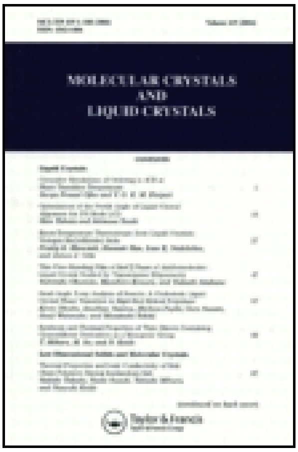

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Barrier Coating for Flexible Display with Intercalated Nanoclay Composite

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Polymer/nanoclay composite layer was coated on plastic substrates for flexible display to improve its barrier properties. Sodium montmorillonite (Na^+-MMT) nananoclay was modified by organic intercalation agents to enhance the d-spacing and compatibility with polymer. Combination of 3-aminopropyl trimethoxysilane(APS) and 3-trimethoxysilyl propyl methacrylate(MAPTMS) achieved d-spacing as 5.78 nm at the best ratio of 1:3 as predicted in mechanism study. Modified nanoclay formed a pre-polymer mixture with polyurethane-acrylate (PUA) to make a composite layer by UV-curing process. For PEN substrate oxygen transmittance rate(OTR) was much reduced to below 0.22 cc/m^2 day, which was much better than the other composite layer with common nanoclay. Water vapor transmission rate(WVTR) was also reduced after nanoclay composite layer formation on polyethylene naphthalate(PEN) and polyethersulfone(PES) substrates. Excess amount of nanoclay tended to agglomerate to deteriorate the barrier properties. Optical properties of PUA/clay composite layer were slightly affected and showed good performances for their application to display devices.

Keywords Nanoclay; composite layer; barrier property; plastic substrate

1. Introduction

Flexible display is expected to be a main part of future display technology, due to its several advantages over the conventional display devices made of glass substrate. Many materials and parts are required in developing flexible display, and substrate with light weight, flexibility and transparency is the most important one among those [1,2]. Plastic substrates are recommended for this purpose, but they have serious problems in terms of barrier properties to water vapor and oxygen, because liquid crystal and organic light emitting diode (OLED) materials are weak to water vapor and oxygen attack [3]. Therefore, barrier properties should be equipped with the plastic substrates, and various barrier coating processes on plastic substrate have been attempted

Several research groups reported that the deposition of oxide layer coating with SiO_x, Al_xO_y had promoted the barrier properties of the plastic substrates [4,5]. However, deposition processes of oxide layer are usually much complicated batch processes requiring

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*Address correspondence to Prof. Sung Soo Kim, Department of Chemical Engineering, Regional Innovation Center for Components and Materials for Information Display, Kyung Hee University, Yongin 446-701, Korea. Tel: (+82)31-201-3257; Fax: (+82)31-204-3294. E-mail: sungkim@khu.ac.kr high vacuum and high temperature. Therefore, they require too much cost to be applied to production scale.

To overcome these demerits, nanoclay composite layer formed by relatively simple process was proposed, which is based on the hybrid of organic polymer and inorganic nanoclay [6]. Nanoclay is a promising material, because it has a 1 nm-thick planar structure, high in-plane strength, and a high aspect ratio [7]. Nanoclay composite layer is usually formed by conventional wet coating process, which requires quite low cost and can be performed by continuous process for mass production scale.

Since the development of clay/polyamide nanocomposite by Toyota's research group [8,9] in 1990, a number of clay/polymer nanocomposites layer have been investigated to enhance the thermal stability [10,11] as well as the mechanical properties [12]. High aspect ratio of nanoclay was proved to improve the barrier properties [13–15], because it might attribute the reduction in straightway movement of water vapor and oxygen molecule, which results in increasing the effective paths for diffusion of each molecule [16]. Several reports have shown that the dispersion of nanoclay and the morphology of the nanocomposite depend on various factors, such as the mixing method [17], mixing speed [18], and clay content [19].

In this study, we prepared poly urethane-acrylate (PUA)/nanoclay composite layers using the modified clay with organic intercalation agents. Interlayer distance of nanocly was increased by using intercalating agents synthesized with silane coupling agent by sol-gel process. Several process parameters were investigated for improvement of barrier properties. Application of shear force during the coating process was also examined to improve the barrier properties.

Experimental

Materials

Na^+-MMT with cationic exchange capacity (CEC) of 90 mEq/100 g was supplied by Southern Clay Product Co., USA. 3-Aminopropyl)trimethoxysilane(APS), and 3-(Trimethoxysilyl) propyl methacrylate (MAPTMS) were used as intercalation agents and supplied by Aldrich Co. Isophorone diisocyanate (IPDI), poly (ethylene glycol) (PEG), 2-hydroxyethyl acrylate (HEA) were used for PUA formation with dibutyltin dilaurate (DBTDL) as a catalyst, which were also supplied by Aldrich Co. 1, 6-hexamethyldiol diacrylate (HDDA) and trimethylolpropane-triacrylate (TMPTA) were added to make coating solution, and they were purchased from Miwon Co., Korea. 1-Hydroxy-cyclohexyl-phenyl-ketone (HCPK) was used as a photo initiator, which was manufactured by Ciba Specialty Chemicals and supplied by Shin Young Radchem.Co., Korea. polyethylene naphthalate (PEN)(Q65) substrate was provided by Teijin DuPont Films and polyethersulfone (PES) substrate (SBT200) was provided by i-components Co., Korea.

Intercalation of Na^+-MMT

The mechanism of clay modification was represented in Fig. 1(a). It is very important to disperse the nanoclay within the polymer matrix, and also the polymer should be penetrated into the spacing between the nanoclay layers. Therefore, intercalating agent were synthesized by sol-gel process from MAPTMS with acrylate group and APS with ammonim group, and intercalation of nanoclay increased the d-spacing of nanoclay and enhanced the compatibility of nanoclay with polymer matrix.

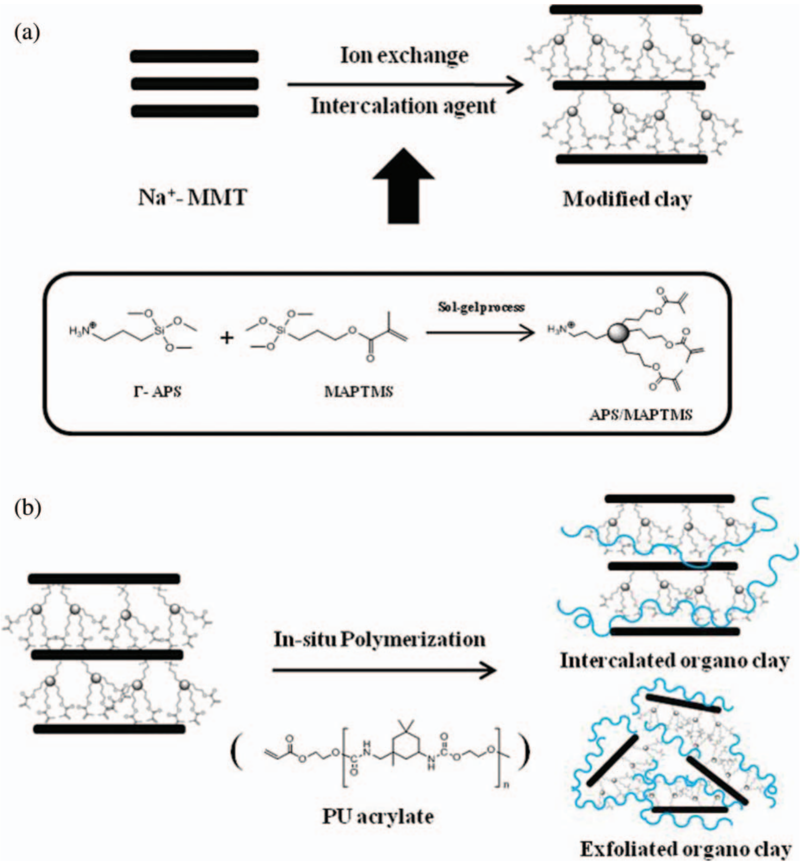

Figure 1. Mechanisms of (a) clay modification with intercalation agent and (b) PUA/modified clay composite formations.

The synthesis of intercalation agent was conducted by the following procedure. Specified amount of APS and MAPTMS were added in 100 ml of anhydrous ethanol at several compositions as APS:MAPTMS = 1:1. 1:2, 1:3, 1:4. 1ml of distilled water was added and the mixture was vigorously stirred at 60°C for 24 hrs. Na^+-MMT was modified with organic intercalation agents (APS/MAPTMS) to increase the interlayer spacing and to improve the compatibility with polymer. Under nitrogen atmosphere, 5.0 g of Na^+-MMT was dispersed in 200 ml of distilled water at room temperature for 1 hrs, and 10 g of APS/MAPTMS was added to the Na^+-MMT suspended solution and stirred vigorously at 70°C for 2 hrs. The solution were repeatedly centrifuged and rinsed with distilled water and dried for characterization.

Composite Layer Formation via iN-Situ Polymerization

The mechanism of polymer/nanoclay composite formation was represented in Fig. 1(b). Modified Na^+-MMT with intercalating agent was added to 40 ml of DMF, and was stirred under nitrogen atmosphere at room temperature for 1 hr. Then it was blended with PEG and IPDI at 70°C for 2 hrs for synthesis of polyurethane via in-situ polymerization with 0.01wt% of DBTDL as a catalyst and then cooled to 50°C. HEA was added for grafting acrylate functional group and stirred for 1.5 hrs, and 1, 4-butanediol was added and stirred at room temperature for 2 hrs. PUA/nanoclay composite solution was mixed with HDDA, TMPTA, and HCPK at room temperature for 3 hrs, and solvents were vaporized by vacuum distillation for 1 hr. PEN, PES substrates were cleaned in methanol for 10 min by using an ultrasonicator, and dried at 80%. To increase the adhesion between substrate and coating layer, the plastic substrate was oxygen plasma treated for 1 min. Solution coating was conducted on PEN, PES substrates by using a bar coating apparatus at a coating thickness of 2 microns, and then it was UV-cured for 3 min at 1 kW by using a high pressure mercury lamp.

Characterizations

The chemical structure of the modified clay by intercalating agent were confirmed by Fourier transformed infrared (FTIR), System 2,000, Perkin Elmer Co. The X-ray diffraction (XRD) patterns were obtained from a Rigaku D/Max-rA rotating anode X-ray diffractometer equipped with a Cu Ka tube and Ni filter (k = 0.1542 nm). The light transmittance of the nanoclay composite film was measured using a color filter spectral multi channel spectrophotometer, MCPD-3000 of Otsuka Co., Japan. Haze was determined using a NDH 5000, Nippon Denshoku Co. Japan. The barrier properties of the substrates were characterized by measuring oxygen transmission rate (OTR) and water vapor transmission rate (WVTR). OTR and WVTR were determined by using the OXTRAN-W model 2/21 and Permatran-W model 3/33, Mocon Inc., USA., respectively.

Results and Discussion

Clay Modification

The FTIR spectra of modified Na$^+$-MMT by APS/MAPTMS at various concentration were compared with original Na$^+$-MMT in Fig. 2. The modified clay showed new absorption peaks at 2,800 □$^{-1}$ and 2,900 □$^{-1}$ for $-CH_2$ and $-CH_3$ stretching vibration, respectively and these peaks were increased with MAPTMS content. It also showed the absorption peaks at 1,720 cm^{-1}, 1,640 cm^{-1} for C=O, C=C, respectively from acrylate groups, and

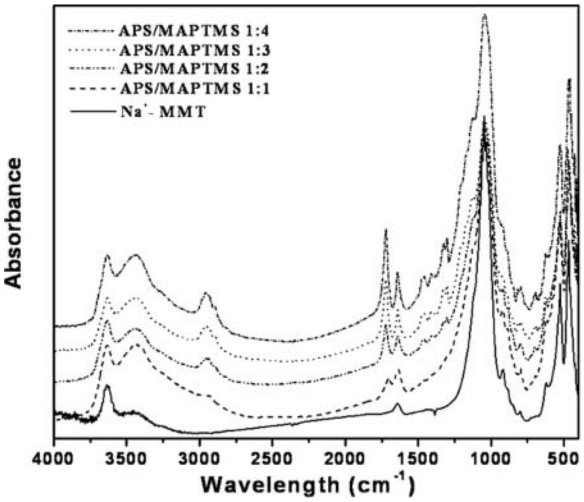

Figure 2. FT-IR spectra of clay modification with APS/MAPTMS.

Table 1. XRD results of nanoclay modified with APS/MAPTMS at various ratios

APS/MAPTMS ratio	2θ (degree)	d_{001} (nm)
Unmodified Na-MMT	7.2	1.4
1:1	3.1	2.9
1:2	2.23	3.8
1:3	1.52	5.78
1:4	1.64	5.1

both peaks increased with MAPTMS content. These results indicated that the nanoclays were successfully modified with APS/MAPTMS, and more acrylate groups were formed with the increase of relative amount of MAPTMS.

The X-ray diffraction(XRD) patterns of modified clay and Na^+-MMT were presented in Fig. 3, where Na^+-MMT have broad diffraction peak appeared at $2\theta = 7.42^o$, corresponding to a d-spacing of 1.44 nm. The d-spacing of modified clay was increased with relative amount of MAPTMS as summarized in Table 1. Maximum d-spacing of Na^+-MMT was achieved by modification with intercalating agent to reach 5.78 nm at mole ratio of APS:MAPTMS = 1:3. Optimum ratio of APS:MAPTMS was 1:3 and it corresponded with the mechanism proposed in Fig. 1(a). Above the APS:MAPTMS = 1:3, the d-spacing could not increase anymore, and it decreased to 5.1 nm at APS:MAPTMS = 1:4. These result showed that increase of relative amount of MAPTMS in intercalating agent could not further increase the d-spacing of clay.

Based on the results obtained for FT-IR and XRD analyses it could be concluded that nanoclay was well modified by the intercalating agent with acrylate group made of APS and MATPMS. Relative amount of MATPMS in intercalating agent had influences on the d-spacing, which showed the maximum values at APS:MAPTMS = 1:3.

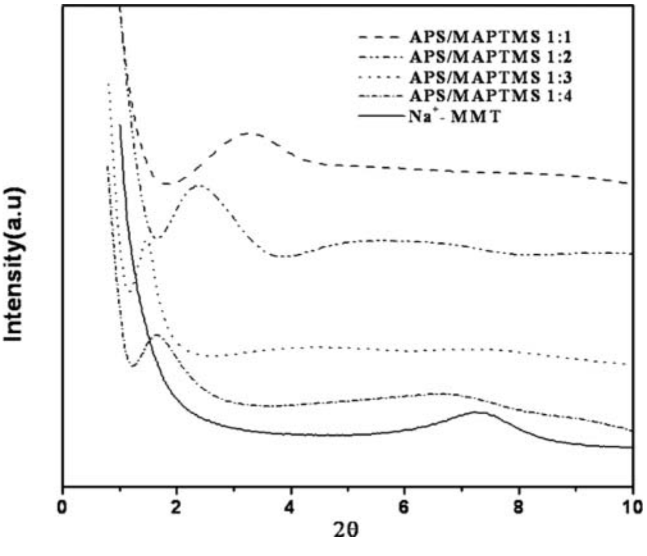

Figure 3. XRD pattern of clay modification with APS/MAPTMS.

PUA/Clay Composite Layer Formation on PEN, PES Substrate

Figure 4(a) showed the XRD patterns of the PUA/nanoclay composite coating on PEN with various clay contents. At the clay content of 1wt% the diffraction peak was shifted to the lower angle, which means intercalation. However, increase of clay content to 3 to 5 wt% resulted in no diffraction peak, which can be interpreted as exfoliation of nanoclay. However, the composite containing 7 and 10wt% of clay showed the diffraction peaks again due to the agglomeration of excess nanoclay. It was confirmed that the clay was exfoliation in composite layers at 3–5 wt% of clay content, which has been coupled with improving the barrier properties [20].

The XRD patterns of the PUA/nanoclay composite coating on PES with various clay contents were presented in Fig. 4(b). Increase of clay content up to 5 wt% shifted the

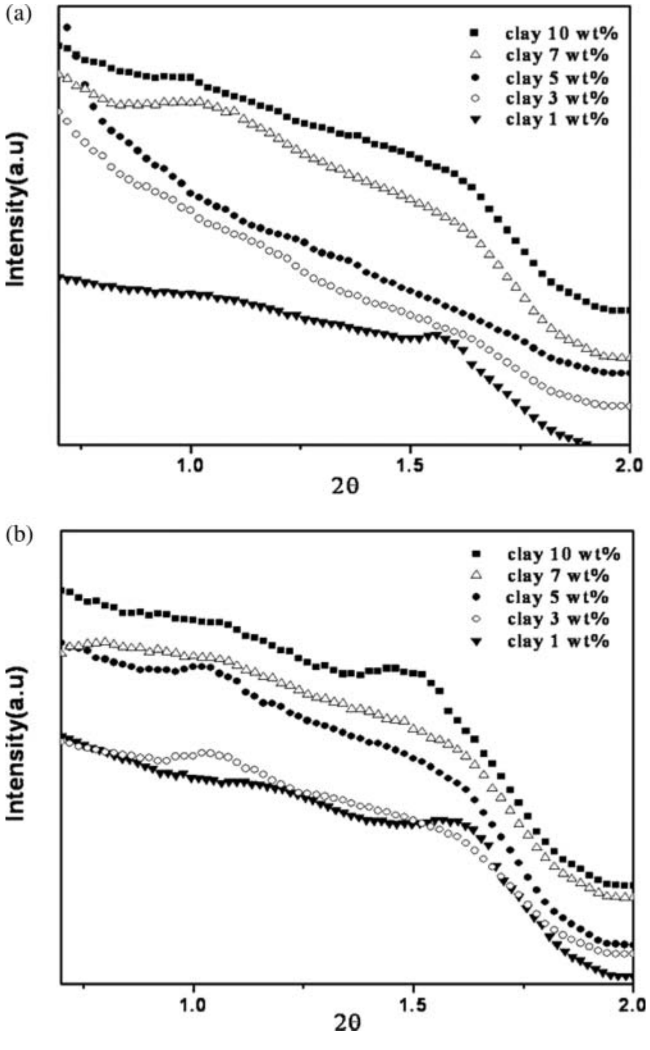

Figure 4. XRD pattern analysis of polymer/naoclay composite layers on PEN(a) and PES(b) films with different clay content.

diffraction peak to lower angle to represent the intercalation, and at 7wt% no peak is observed to stand for the exfoliation. At 10wt% diffraction peak appear again due to the agglomeration of excess nanoclay.

Barrier properties of PUA/clay composite coated on PEN and PES substrates were determined for different clay contents as shown in Fig. 5. Basically bare PEN has better barrier properties than bare PES. PEN substrate showed the minimum OTR values at 3 and 5wt% of nanoclay contents shown in Fig. 5(a), which corresponded with the exfoliation state as proved in XRD data in Fig. 4(a). WVTR for PEN substrate also showed the minimum around the nanoclay content of 3 wt%. These results indicated that exfoliated nanoclays of plate structure formed a planar barrier layer which caused the longer diffusion path for oxygen molecules [21,22].

WVTR and OTR of PES film were also enhanced by the nanoclay composite layer formation on it as shown in Fig. 5(b). However, enhancement of barrier properties of PES

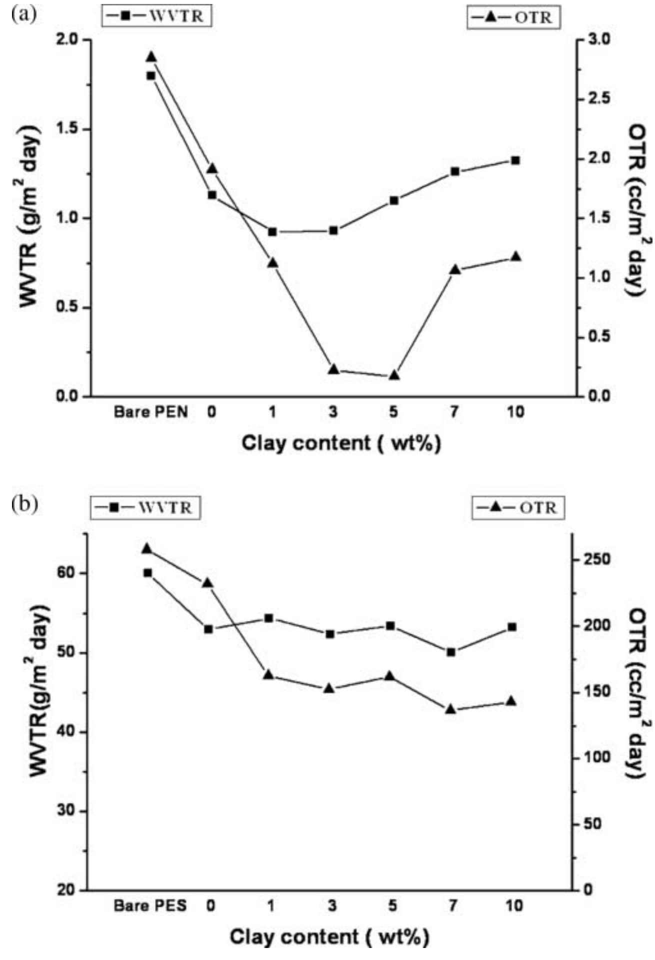

Figure 5. OTR and WVTR of PUA/nanoclay composite layer coating on PEN(a) and PES(b) substrates with different clay contents.

Table 2. Light transmittance and haze of PUA/nanoclay composite layer formed on PEN, PES substrates with different clay contents

	PEN		PES	
Clay content (wt%)	Haze	Light Transmittance at 550 nm (%)	Haze	Light Transmittance at 550 nm (%)
0	0.87	100	0.11	100
1	1.59	98.1	0.72	98.1
3	1.74	97.7	1.19	93.7
5	1.83	97.2	1.43	92.6
7	3.02	91.9	2.37	91.2
10	4.41	86.0	2.87	89.2

film was not as much as PEN film, since bare PES film itself has inferior barrier properties to bare PEN film. Barrier properties achieved in this work were not as good as those for commercial applications. However, the process developed requires less cost than other processes and can be performed as a continuous process for mass production. It can be combined with inorganic layer deposition process to ensure the excellent barrier properties. Further works to enhance the barrier properties are conducted for both nanoclay composite process optimization and hybrid process deveopment with atomic layer deposition process. Both WVTR and OTR decreased with nanoclay content up to 7wt%, which also corresponded with the XRD results in Fig. 4(b). Nanoclay content had influences on barrier properties of both PEN and PES films, but excess amount of nanoclay tended to agglomeration to deteriorate the properties. It could be also concluded that nanoclay composite coating depended on the kinds of substrate surface even though same coating solution was applied.

Optical property changes were summarized in Table 2 for PEN and PES films after nanoclay composite layer formation with different nanoclay content. The light transmittance decreased and haze increased with nanoclay content for both films as expected. But both changes were acceptable in terms of display application. Too high nanoclay content caused the agglomeration of nanoclay to deteriorate the optical properties. Especially for PEN film 10 wt% of nanoclay seriously deteriorated both transmittance and haze.

Conclusions

PUA/nanoclay composite layers were successfully formed on PEN and PES substrates. The interlayer spacing of modified clay with new functional organic intercalation agent was increased from 1.44 nm (Na^+-MMT) to 5.78 nm. Optimum ratio of APS:MAPTMS = 1:3, which was predicted in mechanism study. Modified clays had good compatibility with polymer and polymer could penetrate into the space between the layers. PUA/clay composite layer enhanced the barrier properties of PEN and PET substrates. Especially OTR was remarkably decreased for PEN, and optimum clay content was at 3–5 wt%, at which they were fully exfoliated. PES showed relatively inferior barrier properties to PEN, and showed gradual decreases of WVTR and OTR with nanoclay content up to 7 wt%. Excess amount of nanoclay tended to agglomerate with each other and deteriorated the properties. Optical properties of PUA/clay composite layer showed relatively satisfactory performances of PEN and PES substrates for their application to display devices. Hybrid process development with atomic layer deposition process is conducted to secure the barrier properties for commercial applications.

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References

[1] Logothetidis, S. (2008). *Mater. Sci. Eng. B.*, *152*, 96.
[2] Bae, S. J., Lee, J. W., Park, J. S., Kim, D. Y., Hwang, S. W., Kim, J. K., & Ju, B. K. (2006). *Jpn. J. Appl. Phys.*, *45*, 5970.
[3] Mo, Y. G. (2008). *News & Information for Chemical Engineers*, *26*(3), 306.
[4] Bieder, A., Gruniger, A., & Rudolf von, Ph. (2005). *Surface & Coatings Technology*, *200*, 928.
[5] Carcia, P. F., *et al.* (2009). *J. Appl. Phys.*, *106*, 023533.
[6] Triantafyllidis, K. S., LeBaron, P. C., Park, I., & Pinnavaia, T. J. (2006). *Chem. Mater.*, *18*, 4393.
[7] Tjong, S.C. (2006). *Materials Science and Engineering*, *53*, 73.
[8] Kojima, Y., Usuki, A., Kawasumi, M., Okada, A., Fukushima, Kurauchi, T., & Kamigaito, O. (1993). *J. Mater. Res.*, *8*, 1185.
[9] Yano, K., Usuki, A., & Okada, A. (1997). *J. Polym. Sci., Part A: Polym.Chem.*, *35*, 2289.
[10] Leszczy′nska *et al.* (2007). *Thermochimi. Acta*, *454*, 1.
[11] Xidas, P. I., & Triantafyllidis, K.S. (2010). *European Polymer Journal*, *46*, 404.
[12] Miyuki Harada, Takeharu Miyamoto, & Mitsukazu Ochi. (2009). *J. Polym. Sci., Part B: Polym. Phys.*, *47*, 1753.
[13] Toselli, M., Pilati, F., & Marini, M. (2008). *European Polymer Journal*, *44*, 3256.
[14] Ploehn, H. J., Liu, C., (2006). *Ind. Eng. Chem. Res.*, *45*, 7025.
[15] Xu, R., Manias, E., Snyder, A. J., & Runt, J., (2008). *Macromolecules*, *34*, 337.
[16] Choudalakis, G., & Gotsis, A.D. (2009). *European Polymer Journal.*, *45*, 967.
[17] Heidarian, M., Shishesaz, M. R., Kassiriha, S. M., & Nematollahi, M. (2011). *J. Coat. Technol. Res.*, *8*(2), 265
[18] Bae, H. J., *et al.* (2009). *LWT—Food Science and Technology.*, *42*, 1179.
[19] Sothornvit, R., Hong, S. I., An, D. J., & Rhim, J. W., (2010). *LWT—Food Science and Technology*, *43*, 279.
[20] Tan H., *et al.* (2008). *Polymer Degradation and Stability*, *93*, 369.
[21] Grunlan. J.C., Grigorian, A., Hamilton, C. B., & Mehrabi, A. R., (2004). *J. Appl. Polym. Sci.*, *93*, 1102.
[22] Rhim, J.W., *et al.* (2009). *LWT—Food Science and Technology*, *42*, 612.