can fit well with human skin, even if at the joint. At the same time, with the movement of the limb, the tape also has good extensibility to adhere to the skin. In addition to being a bactericidal adhesive tape, it has the potential to be used as a sensor carrier to monitor human activities