

Article

Layer-by-Layer Assembled Nano-Composite Multilayer Gas Barrier Film Manufactured with Stretchable Substrate

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Abstract: Most gas barrier films produce cracks that lead to a significant loss of gas barrier integrity when strain is applied. In order to fabricate stretchable gas barrier films with low water permeability and high endurance after stretching, we used polydiallyldimethylammonium (PDDA) mixed with graphene oxide (GO) and poly (vinyl alcohol) (PVA) mixed with montmorillonite (MMT). These films were manufactured by layer-by-layer assembly on an Ecoflex/polydimethylsiloxane (PDMS) substrate with pre-strain applied. A total of 30 layers of PDDA (GO)/PVA (MMT) coated on the substrate exhibited a low water vapor transmission rate of 2.5×10^{-2} g/m² day after 100 cycles of stretching (30% strain). In addition, they exhibited a high light transmittance of 86.54%. Thus, the prepared stretchable gas barrier film has potential applications as a barrier film in transparent and stretchable electronic devices.

Keywords: layer-by-layer; pre-strain; stretchable; nano-composite



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1. Introduction

As the demand for flexible and stretchable electronic devices increases, flexible and stretchable gas barrier films are in great need to prevent moisture from entering devices to increase the lifetime and stability of electronics and display devices [1–3]. However, conventional gas barrier films are manufactured using an inorganic film, where cracks or pinholes are generated when the gas barrier film is bent or stretched, and water can penetrate through these defects [4]. Additionally, inorganic layers have been fabricated by vacuum processes. However, vacuum processing has the disadvantages of low production efficiency and high production costs [5]. To solve this problem, we fabricated a stretchable gas barrier film using nano-materials and polymers in place of inorganic layers. Instead of a vacuum process for depositing inorganic layers [6–8], a layer-by-layer (LBL) assembly method based on solution processing via electrostatic attraction was used to deposit the passivation layer [9–11]. As nano-materials to lengthen the moisture permeation path of water, graphene oxide (GO) and montmorillonite (MMT) were used. Since GO exhibits a large aspect ratio and MMT is a plate-like material, they were suitable for gas barrier films [12–15]. In addition, the transmittance is an important factor in our gas barrier film because a high transmittance is essential for the film to be applied to construct a display [16]. Therefore, in our paper, GO and MMT were used to form a flexible gas barrier film for improved transmittance and a decrease in the water vapor transmission rate. Furthermore, polydiallyldimethylammonium (PDDA) and poly (vinyl alcohol) (PVA) were used as suitable polymers to be mixed with GO and MMT.

Polydimethylsiloxane (PDMS) and the Ecoflex series (here, Ecoflex 00-30) are commonly used stretchable substrates. However, each has specific strengths and weaknesses.

PDMS exhibits low stretchability and high transmittance, rendering it suitable for transparent applications, whereas Ecoflex exhibits high stretchability and opaque characteristics. Both materials are types of silicone rubber, which means that they are miscible [17–19]. Thus, we attempted to mix PDMS and Ecoflex as a stretchable gas barrier film substrate. When a passivation layer was laminated on the stretchable substrate, pre-strain was applied and laminated to eliminate spaces between the nano-clays when the substrate was stretched. The water vapor transmission rate (WVTR) characteristics and surfaces of the substrates fabricated after applying 10% and 30% pre-strain and without applying pre-strain were compared. The oxygen transmission rate (OTR) was measured via MOCON, and the WVTR of the stretchable gas barrier film was measured via the Ca test method using the electrical properties of calcium [20,21]. The fabricated stretchable gas barrier film was confirmed to be suitable for use in stretchable electronic devices.

2. Materials and Methods

GO (500 mg/L) was purchased from the Graphene Supermarket, and Na⁺-MMT was purchased from Southern Clay Products, Gonzales, TX, USA. PVA (M_w = 30,000–70,000, 87–90% hydrolysed) and PDDA (M_w = 200,000–350,000, 20 wt% H₂O) were purchased from Sigma-Aldrich (Seoul, Korea). The substrate was prepared using a mixture of PDMS and Ecoflex 00-30 at a weight ratio of 8:2. PDMS was purchased from the Dow Corning, and the PDMS base and curing agent were mixed at a weight ratio of 10:1. Ecoflex was purchased from Smooth-on, and the Ecoflex base and curing agent were mixed at a weight ratio of 1:1. The mixture of PDMS and Ecoflex 00-30 was cured at 60 °C for 5 h. Subsequently, 0.01 wt% GO was magnetically stirred (450–550 rpm) in 200 mL of DI water for 24 h to achieve a uniform dispersion. To prepare a cationic solution, the GO solution was mixed with 0.02 wt% PDDA in DI water for 24 h and stirred for an additional 24 h. The PDDA (GO) solution combined the functional groups on the GO surface and PDDA via electrostatic attractions, resulting in a positive charge on the surface of the resulting material [22,23]. To obtain a uniform MMT particle size, 0.05 wt% MMT was magnetically stirred (450–550 rpm) in 400 mL DI water for 24 h and centrifuged at 4500 rpm for 1 h. Afterwards, the solution containing the large MMT particles was extracted and centrifuged at 1700 rpm for 15 min to obtain a solution with uniform-size MMT particles of 2 to 4 µm. The prepared MMT solution was mixed with a 0.5 wt% PVA solution and then stirred at 85 °C for 24 h at a ratio of 3:1, and the mixture was additionally stirred at room temperature for 24 h. This solution contained a negative charge on the surface [24]. The prepared mixed stretchable substrate was treated with ultraviolet (UV) ozone for 30 min to create OH[•] radicals on the surface [25]. The stretchable gas barrier film was subsequently fabricated by LbL assembly between the cationic solution of PDDA (GO) and anionic solution of PVA (MMT). The calcium test method was used to analyze the WVTR characteristics of the fabricated stretchable substrate, and the MOCON OX-TRAN 2/21 MH (as specified in ASTM D-3985) analysis method at 23 °C and 50% RH was used for OTR analysis. The WVTR and OTR values of the gas barrier film were measured using the property that the resistance of Ca changes due to its role as an insulator when Ca reacts with water and oxygen, decreasing the current under a constant applied voltage. The Ca test method can accurately measure ultra-low water vapor permeability on the order of 10^{−6} g/m² day with high sensitivity and structural compatibility. A zeta potential analyzer (ELSZ-1000, Otsuka Electronics, Osaka, Japan) was used to characterize the electrostatic attraction between the prepared PDDA (GO) and PVA (MMT) solutions. Scanning electron microscopy (SEM) was used for the surface analysis of the stretchable gas barrier film. For transmittance analysis of the film, an ultraviolet–visible (UV-Vis) spectrophotometer (Cary 5000, Varian Instruments, Palo Alto, CA, USA) was used in the range of 400 to 800 nm.

3. Results

3.1. Preparing Stretchable Substrate

Using PDMS as a stretchable substrate results in high transmittance, but limited stretchability, whereas Ecoflex substrates provide better stretchability than PDMS but have very low transmittance. To overcome these challenges, an optimum ratio between the trade-off relation of transmittance and stretchability was determined by testing mixtures of Ecoflex/PDMS as a substrate at a weight ratio of 8:2 [26]. Figure 1 shows that at 550 nm, the transmittance values of PDMS, Ecoflex, and the mixed Ecoflex/PDMS substrates are 100%, 46.45%, and 86.54%, respectively. The PDMS and Ecoflex mixture at a weight ratio of 8:2 was confirmed to be suitable for use as a stretchable substrate with sufficient transmittance. OH- radicals were generated on the substrate surface by UV-O surface treatment for 30 min on the mixed PDMS and Ecoflex sample. The thickness of the fabricated substrate is 300 μm .

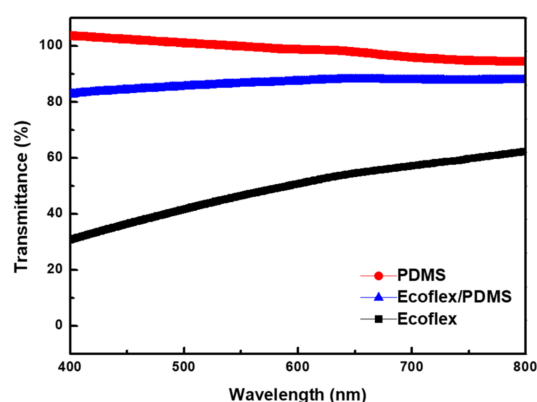


Figure 1. Light transmittance of the prepared stretchable substrates.

3.2. Analysis Using Zeta Potential and Stretchable Gas Barrier Film Fabrication

Using a zeta potential analyzer (ELSZ-1000, Otsuka Electronics), the surface charges of the solutions used for the LbL deposition were determined. As shown in Figure 2, the GO solution exhibited a zeta potential value of -33.6 before mixing with PDDA, but after mixing with PDDA at a ratio of 1:2, the PDDA (GO) solution showed a positive charge of 34.95 . The MMT solution exhibited a zeta potential value of -0.54 before mixing with PVA, which changed to a negative charge of -8.4 after mixing at a ratio of 3:1 with PVA. When MMT was mixed with PVA, the PVA permeated between MMT and bonded with the MMT to increase the diffusion path of water. As confirmed by the zeta potential analysis, the PDDA (GO) solution exhibited a positive charge, and the PVA (MMT) solution was negatively charged, meaning each layer can be stacked alternately by electrostatic interactions. Herein, 30 alternating layers of PDDA (GO) and PVA (MMT) were stacked on the stretchable substrate. The thickness of the fabricated layer by the LbL process is about 150 nm. The LbL process, the solution process used in this paper, has the advantage of being able to be utilized in a large-area lamination because it stacks each layer by electrostatic forces. In addition, after drop casting, it is then rinsed with DI water and then laminated to a thickness on the nano-scale. The drop casting method is more suitable than spin coating for the fabrication of a uniform multilayer film while maintaining pre-strain on the substrate.

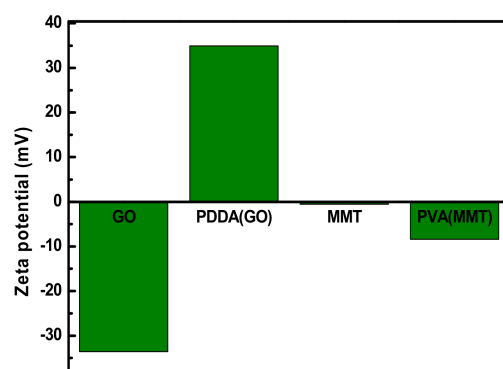


Figure 2. Zeta potential values of the GO, PDDA (GO), MMT, and PVA (MMT) solutions.

3.3. Analysis Using FTIR and SEM

The result from FTIR analysis (LabRam ARAMIS IR2, HORIBA JOBIN YVON) confirmed the incorporation between the GO and MMT. The FTIR pattern of GO in Figure 3 shows bands at 1045 cm^{-1} (C-O-C stretch of epoxy group), 1385 cm^{-1} (C=C bending), 1625 cm^{-1} (-OH bending), and 1710 cm^{-1} (C=O stretch of carboxyl group). The pattern of MMT shows bands at 1035 cm^{-1} (Si-O stretching band), 1630 cm^{-1} (O-H bending band), 3450 cm^{-1} (-OH stretch from free H_2O), and 3630 cm^{-1} (-OH stretch band). The FTIR patterns of MMT such as Si-O and O-H appeared in the GO-MMT composite. The barrier layer was fabricated via drop casting a stretchable substrate without pre-strain, as shown in Figure 4, to fabricate a barrier layer on the stretchable substrate without applying pre-strain [27]. The stretchable gas barrier film was stretched and relaxed. The surfaces of the stretchable gas barrier films fabricated via drop casting without pre-strain and after applying 10% and 30% pre-strain to the stretchable substrate were subsequently analyzed by SEM. Figure 5 shows SEM top-view images of the sample after 30 layers of PDDA (GO)/PVA (MMT) were prepared by LbL deposition at different strains (0%, 10%, and 30%). PDDA (GO) and PVA (MMT) were well deposited on the mixed Ecoflex and PDMS substrate, as shown in Figure 5a–c, which show the surface of the 30-layer laminate of PDDA (GO)/PVA (MMT) after 0%, 10%, and 30% pre-strain, respectively. After pre-strain was applied, it was confirmed that many wrinkles appeared on the surface of the substrate where the barrier layer was laminated and subsequently relaxed. The SEM image in Figure 6 shows the surface of the substrate after 100 cycles of stretching (30% strain) of the stretchable gas barrier film fabricated by applying different pre-strains (0%, 10%, and 30%). The barrier layer could not withstand 30% stretching, as indicated by the large number of cracks in the stretched samples without pre-strain (Figure 6a). The 10% pre-strain sample (Figure 6b) showed less cracks than the samples prepared without pre-strain, but a few cracks were still observed. In contrast, the 30% pre-strain sample showed high durability after 100 stretching cycles. It was confirmed that the gas barrier film was able to withstand stretching well due to wrinkles formed by applying pre-strain. Thus, it can be concluded that the barrier layers are vulnerable to stretching but show high durability during contraction.

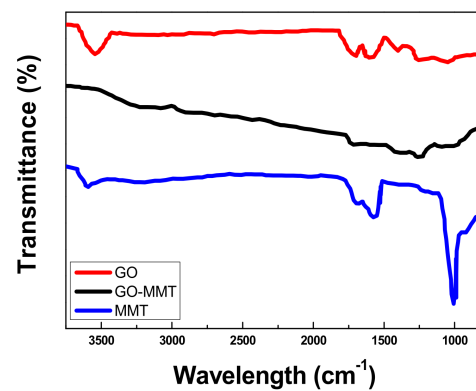


Figure 3. FTIR patterns of GO, MMT, and GO-MMT.

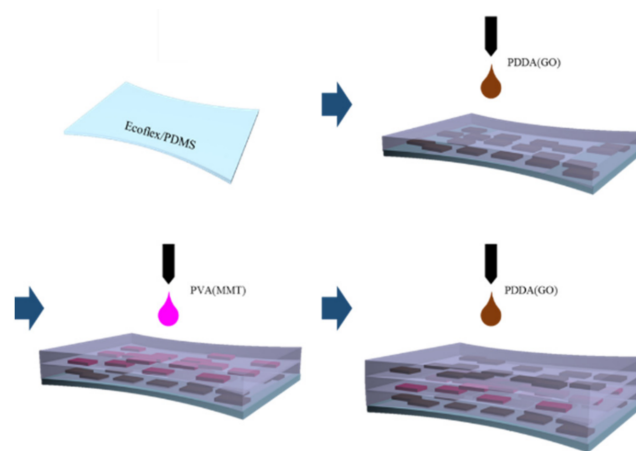


Figure 4. Schematic of the multilayered films deposited on an Ecoflex/PDMS stretchable substrate with pre-strain using LbL assembly.

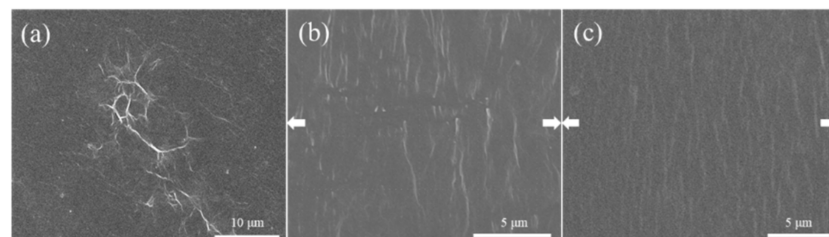


Figure 5. SEM surface images of the 30 laminated PDDA (GO)/PVA (MMT) layers on a stretchable substrate applying strains of (a) 0%, (b) 10%, and (c) 30%.

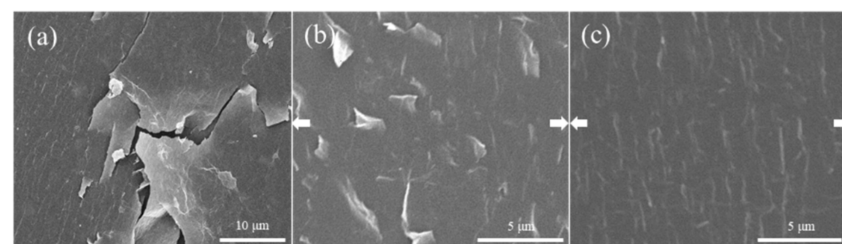


Figure 6. SEM surface images after stretching test on substrates with (a) 0%, (b) 10%, and (c) 30% pre-strain applied.

3.4. WVTR and Light Transmittance of Stretchable Gas Barrier Film

We compared the WVTR values of 30 laminated layers of PDDA/PVA (MMT), PDDA (GO)/PVA, and PDDA (GO)/PVA (MMT). When GO and MMT are laminated, compared to when each is used alone, the materials are more stably bonded by hydrogen bonding of crosslinking effects between GO and MMT, thus filling the vacancies formed when the layers are laminated individually and extending the diffusion path length for a water molecule. As shown in Figure 7, the WVTR value of the PDDA (GO)/PVA (MMT) films was greatly reduced. We compared the WVTR values after 100 stretching cycles (30% strain) of the 30 laminated layers of PDDA (GO)/PVA (MMT) on the stretchable substrate subjected to the applied pre-strain. The WVTR values of the gas barrier films were analyzed using the Ca test method. Figure 8a shows that the WVTR values of the samples with a 30-layer PDDA (GO)/PVA (MMT)-coated stretchable substrate without pre-strain, with 10% pre-strain, and with 30% pre-strain were 8.8 , 2.8×10^{-1} , and 2.5×10^{-2} g/m²·day. The OTR values of the films were analyzed by MOCON. As shown in Figure 8b, the 30-layer PDDA (GO)/PVA (MMT)-coated stretchable substrate without pre-strain was 178 cc/m²·day, which decreased to 43.88 and 11.91 cc/m²·day for the samples subjected to 10% and 30% pre-strains, respectively. Wrinkles were formed in the film with the gas barrier laminated after applying 30% pre-strain. Therefore, when the stretching test (30% strain) was performed, the barrier layer did not crack, and the stretchable gas barrier film showed improved WVTR and OTR values. As light transmittance is also important for gas barrier films, the transmittance of the 30-layer PDDA (GO)/PVA (MMT)-coated Ecoflex/PDMS substrate was measured using a UV-Vis spectrophotometer. Figure 9 shows the transmittance values of the uncoated Ecoflex/PDMS substrate and the 30-layer coating of the PDDA (GO)/PVA (MMT) substrate at 550 nm were 86.54% and 80.84%, respectively. This shows that the PDDA (GO)/PVA (MMT) 30-layer stretchable gas barrier film was sufficiently transparent. Therefore, this stretchable gas barrier film can be used in electronic devices requiring transparency and stretchability.

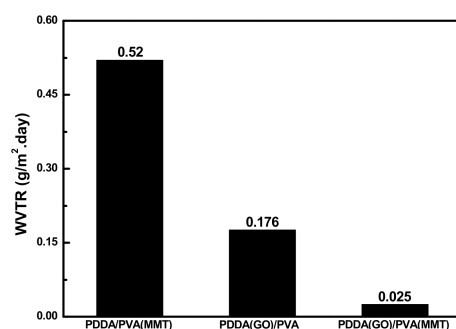


Figure 7. WVTR results of PDDA/PVA (MMT), PDDA (GO)/PVA, and PDDA (GO)/PVA (MMT) gas barrier films.

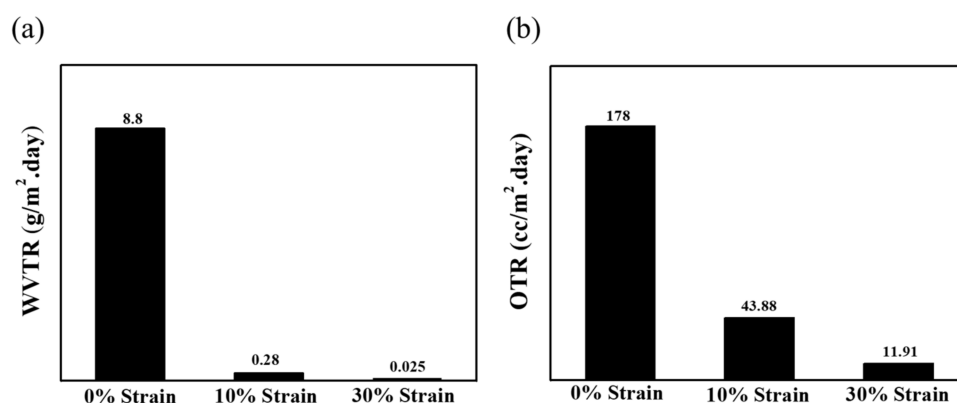


Figure 8. (a) WVTR and (b) OTR values of the prepared stretchable gas barrier films.

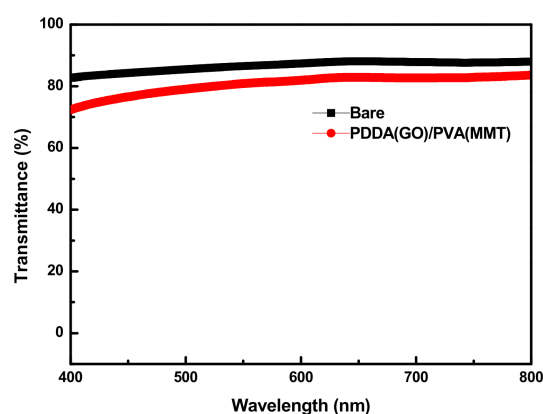


Figure 9. Light transmittance of the bare Ecoflex/PDMS substrate and 30 laminated PDDA (GO)/PVA (MMT) layers on the Ecoflex/PDMS substrate.

4. Discussion

Herein, we fabricated a substrate with 86.54% transmittance by mixing PDMS and Ecoflex in an 8:2 weight ratio. After applying various pre-strains (0%, 10%, 30%) to the Ecoflex/PDMS substrate, PDDA (GO) and PVA (MMT) solutions with opposite charges were laminated using the LbL method, a non-vacuum process to form barrier layers with good interlayer bonding via electrostatic attraction. LbL assembly by absorption from the solution is a good approach to the fabrication of near perfectly oriented and aligned nano-material/polymer multilayers. The experimental results confirm that the method of laminating barrier layers after applying pre-strain produced wrinkles. These wrinkles allow strain to be endured on the surface of the barrier layer, preventing cracks during the stretching test and resulting in an improved WVTR. The 30-layer coated Ecoflex/PDMS substrate had a low WVTR rate of 2.5×10^{-2} g/m² day after 100 cycles of the stretching test. These studies found that the nano-material/polymer multilayer structure has a strong tendency to be suitable as a stretchable gas barrier film. The PDDA (GO)/PVA (MMT) multilayer coated Eco-flex/PDMS gas barrier film shows great potential for use in stretchable applications. In addition, this simple and fast method can be suitable for stretchable gas barrier fabrication technologies.

Author Contributions: Conceptualization, S.K. and T.K.; methodology, S.K.; software, S.K.; validation, S.K., T.K. and B.-K.J.; formal analysis, S.K.; investigation, S.K.; resources, B.-K.J.; data curation, S.K. and T.K.; writing—original draft preparation, S.K.; writing—review and editing, B.-K.J.; visualization, S.K.; supervision, B.-K.J. and D.K.; project administration, B.-K.J.; funding acquisition, B.-K.J. and D.K. All authors have read and agreed to the published version of the manuscript.

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