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### **A capillary water retention effect to improve medium-temperature fuel cell performance**

Lee, So Young; Shin, Dong Won; Wang, Chenyi; Lee, Kang Hyuck; Guiver, Michael D.; Lee, Young Moo

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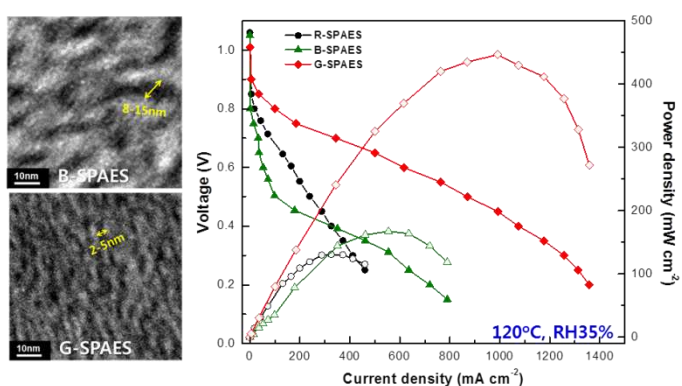


## Graphical abstract

A capillary water retention effect to improve medium-temperature fuel cell performance

So Young Lee, Dong Won Shin, Chen Yi Wang, Kang Hyuk Lee, Michael D. Guiver, Young Moo Lee

Small hydrophilic domain sizes (< 5 nm) improve fuel cell performance due to capillary water retention effect at 120 °C, 35%RH



## Highlights

A capillary water retention effect to improve medium-temperature fuel cell performance

So Young Lee, Dong Won Shin, Chen Yi Wang, Kang Hyuk Lee, Michael D. Guiver, Young Moo Lee

- ♦ Morphology in sulfonated polymer membrane influences fuel cell performance at  $>80\text{ }^{\circ}\text{C}$ .
- ♦ Phase separated morphology and hydrophilic domain size of three types of sulfonated poly(arylene ether sulfone)s (SPAES) improve the medium temperature fuel cell performance.
- ♦ Graft SPAES (G-SPAES) with small hydrophilic domain sizes ( $< 5\text{ nm}$ ) shows excellent fuel cell performance due to capillary water retention effect at  $120\text{ }^{\circ}\text{C}$ , 35%RH.

# A capillary water retention effect to improve medium-temperature fuel cell performance

So Young Lee <sup>1</sup>, Dong Won Shin, <sup>1</sup>Chen Yi Wang, <sup>2</sup> Kang Hyuk Lee, <sup>2</sup> Michael D. Guiver, <sup>2,3</sup>  
Young Moo Lee <sup>1,2,\*</sup>

<sup>1</sup> Department of Chemical Engineering, Hanyang University, Seoul, Republic of Korea, 133-791.

<sup>2</sup> WCU Department of Energy Engineering, Hanyang University, Seoul, Republic of Korea, 133-791.

<sup>3</sup> National Research Council Canada, Ottawa, Ontario, K1A 0R6, Canada.

## Abstract

We demonstrate for the first time that small and narrow hydrophilic conducting domain morphology in sulfonated hydrocarbon membranes leads to much better fuel cell performance at medium temperature and low humidity conditions than those with larger hydrophilic domains. A comparison of three types of sulfonated poly(arylene ether sulfone)s (SPAES) with random, block, and graft architecture indicates that small hydrophilic domain sizes (< 5 nm) appear to be important in supporting water retention under low relative humidity (RH) conditions intended for medium temperature (> 100°C) fuel cell applications. The graft copolymer outperformed both a random copolymer and multiblock copolymer at 120 °C and 35% RH fuel cell operating conditions due to capillary condensation of water within the 3-5 nm hydrophilic domains.

**Keywords:** fuel cell; polymer electrolyte membrane; medium-temperature; sulfonated pol(arylene ether sulfone); morphology;

## **1. Introduction**

Proton exchange membrane fuel cells (PEMFCs) are being studied as clean energy conversion devices due to their high efficiency and environmental friendliness.[1] In particular, medium-temperature proton exchange membrane fuel cells (MT-PEMFCs), operated above 100 °C, have some benefits. [1-3] Carbon monoxide (CO) impurities in the hydrogen feed gas affect the fuel cell performance by adsorbing to the platinum surface and poisoning the platinum electro-catalyst. The adsorption of CO is lessened at elevated temperature leading to higher resistance of the catalyst to fuel impurities; thus operation at high temperature would simplify the fuel cell system by reducing the level of hydrogen purification necessary. In recent years, MT-PEMFCs have been recognized as a promising solution to meet the technical challenges for transportation applications. In 2009, the US Department of Energy (DOE) set the target for PEM performance for operation for 500 h at 120 °C without external humidification.[4] However, there are challenging technical obstacles to overcome, such as low proton conductivity and cell performance drop due to the evaporation of water molecules.

It is well-known that phase-separated morphology affects PEMFC performance under partially hydrated conditions or at elevated temperature [5, 6]. Among PEMs with various types of architecture, block copolymers and aligned polymers have well-defined hydrophilic ionic channels, which increase the connectivity between the hydrophilic domains and improve proton

conductivity and fuel cell performance under low relative humidity conditions. Also, well-defined morphology enhances the self-diffusion coefficient of water, resulting in the better retention of free water within the membrane.

In the present work, three representative sulfonated poly(arylene ether sulfone)s (SPAES) having different architecture and microstructures were used to investigate the influence of polymer morphology on electrochemical properties, leading to insight into the effective molecular design of sulfonated aromatic PEMs for MT-PEMFC. To this end, water transport, proton conductivity, and electrochemical polarization behavior of random, multiblock, and graft SPAES membranes were investigated under controlled temperature and RH.

## **2. Experimental Section**

### **2.1 Preparation of Random and Multiblock and Grafting SPAES Membranes**

Sulfonated PEMs with three types of polymer architecture, random and multiblock copolymer (R-SPAES and B-SPAES) [7-9] and grafted side chain polymer (G-SPAES) [10] were prepared by nucleophilic aromatic substitution reaction. B-SPAES was synthesized in a similar manner with phenoxide terminated hydrophilic oligomer and halide terminated hydrophobic oligomer.

Three types of SPAESs were dissolved as 10-15 wt% solutions in DMSO or DMAc. The polymer solutions were filtered and cast onto glass plates. The cast solutions were dried in an oven at 60 °C in an inert environment for at least 12 h and then residual solvent was removed under vacuum at 120 °C. The salt form ( $K^+$  form) membranes were acidified by boiling in a 0.5

1 M sulfuric acid solution for 2 h, followed by washing with boiling deionized water for 2 h to  
2 convert membranes into the acid form ( $H^+$  form).

## 3 **2.2 Characterization and Measurements.**

4 For transmission electron microscopy (TEM) observation, the membranes were stained  
5 with lead ion ( $Pb^{2+}$ ) by immersing 0.5 M lead acetate aqueous solution. The stained membranes  
6 were embedded in epoxy resin, microtomed to 70 nm thickness with a RMCMTX Ultra  
7 microtome, and placed on copper grids. TEM images were taken with a Carl Zeiss LIBRA 120  
8 energy filtering transmission electron microscope using an accelerating voltage of 120 kV.

9 Proton conductivity of each membrane sample at various temperature and relative humidity  
10 conditions was estimated using a 4-probe conductivity cell connected with an electrochemical  
11 interface (Solartron 1287) in combination with an impedance/gain-phase analyzer (Solartron  
12 1260) in the frequency range from 10 Hz to 100 kHz.

13 The membrane electrode assembly (MEA) with an active area of  $5\text{ cm}^2$  and Pt loading of  
14  $0.5\text{ mg cm}^{-2}$  was fabricated *via* the screen printing method [11]. The single cell was mounted in a  
15 commercial fuel cell testing station (SMART PEMFC test system, WonATech, Seoul, Korea)  
16 which was supplied with temperature and humidity controlled gases.  $H_2$  and  $O_2$  were supplied at  
17 a flow rate of  $100\text{ cm}^3\text{ min}^{-1}$  at various cell temperatures ( $80^\circ\text{C}$ ,  $100^\circ\text{C}$ , and  $120^\circ\text{C}$ ) and relative  
18 humidity conditions (100%, 85%, and 35%) at a 1.5 atm back-pressure state.

## 20 **3. Results & Discussion**

21 The synthesis of three representative SPAESs membranes was confirmed in previous  
22 studies [7-10]. The three SPAES were synthesized to have similar  $IEC_w$  values (1.70~1.75 meq

1  $\text{g}^{-1}$ ) by carefully controlling the feed ratio of sulfonated to nonsulfonated monomers, and the  
2 length of the block segments.

3 The cross-sectional nanophase-morphologies of three SPAESs were investigated using  
4 transmission electron microscopy (TEM) for lead-stained samples, as shown in Figure 1. In these  
5 images, the dark phase represents hydrophilic domains containing sulfonic acid groups, which  
6 were exchanged with lead cations. Nafion<sup>®</sup> 212 membrane has distinct and well-connected  
7 hydrophilic clusters of ca. 5~10 nm size, as reported earlier [12]. Three SPAESs exhibited  
8 different hydrophilic domain sizes and connectivity despite their similar IEC values. R-SPAES  
9 shows relatively featureless morphology indicating the absence of well-defined ionic cluster,  
10 with the hydrophilic domains distributed randomly within the hydrophobic matrix, shown as the  
11 bright phase (Figure 1a,b). In contrast, B-SPAES (Figure 1c,d) and G-SPAES (Figure 1e,f)  
12 exhibit well-defined, nanophase-separated morphologies, which are responsible for high proton  
13 conductivity at low humidity. Especially at higher magnification (Figure 1d, f), the G-SPAES  
14 membrane exhibits narrower and smaller interconnected hydrophilic channel sizes of ca. 2-5 nm,  
15 while B-SPAES exhibits the largest interconnected hydrophilic channel sizes in the range of ca.  
16 8-15 nm.

17 The hydrophilic domain size significantly affects water retention and release in PEMs,  
18 particularly at low RH and elevated temperature ( $>100\text{ }^{\circ}\text{C}$ ) conditions. Park et al. reported that  
19 aliphatic PEMs with hydrophilic domain widths of less than 5 nm showed an increase in proton  
20 conductivity with increasing temperature under low RH conditions, due mainly to the effect of  
21 capillary condensation and confinement of water within the narrow hydrophilic domains [13, 14].  
22 In this regard, G-SPAES with narrower hydrophilic channel size ca. 2-5 nm is expected to



maintain high proton conductivity by high water retention than B-SPAES particularly under high temperature ( $>100\text{ }^{\circ}\text{C}$ ) and low humidity conditions.

The humidity dependence of proton conductivity for the sulfonated aromatic PEMs and Nafion<sup>®</sup> 212 membrane is compared at  $80\text{ }^{\circ}\text{C}$ , as shown in Figure 2a. Proton conductivities of the membranes decreased, as applied humidity was reduced from 100 % RH to 30 % RH, indicating that the presence of water in the membrane enhances ionic conduction by both Grotthuss and vehicular mechanism. The conductivity of Nafion<sup>®</sup> 212 and R-SPAES showed significant declines compared with that of B-SPAES and G-SPAES at above 50% RH, implying that their proton conductivity was more dependent on humidity than that of B-SPAES and G-SPAES. Interestingly, below 50% RH, G-SPAES showed a more stable ionic conductivity than that of B-SPAES and its proton conductivity is comparable to that of Nafion<sup>®</sup> 212.

This similar proton conduction behavior was also exhibited in Figure 2b and plotted as function of temperature at ambient RH, which decreased from 100 % RH to 35% RH as temperature increased from  $80\text{ }^{\circ}\text{C}$  to  $120\text{ }^{\circ}\text{C}$ . The proton conductivities of the three SPAESs and Nafion<sup>®</sup> 212 were comparable to one another at  $80\text{ }^{\circ}\text{C}$  and 100% RH. As the temperature was increased, both B-SPAES and G-SPAES were able to better retain proton conductivity compared with R-SPAES, because of their well-ordered phase separated morphologies. Although B-SPAES had higher proton conductivity than that of G-SPAES below  $100\text{ }^{\circ}\text{C}$ , G-SPAES exhibited the highest proton conductivity of about  $0.011\text{ S cm}^{-1}$  at  $120\text{ }^{\circ}\text{C}$ . The more stable proton conduction behavior of G-SPAES under low RH conditions may result from an increase in water retention capability *via* synergistic effects of high sulfonic acid concentration ( $(\text{IEC}_{\text{v(wet)}}) = \sim 1.86$

meq cm<sup>-3</sup>) [10] and capillary hydrophilic domains enhancing strong complexation of water molecules with sulfonic acid groups.

To investigate the impact of the different polymer morphologies on fuel cell performance, the current-voltage polarization characteristics of H<sub>2</sub>/O<sub>2</sub> single cells using each of SPAESs, were evaluated at three different temperatures and RH conditions (Figure 3). As shown in Figure 3a, the current voltage polarization of three SPAESs and Nafion<sup>®</sup> 212 membrane were obtained at 80 °C and 100% RH. As anticipated from the proton conductivity data and well-developed hydrophilic channels, the performance of the B-SPAES was superior to that of other SPAES and Nafion<sup>®</sup> 212. At 0.5 V, its current density and maximum power density were ~160%, ~170% and ~115% higher than those of G-SPAES, R-SPAES and Nafion<sup>®</sup> 212, respectively.

However, when the cell temperature was further increased and RH was correspondingly reduced, the current-voltage polarization curve of B-SPAES declined rapidly compared with those of G-SPAES and R-SPAES (Figure 3b and 3c). This drastic reduction in single cell performance with decreasing RH (or dry states) is typically observed in many sulfonated hydrocarbon PEMs and is associated with the evaporation of proton carrier water molecules. For example, when the cell temperature and RH were changed from 100 °C and 85% RH to 120 °C and 35%, current density and maximum power density of B-SPAES at 0.5 V sharply decreased from 1289 mA cm<sup>-2</sup> and 650 mW cm<sup>-2</sup> to 104 mA cm<sup>-2</sup> and 150 mW cm<sup>-2</sup>.

Interestingly, in the case of G-SPAES, the extent of reduction in cell performance was largely alleviated with the operation condition changing from 100 °C and 85% RH to 120 °C and 35%, which is probably due to water retention capability of small hydrophilic domain size (2-5 nm) in the polymer. Wide and large well-developed hydrophilic domains of B-SPAES (8-15 nm)

1 had excellent proton transport properties at a temperature of 100 °C and 85% RH conditions.  
2 However, as the temperature increased above 100 °C, the wider channels led to the proton carrier  
3 water molecules being lost more readily, resulting in B-SPAES performing more poorly at 120°C  
4 and 35% RH.

#### 5 6 **4. Conclusions**

7 Morphology and hydrophilic domain size were compared for three SPAESs copolymers  
8 with random, multiblock and grafted side-chain architecture and were found to significantly  
9 affect the proton conduction, particularly at elevated temperatures and low RH conditions. B-  
10 SPAES and G-SPAES, having well-defined, nanophase-separated morphologies exhibited less  
11 dependence on humidity; thus they showed relatively good proton conductivity at 80 °C and low  
12 RH compared with R-SPAES and Nafion<sup>®</sup> 212. G-SPAES, with a narrow hydrophilic domain  
13 size of less than 5 nm showed higher water retention properties for proton transport, particularly  
14 at 120 °C and low RH compared with that of B-SPAES having a relatively large and wider  
15 hydrophilic domain size of about 8-15 nm. Thus the fuel cell performance of G-SPAES  
16 performed much better than that of B-SPAES, R-SPAES and Nafion<sup>®</sup> 212 at 120 °C and 35  
17 RH%. Phase separated morphology and hydrophilic domain size plays a key role in improving  
18 the medium-temperature fuel cell performance.

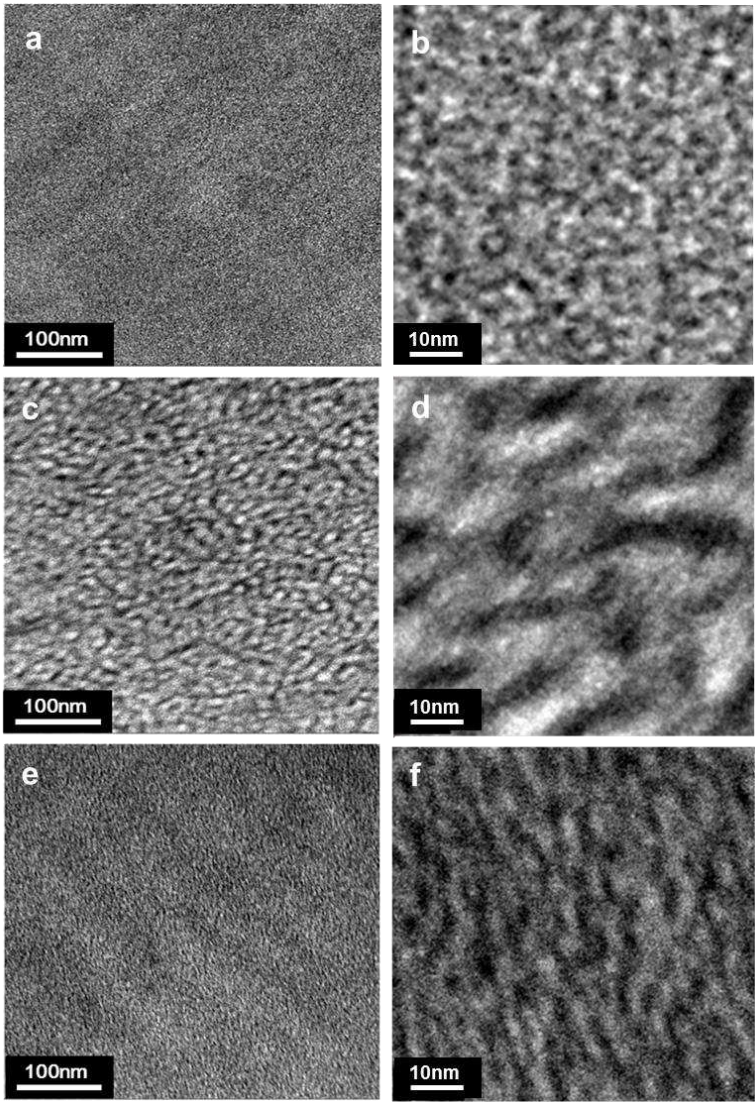
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23 University) program through the government of Korea (No. R31-2008-000-10092-0)

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Figure 1. TEM images of sulfonated hydrocarbon PEMs; a.R-SPAES b. Magnified image of R-SPAES, c. B-SPAES, d. Magnified image of B-SPAES , e. G-SPAES, f. Magnified image of G-SPAES

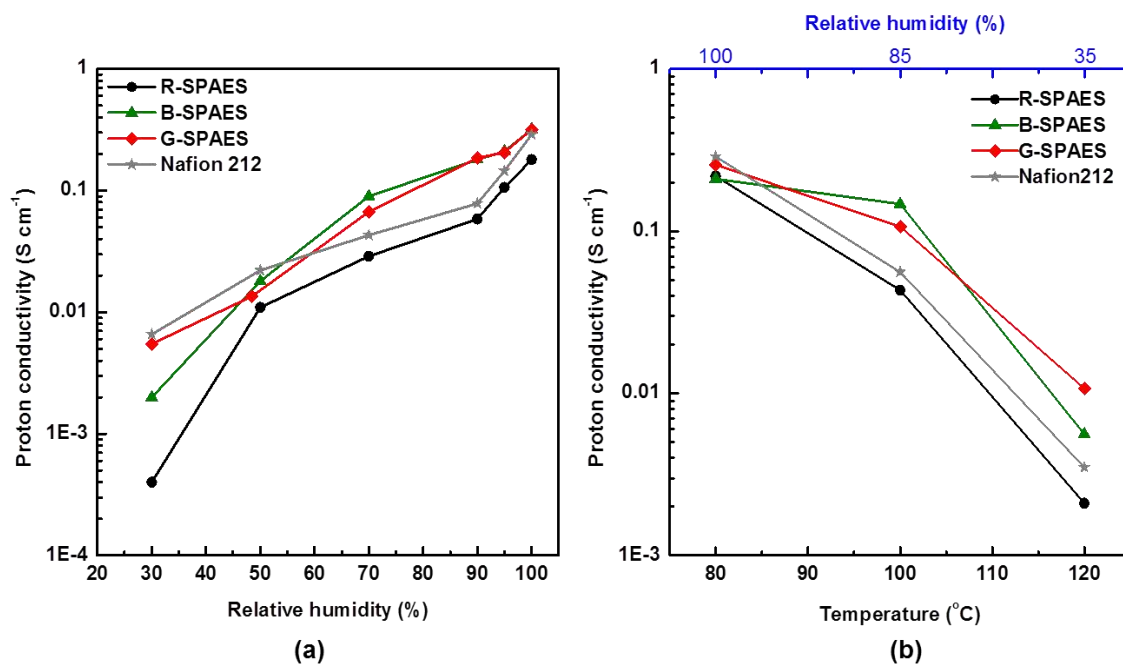


Figure 2. (a) Proton conductivity of SPAESs and Nafion<sup>®</sup> 212 at 80  $^{\circ}C$  as function of RH%, and (b) proton conductivity of SPAESs and Nafion<sup>®</sup> 212 as a function of temperature and RH%

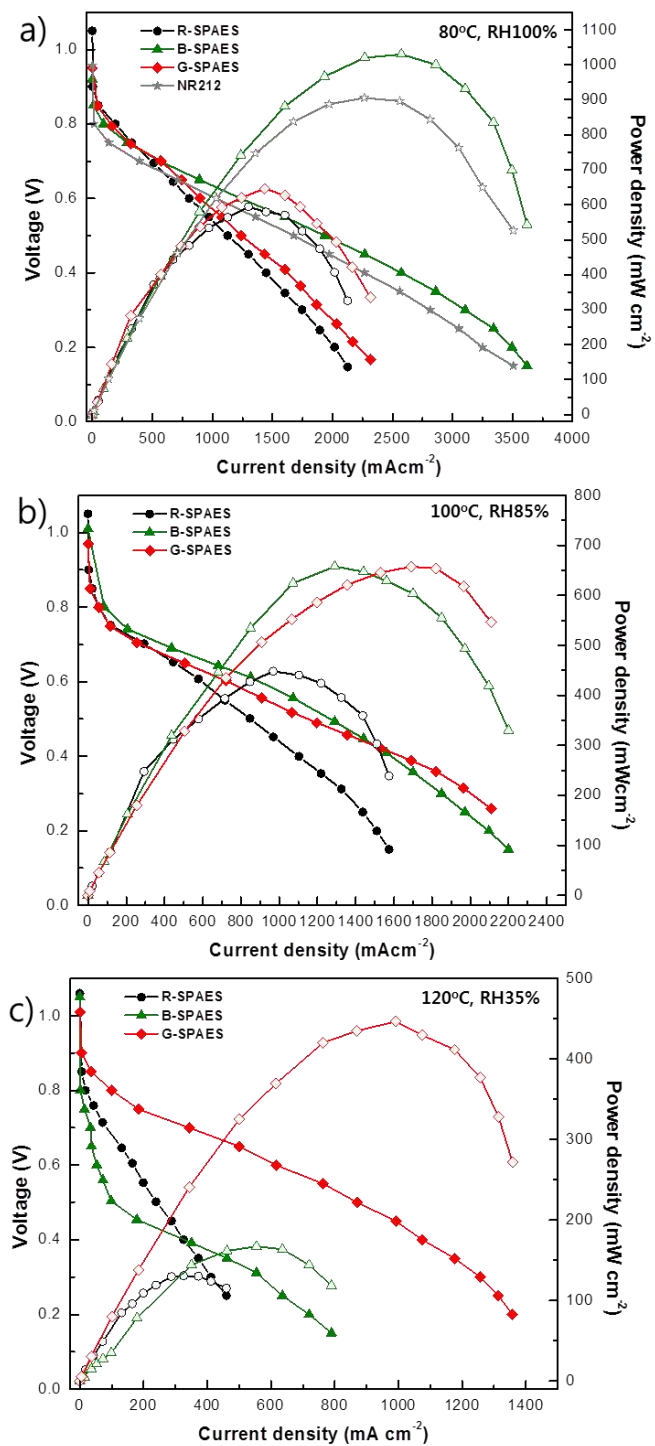


Figure 3. The  $H_2/O_2$  single cell performance of SPAES PEMs at different temperatures and RH conditions. Note that single cell performance of Nafion<sup>®</sup> 212 membrane was not obtained above 80°C temperature, due to thermal dehydration and deformation resulting from low  $T_g$ .