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Barrier Coating on PES Substrate by Formation of Inorganic and Silane-Nanoclay Composite Layer

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Several methods to enhance the barrier property of plastic substrate were tested. Inorganic layer of SiN_xO_y was deposited by PECVD, and barrier properties were enhanced with increased deposition time. Pre-treatment of substrate with Ar/O_2 plasma modified the surface for better deposition of layer with improved barrier properties. Organosilane-nanoclay composite layer was formed by curing the dope solution on the surface through hydrogen bonding formation, and it especially enhanced the barrier property to oxygen. Multilayer formed by combination of inorganic layer on organosilane-nanoclay composite layer attained the best barrier properties among the several methods tested. Inorganic layer and organosilane-nanoclay composite layer were much damaged by bending test to show the deterioration of barrier properties. However, multilayer still retained the barrier property even after the bending test. Multilayer deposited on PES substrate was successful in terms of optical performance for flexible plastic substrate.

Keywords: barrier property; buffer layer; nanoclay; organosilane; OTR; PECVD; PES; WVTR

INTRODUCTION

Flexible display has positioned the future technology as a potential development issues for next generation flat panel display (FPD) strategy. Several research groups have demonstrated display devices

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on flexible substrates that have several advantages of being thin, lightweight, robust, and flexible [1–5]. Metal foils, thin glass and plastic films have been considered to be a good substrates to fabricate the flexible devices [6]. Among these substrates plastic film is a good candidate which has good properties such as high transmittance and flexibility. Moreover, plastic substrates offer the possibility of reduction in productivity due to their compatibility with roll-to-roll processing and printing technology. However, display device performances of plastic films were decreased by diffused water vapor and oxygen through them. Therefore, barrier coatings such as SiO_x, SiO_xN_y, $SiO_xC_yH_z$ on plastic substrates have been investigated to reduce the water vapor and oxygen permeation [7–9]. Although those inorganic coatings represented good barrier properties, the bad adhesion properties between inorganic layer and polymeric substrate were still existed. Several works have also concerned on surface pretreatment using plasma with argon, oxygen and nitrogen to improve the adhesion properties [10,11]. They investigated the influence of plasma pretreatment on inorganic SiN_x barrier layer formation and the adhesion properties.

Organic/inorganic hybrid coatings have been considered for barrier layers and adhesion promoters. Wuu *et al.* reported that a multilayer composed of inorganic and parylene layers had good barrier performance. This was because of the effective coverage of organic layers to decrease the defects of inorganic layer [12]. Singh *et al.* investigated the influence of an organosilane-silica coatings durability on barrier performance and focused on pH effect of solution on permeation behavior [13].

Recently, using nanoclay in organic layer has been considered to enhance the barrier properties. It has been reported that polymer-nanoclay with only a few percent of well-dispersed clay reinforcement have good mechanical and barrier characteristics [14]. Montmorillonite layered silicate with high aspect ratio increased the tortuous path that increase the time for diffusion of gas and moisture through the organic layers [15]. Jang *et al.* studied the layer-by-layer assembly using polymer and clay to form 30-bilayers with good barrier properties [16]. However, the presence of moisture decreased the oxygen barrier properties due to hydrophilic nature of clays. In this study, SiO_xN_y barrier layers were deposited on PES substrate by PECVD. We focused on the effect of deposition time and period on the formation of inorganic layer. Prior to deposition, plasma pretreatment was executed to promote the formation of inorganic layer. Orgnosilane-nanoclay composite was coated by spin coating method as a buffer layer to improve the barrier properties and to enhance the adhesion

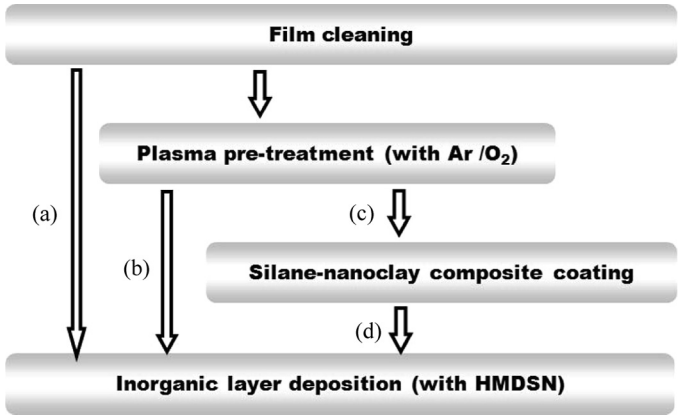

FIGURE 1 Procedure of barrier coating on PES substrates.

stability between the inorganic layer and polymeric substrates. The effect of nanoclay contents in the composite layer on the barrier improvement of substrates was investigated.

In this work several methods of barrier coating on PES substrates were attempted and each process was schematically described in Figure 1; (a) direct inorganic layer deposition by PECVD, (b) plasma pre-treatment of substrate followed by inorganic layer deposition by PECVD, (c) orgnaosilane-nanoclay composite layer coating on plasma pretreated substrate and (d) multilayer formation by inorganic layer deposition by PECVD on orgnaosilane-nanoclay composite layer coated surface, respectively. A comparison of barrier properties between four different types of barrier coating on PES substrates will be discussed.

EXPERIMENTAL

The schematic diagram of PECVD apparatus used in this work is shown in Figure 2. Hexamethyldisilazne (HMDSN, Sigma-Aldrich Co. 98%) was used as liquid source for silicon precursor and was supplied into the reactor by nitrogen bubbling into the reservoir maintained at 60°C. Ar and O_2 gases were also introduced into the reactor for the proper deposition of SiO_xN_y layer at specified rates through the mass flow controller. In order to deposit the SiO_xN_y layer successfully, the deposition time was varied from 1 min to 7 min with a fixed RF power of 350 W. The plasma pretreatment of substrate was

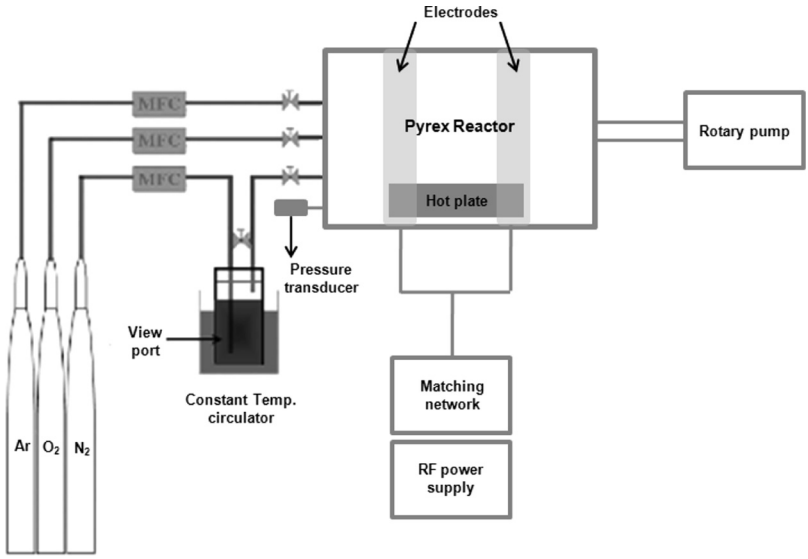

FIGURE 2 Schematic diagram of PECVD.

performed with O_2/Ar gas mixtures was prior to deposition of SiO_xN_y for performance enhancement.

Dimethyl dehydrogenated tallow quaternary ammonium modified montmorillonite-based nanoclay, Closite15A from Rockwood Specialties, were added into prehydrolyzed oragnosilane (γ–APS, Sigma-Aldrich Co. 99%) solution at concentration from 1 to 5 wt% of nanoclay. The organosilane-nanoclay composite solution was stirred for 3 h, and was subsequently ultrasonicated for 3 hr and spin coated at 1500 rpm for 30 sec. The organosilane-nanoclay composite layer was subsequently cured at 100°C for 24 hr under air.

The chemical composition of the plasma pretreated surface of PES and the deposited SiO_xN_y layer were investigated using a X-ray photoelectron spectrometer (XPS, K-Alpha, Thermo electron, UK). The functional groups in the SiO_xN_y and composite layer were characterized by FT-IR (system 2000, Perkin Elmer, USA). Surface images of each layer were obtained by AFM (Nanoscope IIIa, Digital Instrument, USA) and FE-SEM (JEM-2100F, JEOL, JAPAN). The water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) were measured by using Permatran-W (Model 3/33 Mocon Inc. USA) and Oxtran (Model 2/20, Mocon Inc. USA) measurement system, respectively.

RESULTS AND DISCUSSION

Inorganic Layer Deposition

Inorganic layer of SiO_xN_y was deposited by PECVD process on PES substrate with HMDSN source as described in Figure 1(a). Increase of plasma deposition time usually increased the deposition layer thickness as well as the grain size [7]. However, excess deposition time damaged the substrate to result in the pin hole and defect formation. Multiple deposition process was more effective than single deposition process, though total deposition time was same to each other. Multiple deposition reduced the pin holes and macro-defects with less damage than the single deposition, but it still had a few micro-defects to be blocked. In this work multiple plasma depositions for 1 min period were attempted instead of single plasma deposition with longer period to avoid the damages. Effect of deposition time was examined in terms of surface morphology by AFM as shown in Figure 3. With increase of deposition time the grain size on the surface of PES substrate were increased, though the grain shape was not uniform.

Figure 4 showed that longer deposition time resulted in the increase of deposition layer thickness. Roughness of SiO_xN_y layer was rapidly increased until 3 min and then slightly decreased after 3 min. SiO_xN_y was initially deposited in island-like structure to increase the surface roughness, and more SiO_xN_y layer deposition covered the whole surface to reduce the surface roughness. Thickness of the SiO_xN_y increased with increasing deposition time to form uniform SiO_xN_y layer on the PES surface. Formation of SiO_xN_y layer by PECVD

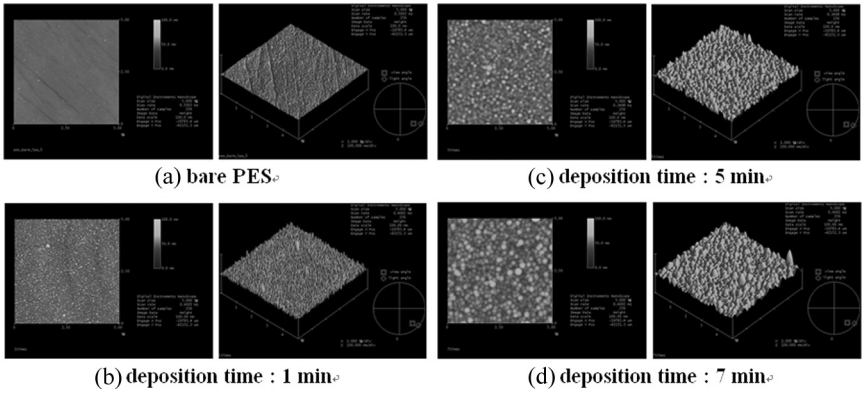

FIGURE 3 AFM images of SiO_xN_y with various deposition times.

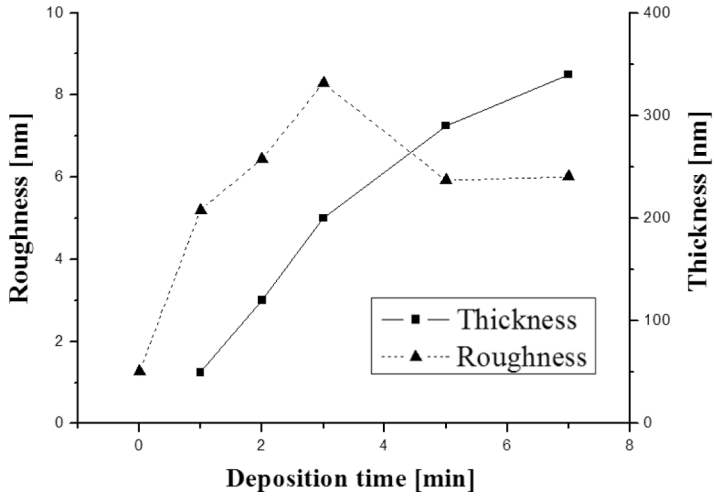

FIGURE 4 Varieties of roughness and thickness of SiO_xN_y with various deposition time.

reduced WVTR and OTR of the layered PES samples, and gradual decreases of both WVTR and OTR were observed as shown in Figure 5.

In order to improve the adhesion stability of SiO_xN_y layer to PES substrates and to promote the formation of SiO_xN_y layer on the

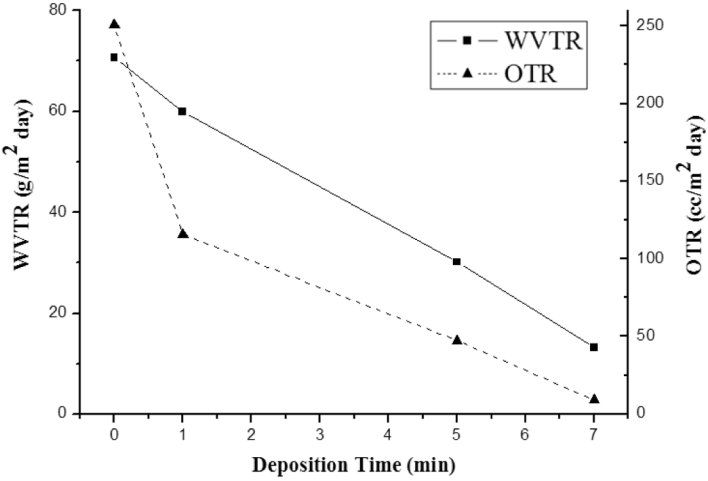

FIGURE 5 WVTR and OTR of SiO_xN_y barrier PES samples with deposition times.

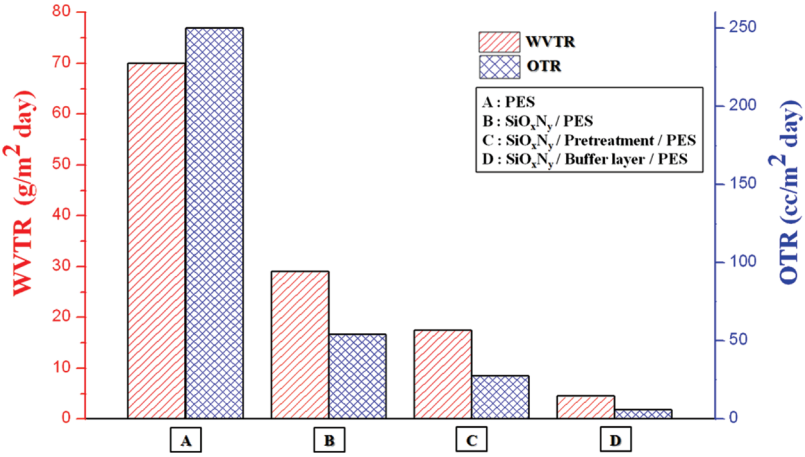

FIGURE 6 A comparison of WVTR and OTR value of PES substrates.

surface, plasma pretreatment with Ar/O_2 gas mixtures was attempted as denoted by Figure 1(b). Figure 6 compared the WVTR and OTR measurement results between the inorganic layer formation on bare PES and plasma pretreated PES substrates, and plasma pretreatment still enhanced the barrier properties of the SiO_xN_y layer on PES substrates. Surface energy of the PES substrates increased due to increased oxygen functionalities by plasma pretreatment, which means that inorganic SiO_xN_y layer was deposited on the PES substrate uniformly.

Organosilane-Nanoclay Composite Layer Deposition

The organic/inorganic hybrid materials have been investigated as the barrier layer itself and interfacial buffer layer between substrate and inorganic barrier layer. Organosilane-nanoclay composite layer was formed on the plasma pretreated PES substrate as denoted by Figure 1(c). The mechanism of organosilane coating on PES substrate was represented in Figure 7. Firstly, organosilane reacted with hydrophilic species on the PES surface. The silanol group in organosilane was produced through the hydrolysis reaction of alkoxy group and then followed by the condensation reaction [14]. Therefore, crosslinking between the hydroxyl group of organosilane and the hydrophilic species of PES surface was formed, which cause the good adhesion properties.

A layered silicate with lamellar stack has been used for the preparation of polymer/nanoclay composites. The nanoclay can offer

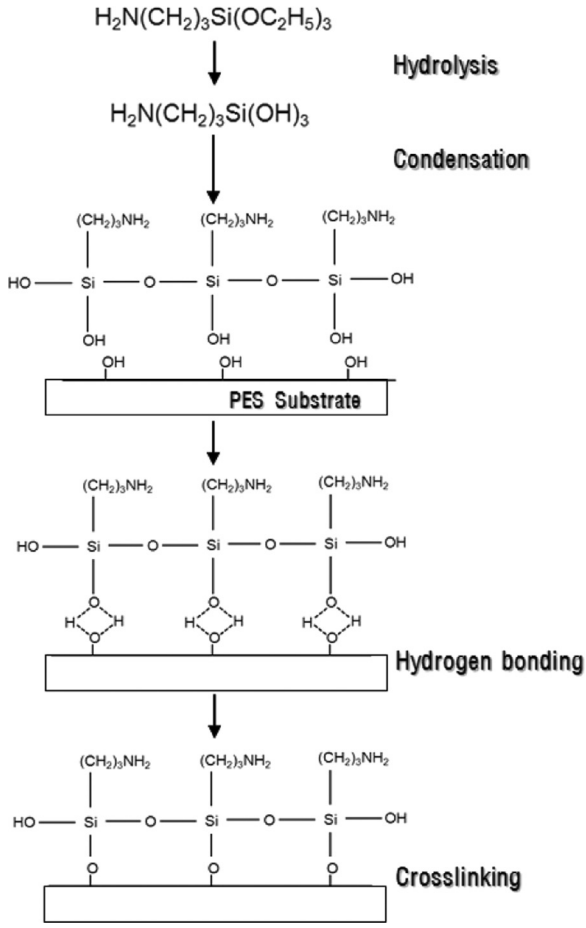

FIGURE 7 The mechanism of organosilane coating on PES substrate.

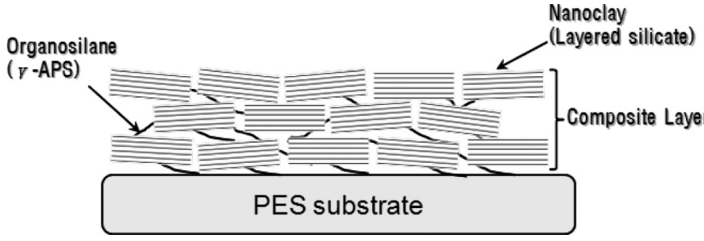

FIGURE 8 Schematic of organosilane-nanoclay composite layer on PES substrates.

barrier characteristics with significantly reduced gas permeability. As represented in Figure 8, when the layered silicate was organically intercalated and exfoliated as about results, the tortuous paths that increase the time for diffusion of gas and moisture were created in coating composite layers, Figure 9(a) showed the FT-IR spectra for organosilane-nanoclay composite solution. When γ–APS was added to the aqueous nanoclay mixture, a new peak appeared at 3300–3400 cm^{-1} broadly. This peak was assigned to the hydroxyl group (–OH) that was generated from hydrolysis reaction between γ–APS and nanoclay in composite solution. One is to modify the clay

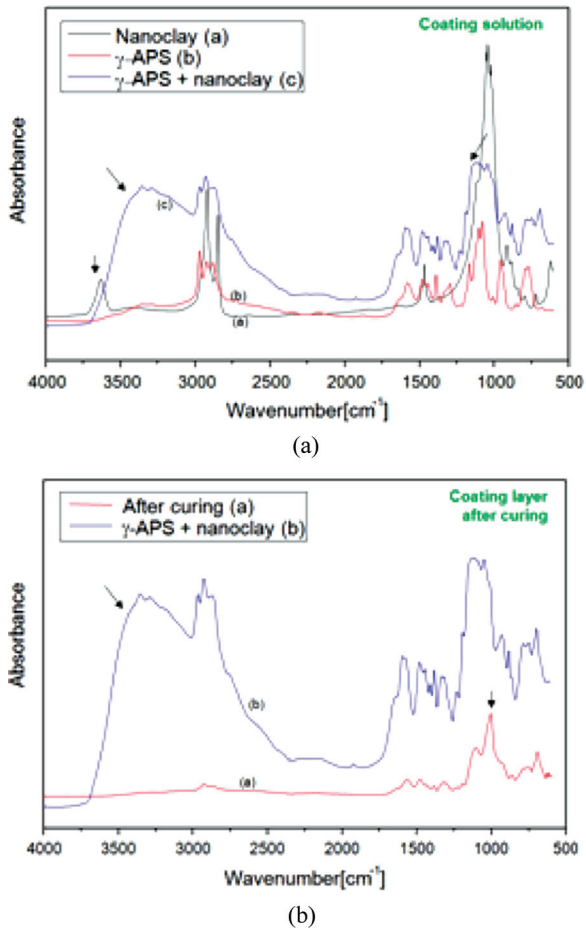

FIGURE 9 FT-IR spectra of organosilane-nanoclay composite coating solution (a) and composite layer (b).

TABLE 1 The Change of d-spacing of Organosilane-Nanoclay Composites

Nanoclay contents in solution (wt%)	2θ-angle (degree)	d-spacing (nm)
Nanoclay powder	2.77	3.185
1	2.294	3.847
3	2.331	3.788
5	2.459	3.590

with the alkoxy group of silane through the condensation reaction of the OH group of clay with the alkoxy group of silane.

Table 1 presented the XRD results of clay powder and organosilane/nanaoclay composites with varying clay contents. Cloisite 15A had an original intergallery distance (d-spacing) of 3.185 nm as calculated from the peak (001) basal plane. After mixing with organosilane, intergallery spacing increased from 3.590 nm to 3.847 with decreasing the clay contents. This indicates the insertion of silane molecules into the clay galleries. When the layered silicate was organically intercalated and exfoliated as about results, the tortuous paths that increase the time for diffusion of gas and moisture were created in coating composite layers (Fig. 8).

FT-IR spectra of the composite layers coated on PES surface was given Figure 9(b). The hydroxyl group (–OH) peak at 3300–3400 cm^{-1} disappeared in coated layer. This indicated that the hydrogen bonding was formed between composite layer and PES substrates. The Si-O-Si peak at 1000–1100 cm^{-1} appeared after forming the composite layer, which indicated that the strong siloxane bond was formed in interphase region. This crosslinking of composite layer on PES surface play an important role to enhance the adhesion stabilities between coating layer and substrates. Therefore, in case of using organosilane-nanclay composite coating as a buffer layer between SiO_xN_y and PES substrate, it could be obtained good adhesion stability as well as improved barrier properties (see Fig. 6(D)). The strong crosslinking caused the siloxane network in the composite layer coated on PES surface, which contributed to enhancement of barrier characteristic [13].

The influence of clay contents on barrier properties of organosilane-nanoclay composite layer coated on PES substrate was shown in Figure 10. When the composite layer was formed on PES without nanoclay, the barrier properties were slightly improved. After adding the nanoclay in composite layer, WVTR & OTR values more decreased. This indicated that the nanoclay in composite layer created the longer tortuous path, as above mentioned.[15] It also could be confirmed that a

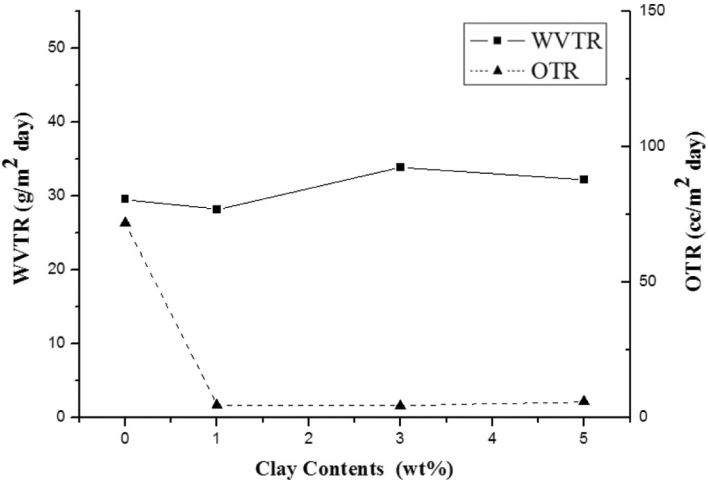

FIGURE 10 Effect on nanoclay contents in the composite layer on WVTR and OTR of PES substrate.

clay content as low as 1 wt% was sufficient to reduced the OTR values. However, the WVTR value could not be more reduced, due to the hydrophilic properties of nanoclays.

The variation of WVTR & OTR values after bending test was indicated in Figure 11. This result showed that the presence of buffer layer using organosilane-nanoclay composites enhanced the barrier properties. After bending test, there was no significant decreasing in

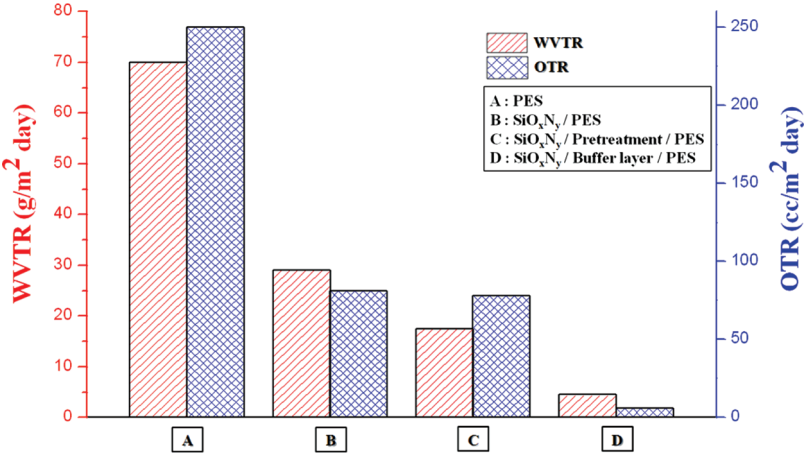

FIGURE 11 WVTR and OTR values after bending test.

its barrier performance. It means that the buffer layer offered a good effect to improve the adhesion stabilities between SiO_xN_y barrier layer and PES substrates.

CONCLUSIONS

SiO_xN_y layer was successfully deposited on PES substrate by PECVD with HMDSN. Plasma pre-treatment with Ar/O_2 increased the surface energy and formed functional groups on PES substrate surface. Plasma pre-treatment also had great influence on PECVD with HMDSN, which reduced the surface roughness and increased the surface contents of O, N and Si. The orgaonsilane-nanoclay composite layer was fabricated by curing the γ APS-nanoclay mixture through hydrogen bonding with the surface of plasma pre-treated PES film. Combination of SiO_xN_y layer and organosilane-nanoclay composite layer achieved quite good enhancement of barrier properties (WVTR and OTR) of PES substrate. The use of the buffer layer between PES and the inorganic layer kept the barrier properties after bending test.

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