

# Temperature-sensitive Composite Membranes with “Double Switch” on Water Vapor Permeability

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**Abstract:** Temperature-sensitive polymer membranes were prepared by combination of shape memory hydrophilic polyurethane (SMPU) and thermo-sensitive poly(N-isopropylacrylamide-co-sodium acrylate) [poly(NiPAAm-co-SA)] hydrogel micro-particles through composite coating method. These two intelligent polymer components endowed the composite membranes with “double switch” on the water vapor permeability. Poly(NiPAAm-co-SA) hydrogel micro-particles exhibited a reversible volume transition at lower critical solution temperature (LCST) around 34-36°C in the experiment. The size of gel particles varied more than 10-fold between temperature above and below LCST. It is likely acted as a sensor of temperature and as a switch to regulate the water vapor permeability of composite membranes. Moreover, there was also a dramatic increase in water vapor permeability (WVP) with an increase in temperature from 35 to 40°C for the shape memory hydrophilic polyurethane basement membranes. Two different procedures for WVP test were employed to simulate different application situations of the composite membranes. The temperature-sensitive water vapor permeability of composite polymer membranes was investigated by varying the content of hydrogel micro-particles. All of the temperature-sensitive membranes could have water vapor permeability controlled in response to temperature changes.

**Keywords:** temperature-sensitive; composite membranes; double switch, water vapor permeability

## 1. Introduction

Nowadays, textile industry shows a huge interest in environmentally responsive or stimuli-responsive materials which could be incorporated into technical textiles [1, 2]. Poly(N-isopropylacrylamide) hydrogel (PNiPAAm) attracts lots of researchers as a best known thermosensitive polymeric network, which exhibits a reversible volume transition at a transition temperature or lower critical solution temperature (LCST) of approximately 33°C [3, 4]. UV grafting of NiPAAm on polymer substrates and plasma polymerization of NiPAAm on polyethylene and polypropylene membranes have been reported in the literature [5-11]. The grafted gels acted as a sensor of temperature and as a valve to regulate the water vapor permeability of the membranes. All the membranes mentioned above benefit from additional functionality related to the change of the hydrogels properties across the lower critical solution temperature (LCST).

In this paper, we prepared temperature-sensitive composite membranes by combination temperature-responsive poly(NiPAAm-co-SA) hydrogel micro-particles with thermo-sensitive polyurethane substrates using composite coating method. The water vapor permeability of obtained composite membranes can be controlled by the two temperature-sensitive components with the temperature variation. This investigation is aim to provide a smart thermo-sensitive membranes with “double switch” on the water vapor permeability for textile producers. There is no doubt that temperature-sensitive textiles produced by polymer will play a significant role in the realization of the smart textile of tomorrow.

## 2. Experimental

### 2.1 Materials

N-isopropylacrylamide (NiPAAm) monomer (WUJING Chemical Co., China) was used as

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supplied. Sodium acrylate (SA) was synthesized from acrylic acid and sodium hydroxide. N, N’-Methylenebisacrylamide(BIS), Tetramethylethylene diamine (TEMED), and ammonium persulfate (APS) were purchased from Sinopharm Chemical Reagent Co.(China) and used as received.

Toluene-2, 4-dissocyanate (TDI;extra pure), 1, 4-butanediol (BDO, chemical pure), N, N-dimethylformamide (DMF, analytical pure), dimethylolpropionic acid (DMPA, chemical pure) and triethylamine (TEA, chemical pure) were purchased from Sinopharm Chemical Reagent Co. China and used as supplied. Poly(butylenes adipate) glycol (PBAG, industrial grade, =2000) was supplied by Lianying Polymer Co. Shanghai, China and used as received. Water for experiment was deionized water.

## 2.2 Preparation of Thermo-sensitive Composite Membranes

Segmented shape memory polyurethanes were synthesized in two steps. Soft segment PBAG with molecular weight ( $\bar{M}_n$ ) 2000 (g/mole) were dried at 120°C under vacuum for 2h before use. Hard segments TDI and BDO were used with PBAG to prepare segmented polyurethanes. A 500ml round bottom, three-necked flask equipped with a mechanical stirrer, nitrogen inlet and condenser was used as a reactor to prepare the polyurethanes. One mole of dehydrated PBAG with four mole TDI was reacted at 70°C for 1.5h. Then, the NCO-terminated pre-polymer was mixed with chain extension BDO at 70°C for another 2h. Ionomers were obtained by neutralizing the COOH groups of DMPA with TEA.

Table 1 showed the basic formulation of the present experiment of shape memory polyurethane.

Poly(NiPAAm-co-SA) hydrogels with mole ratio 98:2 were synthesized using BIS as crosslinking agent. APS and TEMED were used as initiator and accelerator by free radical polymerization. The hydrogels were prepared as follows. NiPAAm and BIS [5% (mol/mol) to NiPAAm] were dissolved in deionized water with the solution concentration 5% by weight. The solution was nitrogen bubbled for 10 min, and then SA solution was added and bubbled with nitrogen for another 5 min. APS [2% (mol/mol) to NiPAAm] and TEMED [5% (mol/mol) to NiPAAm] were subsequently mixed into the aqueous solutions and bubbled with nitrogen for 5 min. The whole reaction was conducted in water bath at required temperature of 35°C for 1h with nitrogen protection, and then stayed at room temperature (18°C) for 1 day. The resulting hydrogels were separated from the vessel and purified by immersing in deionized water for one week to remove unreacted chemicals and fully swell. The water was replaced 3~4 times every day. A total of 100 g equilibrated swelling hydrogels with 20ml deionized water were made into micro-particles by SDF400 Intelligent Dispersion Ball Mill (Weite, China). The obtained micro-particles were screened in order to get the micro-particles with uniform size. From the phenomena of the hydrogels dramatically deswelling and color changing from transparent to opaque around the LCST, the LCST of poly(NiPAAm-co-SA) hydrogels in the experiment were defined at the range of 34-36°C

Table 1 The basic formulation and DSC results of shape memory polyurethane

Sample number	$\bar{M}_n$ of PBAG	PBAG (mol)	Chain Extender (mol)	TDI (mol)	Hard contents (%)	( $T_{s,m}$ ) <sub>start</sub> (°C)	( $T_{s,m}$ ) <sub>peak</sub> (°C)	( $T_{s,m}$ ) <sub>end</sub> (°C)	$\Delta H_m$ (Jg <sup>-1</sup> )
PU204	2000	1	2.24	4.05	31.2	31.3	39.4	46.1	53.76

The composite membranes were prepared as follow. Firstly, a layer of hydrogel particles was coated on the horizontal glass plate evenly. Secondly, a layer of shape memory polyurethane was coated on the hydrogel layer carefully in order to form

continuous surface of the substrate membrane. Thirdly, another layer of hydrogel particles was coated on the top of shape memory polyurethane coating. Keep the composite coating at room temperature for 10 min. The membranes were