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Opinion

Bio-based polymer electrolyte membrane with nanomatrix channel prepared from natural rubber

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Opinion

Natural rubber is a secondary metabolite isolated from *Hevea brasiliensis*, which is the plant-derived rubber material used in industry [1]. Currently, approximately 10^7 hectares of natural rubber plantations fix about 10^8 tons of carbon annually, and produce about 10^7 tons of natural rubber each year [2]. Thus, the manufacturing of functional materials using natural rubber as a starting material has attracted much attention as a means of contributing to Net-Zero Policy Frameworks and Sustainable Development Goals (SDGs), particularly SDG13 (Climate Action). This opinion describes the preparation of bio-based rubbery soft polymer electrolyte membrane with nanomatrix channel from natural rubber.

Bio-based rubbery soft polymer electrolyte membrane with a nanomatrix channel prepared from natural rubber is sustainable functional material that can potentially achieve an efficient proton transportation, which is required for flexible polymer electrolyte fuel cells to generate green electrical energy [3, 4]. This nanomatrix channel is responsible for the proton transportation owing to its nanophase separated structure consisting of hydrophobic polymer particles with a diameter of approximately 1 μm covered with a continuous nanochannel of a hydrophilic functional polymer. As the hydrophobic polymer particles for the nanomatrix channel of bio-based rubbery soft polymer electrolyte membranes, natural rubber, which is isolated from *Hevea brasiliensis* as a latex in which hydrophobic rubber particles with a diameter of approximately 1 μm are dispersed in water, is expected to offer a sustainable green resource.

The bio-based rubbery soft polymer electrolyte membrane is prepared under mild reaction conditions by graft-copolymerizing ethyl *p*-styrenesulfonate (SSEt) onto the surface of natural rubber particles followed by hydrolysis with NaOH, as shown in Figure 1. The resulting graft-copolymer, deproteinized natural rubber-*graft*-poly(styrenesulfonic acid) (DPNR-*graft*-PSS), is characterized by rubber-state NMR spectroscopy. Figure 2 shows TEM images of DPNR-*graft*-PSS with PSS content of 6.5%, 5.3%, and 4.4% [3]. As shown in Figure 2(a), the nanomatrix channel of DPNR-*graft*-PSS(6.5) is formed, in which the natural rubber particles with a diameter of approximately 1 μm are covered with a continuous nanochannel of PSS with a thickness of approximately 10 nm. In contrast, the nanochannel of DPNR-*graft*-PSS(5.3) is partially disconnected (Figure 2(b)). As shown in Figure 2(c), for DPNR-*graft*-PSS(4.4), some lumps of PSS with a diameter of about 50–100 nm exist on the surface of the natural rubber particles, forming a discontinuous nanochannel. These differences in the morphology may be attributed to the difference in the PSS content; that is, the PSS contents of 5.3% in DPNR-*graft*-PSS(5.3) and 4.4% in DPNR-*graft*-PSS(4.4) are considered insufficient to form continuous nanochannel.

Table 1 shows PSS content, ion exchanged capacity (IEC) and proton conductivity (σ) measured at 50°C of untreated natural rubber (DPNR), DPNR-*graft*-PSS, and Nafion117®. The IEC and σ of DPNR are 0.00 meq/g and 0.0 S/cm, respectively, owing to the lack of a sulfonic acid group. Those of DPNR-*graft*-PSS depend significantly on the PSS content. Specifically, the IEC increases from 0.11 to

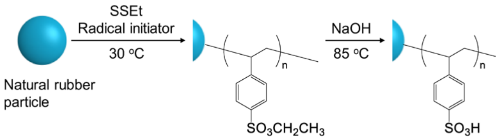

Figure 1 Preparation of DPNR-*graft*-PSS.

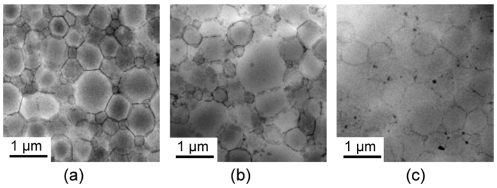

Figure 2 TEM images of (a) DPNR-*graft*-PSS(6.5), (b) DPNR-*graft*-PSS(5.3), and (c) DPNR-*graft*-PSS(4.4).

Table 1 PSS content, IEC and conductivity of DPNR, DPNR-*graft*-PSS, and Nafion117®.

Specimen	PSS content (%)	IEC (meq/g)	Conductivity, σ (S/cm)[a]	σ^* ((S/cm)/meq)[b]
DPNR	-	0.00	0.0	0.0
DPNR-*graft*-PSS(4.4)	4.4	0.11	3.2×10^{-5}	0.015
DPNR-*graft*-PSS(5.3)	5.3	0.15	1.4×10^{-3}	0.50
DPNR-*graft*-PSS(6.5)	6.5	0.22	8.1×10^{-3}	2.6
Nafion117®	-	0.87	4.6×10^{-2}	1.9

[a] Measured at 50°C

[b] $\sigma^* = \dfrac{\sigma}{\mathrm{IEC}\cdot t\cdot A\cdot d}$ t : thickness, A: surface area, d: density

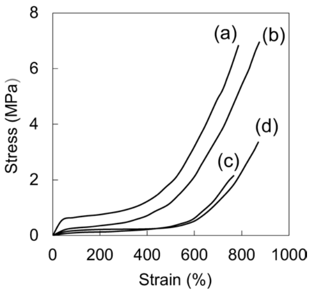

Figure 3 Stress-strain curves of (a) DPNR-*graft*-PSS(6.5), (b) DPNR-*graft*-PSS(5.3), (c) DPNR-*graft*-PSS(4.4), and (d) DPNR.

0.15 and then to 0.22 meq/g with increasing PSS content in DPNR-*graft*-PSS(4.4), DPNR-*graft*-PSS(5.3), and DPNR-*graft*-PSS(6.5), respectively. Similarly, the σ of DPNR-*graft*-PSS increases with increasing PSS content, reaching the highest value of 8.1×10^{-3} S/cm for DPNR-*graft*-PSS(6.5), but it is still lower than that of Nafion117® (4.6×10^{-2} S/cm). In contrast, the proton conductivity per unit equivalent of sulfonic acid (σ^*) of DPNR-*graft*-PSS(6.5) is 2.6 (S/cm)/meq, which is approximately 1.4 times higher than that of Nafion117® (1.9 (S/cm)/meq). This is attributed to the formation of a continuous phase of PSS in the nanomatrix channel.

Figure 3 shows stress-strain curves of DPNR and DPNR-*graft*-PSS. The values of stress and strain at break of DPNR are 3.4 MPa and 870%, respectively. For DPNR-*graft*-PSS(6.5) and DPNR-*graft*-PSS(5.3), the stress increases abruptly at a strain of approximately 400%, reaching 6.9 MPa at break, and the strain at break is similar to that of DPNR, that is, 790 and 880%, respectively. Based on these results, the nanomatrix channel consisting of natural rubber particles and a continuous phase of PSS improves not only the proton conductivity but also the tensile strength of natural rubber. In particular, DPNR-*graft*-PSS(6.5) is proved to be a bio-based rubbery soft polymer electrolyte membrane with outstanding proton conductivity.

The basic technology to prepare bio-based rubbery soft polymer electrolyte membrane has been established by using natural rubber, a plant-derived rubber resource, as the starting material. One of the challenges in the social implementation of the technology is to overcome the poor degradation resistance of natural rubber. Enhancing its durability and developing functional materials using natural rubber as a starting material are expected to contribute to Net-Zero Policy Frameworks and SDGs, and to establish a carbon-neutral society.

Keywords

Natural rubber; Polymer electrolyte membrane; Nanomatrix channel.

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Conflict of interest

The author declares no conflict of interest.

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