Composite Layer Formation on Plastic Substrates for Flexible Display by Using Functionalized Nanoclay

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Abstract: Polymer/nanoclay composite layers were formed by a UV-curing process on plastic substrates for flexible display to enhance their mechanical and barrier properties. Sodium montmorillonite (Na^+-MMT) was modified for intercalation by cationic surfactants having various alkyl chain lengths. Increase of alkyl chain length achieved more intercalation of the nanoclays, and the maximum *d*-spacing was 4.2 nm when modified by cetyltrimethyl ammonium bromide (CTAB). The modified nanoclay was then functionalized by isophorone diisocyanate-2-hydroxyethyl acrylate (IPDI-HEA) having a reactive acrylate group, which enhanced its compatibility within the polymer matrix. The composite layer formation using functionalized nanoclay still improved the mechanical and barrier properties. The pencil hardness was improved to 3H and impact energy increased to 150 mJ, while maintaining the original optical properties of the polyethersulfone (PES) substrate. Oxygen transmittance rate (OTR) was remarkably reduced from 250 to 18.5 cc/m^2 day and water vapor transmission rate (WVTR) was gradually decreased from 60 to 37.7g/ m^2 day with the increase of nanoclay content, respectively. Composite layers with functionalized nanoclay improved the properties of the PES substrate to be used in flexible displays.

Keywords: composite layer, nanoclay, cationic surfactant, barrier property, UV-curing.

Introduction

Plastic substrates are gaining much interest for its application to flexible display, since it has several advantages over the glass substrate such as light weight, flexibility and transparency.[1] Polyimide (PI) films were commercially developed by Dupont as a good candidate for substrate of flexible devices due to its high thermal distortion temperature around 350 ℃. However, they were not optically clear because it has yellowish color, which limit it from being applied to display devices. Therefore, several groups have reported the development of colorless polyimide films on which the flexible devices were demonstrated.[2] Semi-crystalline polymers, such as polyethylene terephthalate (PET), polyethylene naphthalate (PEN) were very promising substrate materials. They showed good transparency when compared to polyimide films and have widely been used for flexible display. Cho *et al*. reported the fabrication of organic light emitting diode (OLED) devices on highly flexible, transparent conductive oxide (TCO) coated PET.[3] Rahy *et al*. also reported that carbon nanotube (CNT) coated PEN films was applicable for flexible electronic devices such as solar cell, OLED and touch panel.[4] However, the low glass transition temperature of these semi-crystalline polymers still remains as drawback to be overcome.

Polycarbonate (PC) and polyethersulfone (PES) belong to amorphous polymer group and were also recommended as good alternatives for flexible plastic substrate. Especially, PES films had optical clarity and quite high operation temperature.[5] Therefore, many research groups studied the demonstration of flexible devices, such as organic thin film transistor (OTFT),[6] liquid crystal display (LCD),[7] and OLED[8-10] on PES substrates. Although intensive researches have been conducted on plastic substrates, there still remain much requirements to be fulfilled for its application to flexible display. Among those requirements, surface hardness and barrier properties to water vapor and oxygen permeation through substrate should be mainly considered. Additional layers were formed on plastic substrate to achieve the required mechanical and barrier performances. Many attempts have been made including thin oxide film formation.

Thin and transparent oxide layers, such as siliconoxide,[11] siliconnitride,[12] and siliconoxynitride[13] have been proposed as excellent barrier layers for flexible substrates. However, oxide layers deposited on polymer film have drawbacks as poor mechanical and adhesion properties, and difference in

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thermal expansion coefficient resulted in the crack formation on the surface.[14] To overcome the aforementioned demerits, new functional coating material and method were proposed to demonstrate the advantages over the conventional polymers. Nanocomposite hybrid layer based on organic polymers and inorganic materials have attracted the interest for the enhancement of the mechanical and barrier properties, and new nanocomposite materials were developed.[15]
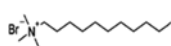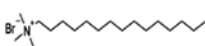
Nanoclay is known to play a role to improve the mechanical properties and barrier properties due to its large aspect ratio.[16] Since polymer/montmorillonite (MMT) composite was proposed by Toyota's research group in 1990's,[17] polymer/nanoclay composites have been intensively investigated. When the polymer/nanoclay composites were prepared by *in situ* polymerization, compatibility of nanoclay with polymer matrix played the main role in improving the performances. Generally, alkylammonium ions are used as good compatiblizing agents in the nanoclay composites.[18] Also, as nanoclays were modified using ammonium surfactants with functional groups, nanoclays has highly intercalated and exfoliated structures. Pinnavaia suggested that organically modified nanoclays using the long alkyl chain showed much larger interlayer distances in nanocomposites.[19] Wang *et al.* focused on the compatibility between organo-nanoclay and polyols.[20] In their works, as MMT was modified by using ammonium ions with long chain, its compatibility with various polyols was improved, which commonly used for synthesizing polyurethane. Additionally, incorporation of layered nanoclays with high aspect ratio in the composites represented the enhancement of the permeation-barrier properties of polymers.[21,22]

High aspect ratio of plate structure of nanoclays was attributed to the reduction in straightforward pathways of water vapor and oxygen molecule through the substrate, which results in the increase the effective path length and tortuosity for molecular diffusion. In this work composite layers were formed on plastic substrates using UV curable polymer and functionalized nanoclays to improve the barrier properties, surface hardness and impact strength of plastic substrate. The nanoclays were modified by cationic surfactants with various alkyl chain lengths, and then reacted with isophorone diisocyanate-2-hydroxyethyl acrylate (IPDI-HEA), subsequently. Effects of nanoclay modification on its compatibility with polymer were investigated in terms of the interlayer distance of nanoclays. Nanoclay content in composite layer was also examined and optimized for improvement of mechanical and barrier properties of substrates without any significant deterioration in optical performances.

Experimental

Materials. Sodium montmorillonite (Na$^+$-MMT) with cationic exchange capacity (CEC) of 90 mEq/100 g was provided by Southern Clay Product InC., USA. Surfactants

Table I. Cationic Surfactants for Nanoclay Modification

Tetramethyl Ammoniumbromide (TAB)	Dodecyltrimethyl Ammoniumbromide (DTAB-C$_{12}$)	Cetyltrimethyl Ammoniumbromide (CTAB-C$_{16}$)

such as tetr-amethylammonium bromide (TAB), dodecyltrimethyl ammonium bromide (DTAB), and cetyltrimethyl ammonium bromide (CTAB) were purchased from Aldrich Co., and specifications of surfactants used were described in Table I. Detailed synthesis and characterization procedures of half adduct of isophorone diisocyanate and 2-hydroxyethyl acrylate (IPDI-HEA, Aldrich Co.) were described elsewhere.[23] An aliphatic polyurethane acrylate, 1,6-hexamethyldiol diacrylate (HDDA) and trimethylolpropanetriacrylate (TMPTA) were supplied by Miwon Co., Korea and 1-hydroxy-cyclohexyl-phenyl-ketone (HCPK) was produced by Ciba Specialty Chemicals and used as a photoinitiator.

Composite Layer Formation Procedure. A schematic drawing of the procedure for the formation of polymer/nanoclay composite layers was presented in Figure 1. The first step was nanoclay modification by cationic surfactants, which was conducted through a cationic-exchange process. To investigate the effect of alkyl chain length on d-spacing of nanoclays, three different types of cationic surfactants, such as TAB, DTAB, and CTAB were used. 4.0 g of Na$^+$-MMT was dispersed in 500 mL of distilled water and stirred at room temperature for 1 h. The cationic surfactants were added to the Na$^+$-MMT suspended solution and stirred vigorously at 80 ℃ for 18 h. Amount of surfactant was two times of Na$^+$-MMT by weight for each cationic surfactant. The modified Na$^+$-MMT was washed repeatedly with distilled water until no AgBr precipitate was found by titrating the filtrate with 0.1 N AgNO$_3$ solutions.

Thus modified Na$^+$-MMTs were dispersed in 150 mL of toluene, and then water was removed by azeotropic distillation. The solution was cooled down to room temperature and mixed with 50 mmol of IPDI-HEA for functionaliza-
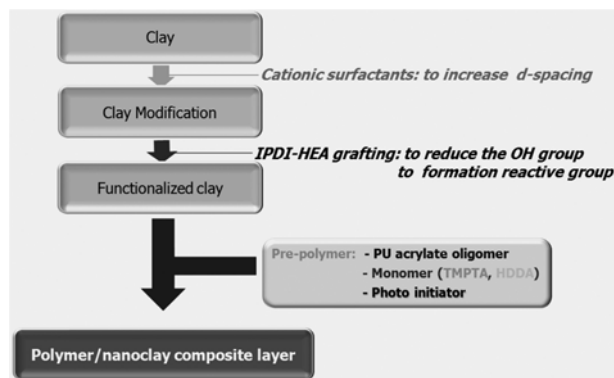

Figure 1. A schematic procedure for the formation of polymer/nanoclay composite layer.

tion of nanoclay. 0.1 wt% of dinbutyltin dilaurate (DBTDL) and 1,000 ppm of *p*-hydroxyanisole were added as a catalyst and antioxidant, respectively. The solution was vigorously stirred at 70 °C for 48 h. The products were collected by filtration and then repeatedly washed with toluene to remove the unreacted IPDI-HEA. Thus obtained functionalized nanoclays were added into the pre-polymer mixtures consisted of PU acrylate, 1,6-hexamethyldiol diacylate (HDDA) and trimethylol propane triacrylate (TMPTA) to make the composite coating solution, into which HCPK was added as a photoinitiator. Coating solution was mixed at room temperature for 5 h, and mixing efficiency was enhanced by ultrasonication for 30 min. The polymer/nanoclay composite solution was spin coated on PES substrate (SBT200, i-component Co., Korea) at 2,000 rpm for 20 s. PES films have little problems in terms of optical properties including birefriengence. They have been already adopted as plastic substrates for LCD, e-paper and electrowetting display devices. Solution coated substrate was UV-cured for 3 min at 1 kW by using a high pressure mercury lamp and coating layer thickness was controlled at 3 μm.

Characterizations. The X-ray diffraction (XRD) patterns were recorded using a Rigaku D/Max-rA rotating anode X-ray diffractometer equipped with a CuK$_\alpha$ tube and Ni filter (*k*=0.1542 nm). The Fourier transformed infrared (FTIR) spectra were obtained using a Perkin Elmer system 2,000 and thermogravimetric analysis (TGA) was performed by using SDT Q600 thermoanalyzer, TA Instruments at a heating rate of 5 °C/min from room temperature to 900 °C under N$_2$ atmosphere. The mechanical properties were measured using pencil hardness tester and falling ball impact tester. Hardness of the cured films was determined by a pencil hardness tester (CKH-100, CK Co., Korea). Falling ball impact energy was determined according to ASTM D5420 using a ball impact tester (Coad 704, Oceansci Co., Korea). The light transmittance of the cured film was measured using a spectrophotometer (MCPD-3000, Otsuka, Japan), and haze was determined using a haze meter (NDH 5,000, Nippon Denshoku, Japan). Water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) were determined using PERMATRAN model 3/33 OXTRAN-W model 2/21 (Mocon Inc., USA), respectively.

Results and Discussion

Nanoclay Modification by Cationic Surfactants. Effects of the alkyl chain length of the cationic surfactants on the intercalation of Na$^+$-MMT layers were examined using various cationic surfactants. Figure 2 showed the FTIR spectra change after the modification of Na$^+$-MMT by cationic surfactants. Modified nanoclays showed the new absorption peaks at 2910 and 2850 cm^{-1} assigned to the stretching vibration of -CH$_2$ and -CH$_3$, and at 1487 and 1475 cm^{-1} assigned to the bending of -CH$_2$ and -CH$_3$, which represented
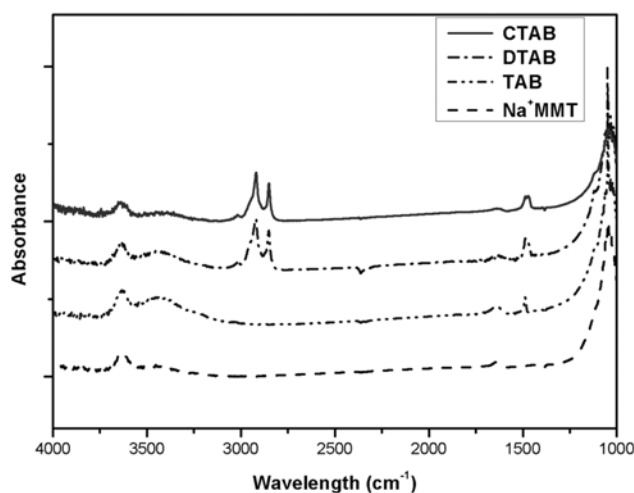

Figure 2. FTIR spectra of nanoclay before and after the modification with cationic surfactants.
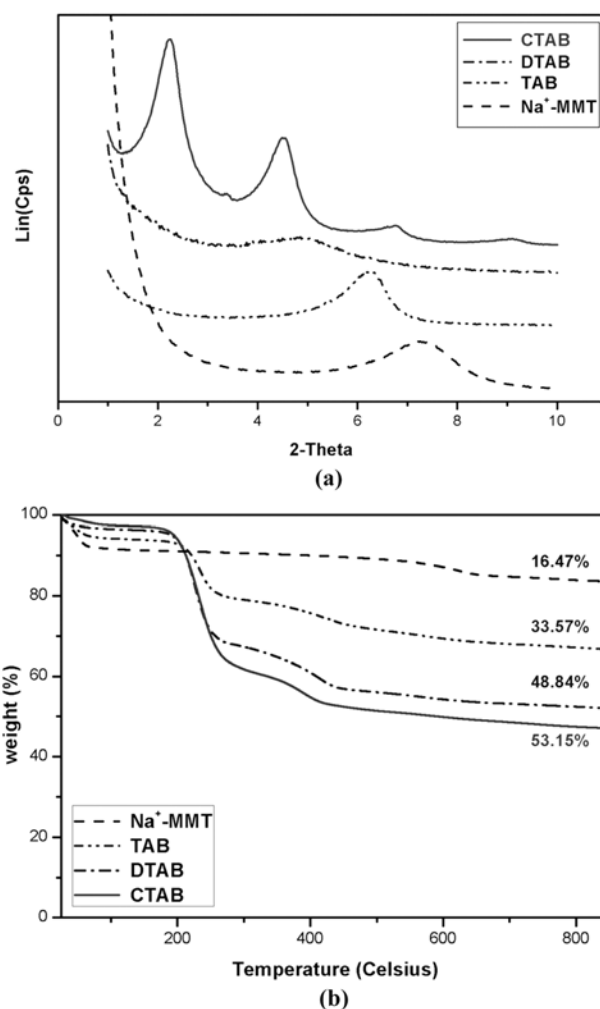

Figure 3. XRD patterns (a) and TGA thermograms (b) of nanoclay before and after the modification with cationic surfactants.

Table II. TGA and XRD Results Before and After the Modification of Nanoclay

| Nanoclays	2θ (degree)	d_{001} (nm)	Δwt (%)
Na$^+$-MMT	7.24	1.22	16.47
TAB(1)	6.25	1.41	33.57
DTAB(12)	4.83	1.83	48.84
CTAB(16)	2.10	4.2	53.15

that the Na$^+$-MMT was successfully modified by every cationic surfactant used. These results were in good agreement with previous observation on the cationic exchange reactions.[24]

The X-ray diffraction (XRD) patterns were also changed after modification by cationic surfactants as presented in Figure 3(a). Na$^+$-MMT showed the broad diffraction peak at $2\theta = 7.42°$, corresponding to d-spacing, $d(001)$ of 1.22 nm. After modification by cationic surfactant the XRD peaks were shifted to lower angle, which means the increase of interlayer spacing of Na$^+$-MMT. Interlayer spacing increased with increasing alkyl chains in cationic surfactant as summarized in Table II. When Na$^+$-MMT was modified with CTAB, the maximum interlayer spacing reached 4.23 nm.

TAB and DTAB performed uniform intercalation by showing single 2θ values, which are smaller than unmodified Na$^+$-MMT. CTAB has longer alkyl chain than TAB and DTAB, and degree of intercalation was much greater than the others by reaching $2\theta = 2.1°$. However, it was not easy for CTAB to evenly penetrate between clay layers due to molecular bulkiness, and degree of intercalation was not uniform by CTAB. Depending on the degree of intercalation several peaks were observed in this case. It was also reported that significant fraction of the initial inorganic phase with a spacing of 2.1 Å remains after curing reaction.[15]

Figure 3(b) shows the TGA curves for the modified Na$^+$-MMT's and unmodified one. Unmodified Na$^+$-MMT underwent 10 wt% weight loss around 80-110 °C due to the vaporization of bound water within the interlayers and also slight weight loss at higher temperature due to the unknown impurrity decomposition.[25] After modification by surfactants the weight loss of the water was not as serious as unmodified one. However, the weight loss above 200 °C was remarkably increased to 33.57, 48.84, and 53.15 wt% when modified by TAB, DTAB and CTAB, respectively. These indicated that the alkyl chain of surfactants chemically adsorbed into the nanoclays was decomposed. Therefore, based on the FTIR, XRD, and TGA results it could be concluded that nanoclay was successfully modified by cationic surfactants, and the interlayer spacing was effectively increased.

Functionalization of Nanoclay. Although the nanoclays were more intercalated through the cationic exchange reactions, they were not easy to be well dispersed within the
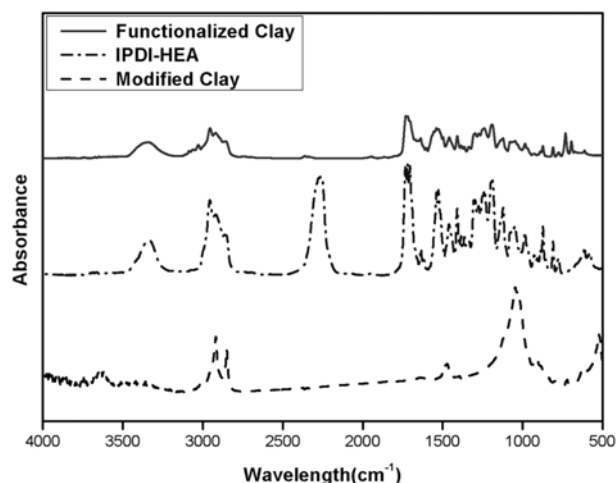
Figure 4. FTIR spectra of nanoclay before and after grafting with IPDI-HEA.
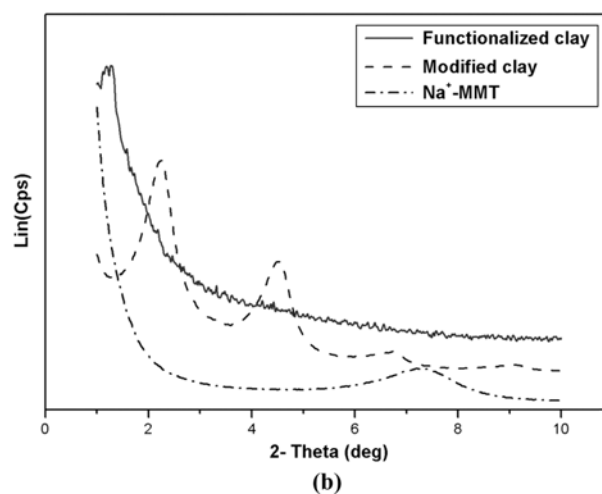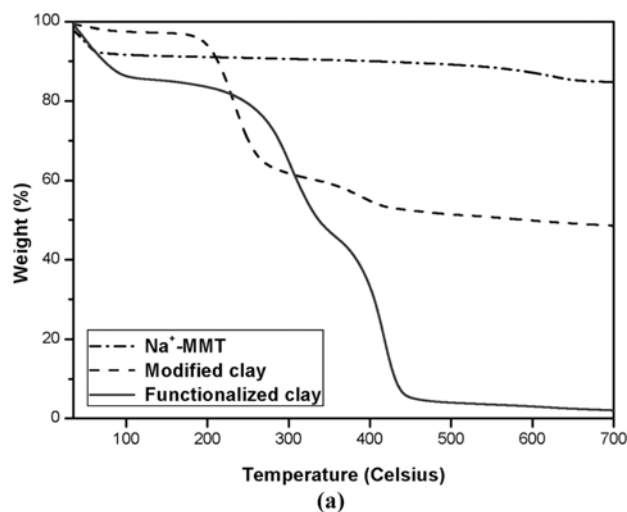
Figure 5. TGA thermograms (a) and XRD patterns (b) of nanoclay before and after grafting with IPDI-HEA.

polymer solution phase. To improve their compatibility with polymer, the modified nanoclays were functionalized by IPDI-HEA having reactive acryl groups. The FTIR spectra of IPDI-HEA, modified Na+-MMT and functionalized Na+-MMT by IPDI-HEA were compared with each other in Figure 4. IPDI-HEA has an absorption peak at 2268 cm^{-1} for NCO and the absorption peaks at 1720 and 1640 cm^{-1} for C=O and C=C from acrylate groups, respectively. After functionalization of Na+-MMT by grafting with IPDI-HEA, FTIR spectra had absorption peaks for C=O, C=C, while -NCO peak was eliminated. These results indicated that the IPDI-HEA was successfully grafted into the interlayer of modified Na+-MMT.

The TGA curves for Na+-MMT, modified and functionalized ones were presented in Figure 5(a). The weight loss of functionalized Na+-MMT was much greater than original and modified ones due to the decomposition of IPDI-HEA. The XRD patterns in Figure 5(b) showed that the interlayer spacing of functionalized Na+-MMT still increased due to the grafting inside the interlayer of modified Na+-MMT. From the XRD and TGA results, it could be found that the IPDI-HEA with reactive acrylate groups was successfully grafted into the interlayer of nanoclays. The acrylate groups in IPDI-HEA should enhance the compatibility of Na+-MMT with PU-acrylate oligomer to make homogeneous coating solution.

Property Changes by Composite Layer Formation. Properties of composite layers coated on PES substrate were investigated for its application to flexible display. Four samples have been tested and compared with each other such as bare PES film, organic layer without Na+-MMT, composite layer with modified Na+-MMT by CTAB and composite layer with functionalized Na+-MMT. CTAB/Na+-MMT=2/1 by weight and functionalized Na+-MMT content was 3 wt%.
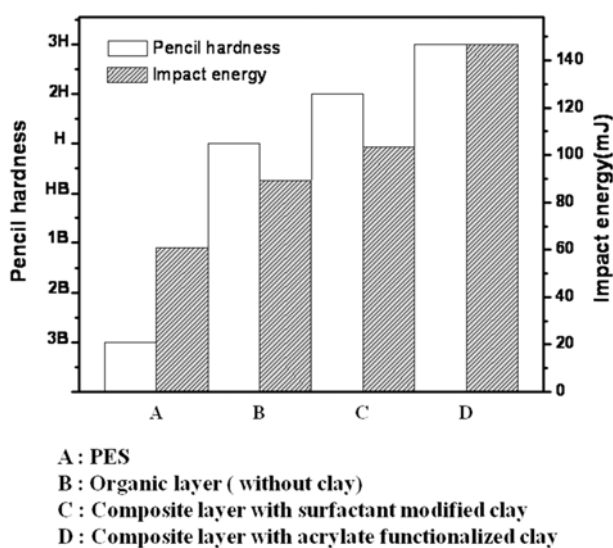
Figure 6. Mechanical property changes by various layer formation on PES substrate.

A : PES
B : Organic layer (without clay)
C : Composite layer with surfactant modified clay
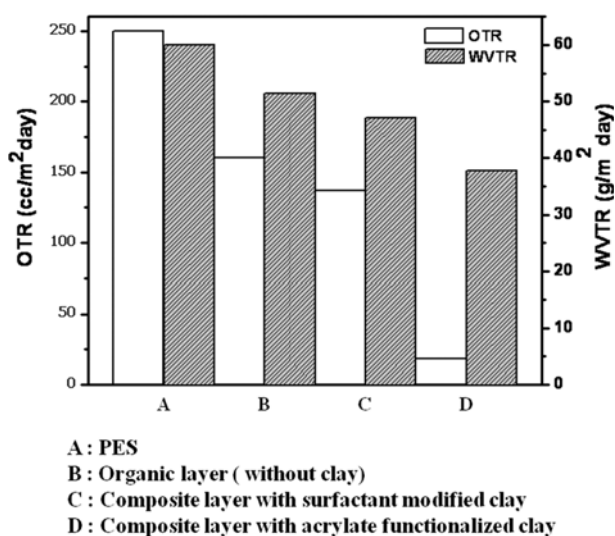D : Composite layer with acrylate functionalized clay

Figure 7. Barrier property changes by various layer formation on PES substrate.

Pencil hardness and impact energy were determined for various samples as presented in Figure 6. Original PES substrate had quite poor surface hardness and impact energy, and they were much improved after UV curing the organic prepolymer without Na+-MMT on PES substrate. When modified Na+-MMT was added to PU-acrylate prepolymer, the mechanical properties were improved due to the intercalation of Na+-MMT. Functionalized Na+-MMT still enhanced both properties due to more enhanced intercalation and miscibility by grafting IPDI-HEA. These results are in good agreement with Wei's work,[26] in which they demonstrated that surface hardness and impact strength of the coated PES substrate were improved by addition of nanoclays with high aspect ratio and platelet structure.

Nanoclays with high aspect ratio and platelet structure in the composite layer tended to decrease the permeation of gas through substrate. Barrier properties of the above mentioned four samples were examined as represented in Figure 7. Original PES film showed poor barrier properties, and organic layer formation by UV curing without nanoclay on PES substrate somewhat decreased the both WVTR and OTR. Addition of modified Na+-MMT made contributions to still reduce WVTR and OTR. However, reductions of WVTR and OTR were not enough to be applied to flexible display. If functionalized Na+-MMT was used in composite layer, OTR was remarkably reduced. These results indicated that the nanoclays within composite layer made the longer diffusion path for oxygen molecules.[27] WVTR was gradually reduced but its reduction was not as great as OTR reduction. Improvement of compatibility of functionalized Na+-MMT with prepolymer enhanced its dispersion in composite coatings.

Effects of Functionalized Na+-MMT Content in Composite Layer. The composite layers were formed on the plastic
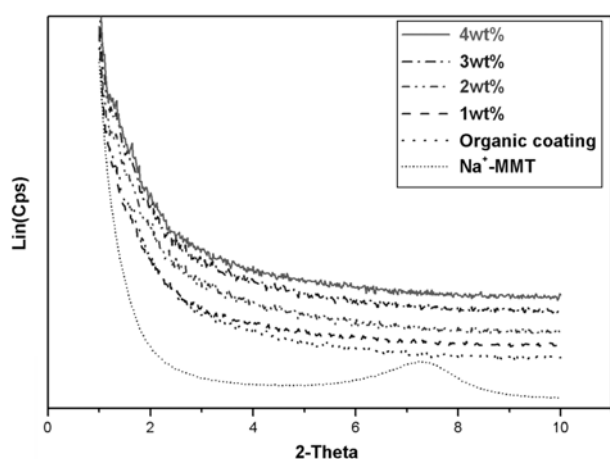
Figure 8. XRD patterns of Na$^+$-MMT and composite layers with various nanoclay contents.

substrates by using various functionalized Na$^+$-MMT contents from 0 to 4 wt%, and their XRD diffraction peaks were obtained as shown in Figure 8. Diffraction peak of *d*-spacing, *d*(001) was observed for Na$^+$-MMT, but no diffraction peaks were observed in organic and composite layers on PES substrates. Organic layer with no nanoclay had to be free from diffraction peak. Composite layer with functionalized Na$^+$-MMT were dispersed uniformly and fully exfoliated in the composite layers for the nanoclay content up to 3 wt%. At 4 wt% of nanoclay content diffraction peak appeared again, which seemed to be caused by the agglomeration of nanoclay and no more exfoliation was valid at high nanoclay content.

Improvement of the compatibility with polymer matrix using reactive group achieved the exfoliation of Na$^+$-MMT. The composite layer with functionalized Na$^+$-MMT was proved to achieve the significant enhancement in mechanical and barrier properties. As presented in Table III, increase of nanoclay contents in composite layers enhanced the mechanical properties such as surface hardness and impact strength. Optical properties were slightly deteriorated with composite layer formation in terms of light transmittance, haze and yellow index as listed in Table IV. However, nanoclay size was much smaller than

Table III. Mechanical Property Variations of Composite Layers with Nanoclay Contents

Nanoclay Contents (wt%)	Pencil Hardness	Falling Ball Impact Strength (mJ)
0	H	89.3
1	H	108.5
2	2H	114.9
3	3H	146.8
4	3H	153.2

Table IV. Optical Property Variations of Composite Layers with Nanoclay Contents

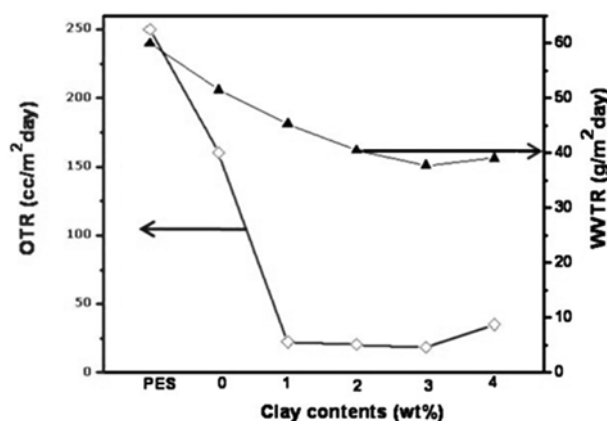| Nanoclay Contents (wt%)	Light Transmittance (%)	Haze	Yellowness Index
0	91.03	0.37	2.45
1	88.98	0.46	3.8
2	90.0	0.72	3.2
3	88.87	0.76	4.9
4	82.4	0.98	6.1

Figure 9. OTR and WVTR of composite layers with various nanoclay contents.

the wavelength of visible light and showed the light transmittance around 90%, which assured its application to optical devices.

Effects of clay content on OTR and WVTR were examined as shown in Figure 9. Both OTR and WVTR were decreased with the increase of clay content in composite layer on the substrate. OTR was decreased to the level less than 10% of original value by addition of clay by 1 wt% and maintained this value up to 3 wt% of clay content. These results indicated that the fully exfoliated clays have good dispersion in composite layer and it increased the tortuous path for oxygen molecules. WVTR was not as much reduced as OTR, but it continuously decreased with clay content up to 3 wt%. At the clay content of 4 wt%, both OTR and WVTR increased again, which corresponded with the diffraction peak formation in Figure 8. Excess clay content caused the agglomeration of nanoclay, which was responsible for returning from exfoliation state to intercalation state again to result in the increases of OTR and WVTR.

Conclusions

The polymer/functionalized nanoclay composite layers were successfully formed on PES substrates *via* UV curing process. Na$^+$-MMT was modified by cationic surfactant to increase the *d*-spacing by intercalation, which means that

polymer could be more inserted into Na^+-MMT layers during the polymerization. Alkyl chain length of surfactant had influence on the intercalation and CTAB increased the *d*-spacing of Na^+-MMT from 1.22 to 4.23 nm. When modified Na^+-MMT was grafted with IPDI-HEA for functionalization, its compatibility with prepolymer was improved to make homogeneous composite layer with well dispersed nanoclays. Polymer/functionalized nanoclay composite layers enhanced surface hardness, barrier property and showed good optical properties. The optimum nanoclay content was 3 wt%, at which the composite layers showed the best performances. However, excess nanoclay content reduced the performance of composited layer due to the agglomeration of nanoclay.

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