Enhancement of physical and optical performances of polycarbonate-based diffusers for direct-lit LED backlight unit by incorporation of nanoclay platelets

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ABSTRACT: Using twin-extrusion compounding followed by compression molding processes, polycarbonate/clay nanocomposite optical diffusers with highly intercalated and exfoliated nanostructure could be prepared for application in direct-lit LED backlight unit. The incorporation of nanoclay platelets with an appropriate level of content substantially improved thermal resistance, as well as thermo-mechanical, and mechanical flexural properties. The optical property of luminance uniformity with respect to both location and viewing angle was also enhanced by the load of nanoclay platelets along with silicone bead, probably due to efficient scattering and diffusion action of the nanoclay. However, excess loading of nanoclay had insignificant effect on the improvement of properties for the nanocomposite diffusers. In addition, the presence of nanoclay platelets in the PC matrix effectively suppressed the moisture absorption rate, suggesting the feasibility of avoiding the warpage phenomena of the optical diffuser during use. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2016, 133, 42973.

INTRODUCTION

The liquid crystal display (LCD) has been widely used in information technology (IT) products because of its sharp picture, high-speed response, and easy access to ultralight and slim structures. In order to provide homogeneous light source on an LCD, a backlight unit (BLU) is necessary because liquid crystals do not emit light.[1–3] A typical BLU of LCD consists of a light source and optical materials. As a light source, the conventional cold cathode fluorescent lamp (CCFL) or flat fluorescent lamp (FFL) have been used, but recently are being rapidly replaced by light-emitting diodes (LED), which have many advantages such as good color reproduction, good durability, low power consumption, and environmental friendliness.[4–6] As optical materials, various types of polymeric sheets or films such as light-guide plates (LGP), diffuser sheets, prism films, and bright enhancement films (BEF), have been used to induce transmission, multiple reflections and refractions of incident light rays.[7–9]

The BLU can be classified into two different types, edge-lit and direct-lit BLU, according to the location of the light source. The edge-lit backlight system, which is capable of slimmer and light-weight LCDs, has been typically utilized for small-sized displays of IT products such as mobile phones and notebook computers, because of its limitation in the achievement of high luminance and good luminance uniformity for large-sized displays. On the other hand, direct-lit backlight system offers the feasibility of production of large-sized display with very high luminance. Among the various polymeric optical materials used in this direct-lit backlight system, the diffuser sheet is the most significant material, as it functions to convert linear or point light sources into uniform planar light sources and thereby increasing the luminance uniformity by scattering and diffusing the light rays emerging from the lamp.[10] For obtaining slimmer displays, however, reducing the distance between the diffuser and lamp can easily give rise to severe thermal deformation of the diffuser because of high heat energy transferred from the lamp located at bottom of BLU. Accordingly, there is a need for development of a diffuser with improved thermal and mechanical properties as well as optical performance.

Recently, incorporation of crosslinked polymeric beads, such as polystyrene (PS), poly(methyl methacrylate) (PMMA), and silicone, has been attempted to improve the physical properties as well as optical performances of compound-type diffusers prepared via extrusion compounding followed by a casting roll process.[11–13] In particular, Kim et al. reported that thermally

induced warpage phenomena, which is a significant problem for the diffuser of direct-lit BLUs, was effectively prevented, and the thermo-mechanical properties were also improved by addition of inorganic glass fibers as reinforcements besides polymeric beads during the extrusion compounding process.[14] In our previous study, we confirmed that the incorporation of inorganic porous silica particles combined with PMMA beads into the polycarbonate (PC) matrix remarkably enhanced the thermal and mechanical properties as well as the luminance uniformity for the compound-type diffuser.[15]

In this study, we attempted an incorporation of organically modified montmorillonite nanoclay platelets as reinforcements to enhance the physical and optical properties of PC-based diffusers of direct-lit LED backlight units. To date, there have been no reports in the literature for optical nanocomposite diffusers prepared by incorporation of nanoclay platelets into the polymers. PC/clay nanocomposite diffusers containing silicone beads as basic diffusing agent were prepared via twin-extrusion compounding followed by hot-melt compression molding. We investigated the nanostructured morphology including the degree of intercalation and exfoliation in the prepared nanocomposites using both XRD analysis and TEM observation. The correlation between the level of clay loading and the resulting optical, thermal, and mechanical properties of the nanocomposite diffusers was also explored. In addition, we examined the effect of nanoclay inclusion on moisture permeation resistance property of the diffusers to present practical guidelines to avoid warpage phenomena.

EXPERIMENTAL

Materials and Preparation

Thermoplastic polycarbonate (PC) as the matrix resin was purchased from Sabic Co. with grade name of 103R. The organically modified montmorillonite (MMT) clay used as the nanoscale inorganic reinforcement in this study was obtained from Southern Clay Products with the commercial name of Cloisite 30B (C30B, CEC (cation exchange capacity): 90 mequiv/100 g) and, was modified with a quaternary ammonium salt containing one methyl, one tallow, and two hydroxyethyl groups. As the basic diffusing agent, organic polysilicone bead purchased from Momentive Performance Materials with an average size of 3 μm in diameter was used.

Prior to the melt-compounding process, PC resin in the form of pellets and polysilicone beads were dried in a convective drying oven at 60°C for 24 h, and powdery nanoclays were dried in a vacuum oven at 80°C for 12 h to eliminate moisture contained within the materials. The melt compounding of PC with the diffusing beads and nanoclay particles (C30B) was performed using a co-rotating intermeshing twin-screw extruder (TEK 30, SM Platek Co.) with screw diameter of 35 mm and screw length-to-diameter ratio (L/D) of 40. In the twin-extrusion compounding process, the screw rotation speed was set as 500 rpm to yield sufficient shear stress level for the break-up of agglomerated nanoclay particles, and a temperature profile ranging from 260 to 300°C, which was determined from melting behavior by DSC experiment, was used. The melt-extruded PC/clay nanocomposite strand emerging from the die was cooled and solidified in a water bath and then cut into cylinder-type pellets with a pelletizer. The compounded nanocomposite pellets were vacuum-dried at 100°C for 4 h before further processing. Finally, the nanocomposite diffuser sheet, with a thickness of 1.3 mm and dimensions of 200 × 200 mm, was prepared by employing a hot-melt compression process, which was operated in three sequential steps of melting, compression, and cooling under pressures of 100, 650, and 100 kg$_f$/cm^2, respectively. When preparing the nanocomposite diffusers, the incorporated nanoclay contents were varied at 3, 5, and 8 wt %, while the amount of added polysilicone bead was fixed at 0.5 wt % in all samples.

Characterization

An X-ray diffractometer (Ultima 3, Rigaku, Japan) with Cu Kα radiation operated at 40 kV and 30 mA was used to quantitatively examine the gallery distance between the intercalated nanoclay platelets and the extent of exfoliation in the nanocomposites. Samples were scanned in the range of 1–14° at a scan rate of 1.0°/min. The basal spacing of the clay was determined from the position of the d_{001} and d_{002} peaks in the X-ray diffraction (XRD) pattern using Bragg's law.

The intercalated or exfoliated nanoclay dispersion in the PC matrix was observed with a transmission electron microscope (TEM, JEM-2100F, JEOL, Japan) at an accelerating voltage of 200 kV. The thin films with a thickness of about 100 nm for TEM observation were prepared by ultramicrotoming the cured epoxies containing the nanocomposite sheet.

The angular luminance of the prepared diffuser was measured by a conoscope instrument (EZ-contrast 160, Eldim S. A.) with a viewing angle of ±88°, according to the standard method of flat panel display measurements standard (FPDM) 2.0 of the Video Electronic Standard Association (VESA). The luminance along the vertical direction was determined by averaging the values measured at 9 different locations on the diffuser sheet using a spectroradiometer (SR-3, Topcon Co.).

Differential scanning calorimetry (DSC, Extar 7000, Seiko Co.) was used to examine the thermal behavior of the glass transition temperature (T_g) for the nanocomposites. The heating thermogram was obtained by heating the sample from room temperature to 250°C at a rate of 10°C/min.

The dynamic viscoelastic properties of the nanocomposite diffusers were measured with a dynamic mechanical analyzer (SS6100, Seiko Co.) with a strain amplitude of 0.1% at a frequency of 1 Hz. The temperature was increased from room temperature to 180°C at a heating rate of 3°C/min.

The mechanical properties of flexural strength and modulus for the nanocomposite diffuser sheets were measured with the three point bending mode of a universal testing machine (H10KT, Tinius Olsen, Germany) in accordance with ASTM D 790. The average value was determined from data obtained by testing five samples with dimensions of 130 mm (length) × 13 mm (width) × 1.3 mm (thickness).

RESULTS AND DISCUSSION

In polymer-based nanocomposite fields, achievement of homogeneous dispersion of highly intercalated and/or exfoliated
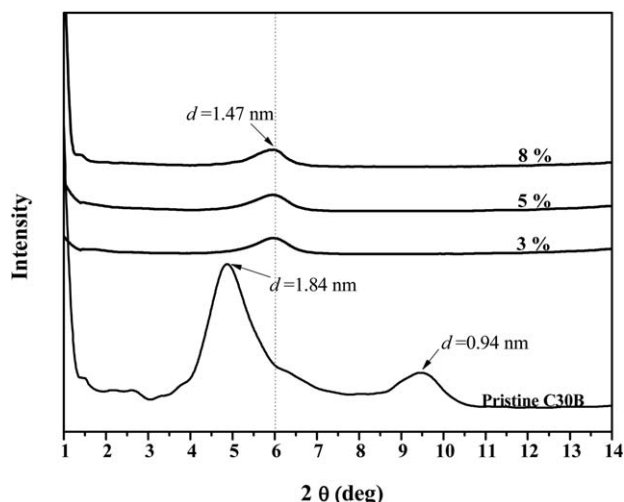
Figure 1. XRD patterns of pristine C30B and PC/clay nanocomposites with various nanoclay loadings.

nanofiller platelets in the polymer matrix has been recognized as the most significant factor for the preparation of high-performance polymer nanocomposites.[16] The twin-extrusion compounding process employed in this study was expected to achieve a highly intercalated or exfoliated nanostructure as well as a homogeneous dispersion of nanoclay platelets in the PC matrix by imparting a high level of energy or shear stress onto the agglomerated nanoclays. Figure 1 shows the XRD patterns of the pristine nanoclay (C30B) and the corresponding PC/clay nanocomposites with various clay contents in the 2θ region of 1–14°. The two strong and weak diffraction peaks of pristine nanoclay were observed at $2\theta = 4.8°$ and 9.6°, which correspond to d_{001} and d_{002} spacing of 1.84 nm and 0.94 nm, respectively. In the nanocomposite samples with various clay loadings, however, the characteristic peak of C30B at $2\theta = 4.8°$ disappeared, while the peak at $2\theta = 9.6°$ corresponding to d_{002} spacing of 0.94 nm shifted to a lower position of $2\theta = 6.1°$, indicating a slightly increased interlayer distance (d_{002}) of 1.47 nm after nanocomposite preparation. This result suggests that intercalated clay tactoids with increased intergallery distance coexisted with partially exfoliated nanoclay platelets, which were responsible for homogeneous nanoclay dispersion in the PC matrix.

TEM observation was also performed to qualitatively examine the nanostructured morphology in conjunction with the XRD measurement. Figure 2 shows the TEM micrographs of ultrami-

crotomed cross-sections of the nanocomposite diffuser sheets with different nanoclay contents. As seen in the images, the intercalated nanoclay tactoids with increased distance between layers and some exfoliated nanoplatelets were observed to be randomly dispersed in the matrix. Especially, in the case of the nanocomposite sample with high clay loading of 8 wt %, intercalated tactoids consisting of a larger number of stacked layers were observed due to the lack of stress for layer delamination. It was revealed from this TEM observation along with XRD analysis that a high extent of intercalation and exfoliation in the PC/clay nanocomposites could be achieved via only single-step melt extrusion process using a twin-screw extruder. In addition, strong physical interaction formed between the carbonyl groups of the PC resin and the hydroxyl groups on the surface of C30B nanoclay appeared to accelerate the diffusion of the PC chain molecules into intergallery spaces between nanoclay platelets, leading to highly intercalated nanostructure.

The optical diffuser in the direct-lit BLU system can easily distorted due to thermal energy generated from the LED source, which may deteriorate the duration of LCD product. Therefore, high thermal resistance is an essential property for the stable use of a diffuser located adjacent to the LED chips. In this study, we investigated the influence of nanoclay incorporation on the thermal resistance of prepared nanocomposite diffusers in terms of glass transition behavior. Figure 3 shows the heating thermograms obtained from the DSC experiment. The incorporation of nanoclay platelets was shown to increase the glass transition temperature (T_g) of the PC in the nanocomposites. For instance, T_g was increased from 150°C for the PC diffuser without nanoclay to 152°C when incorporated with 5 wt % nanoclay. This improvement in the thermal resistance may originate from the more restricted chain mobility of PC molecules in the nanocomposites by the strong intermolecular bonding between hydroxyl groups on the nanoclay surface and the functional groups of the PC molecules. Such a reinforcing effect in the thermal property has been reported in the many other studies, in which various types of nanofillers, such as nanosized silica particles,[17,18] cellulose nanofiber,[19,20] graphene oxide nanosheets,[21,22] and nanoclay platelets,[23–25] have been used to prepare nanocomposites.

Dynamic mechanical analysis (DMA) was also conducted to examine the influence of nanoclay incorporation on the thermo-mechanical properties of the prepared nanocomposite diffusers. Figure 4(a) shows the storage modulus of PC/clay nanocomposites
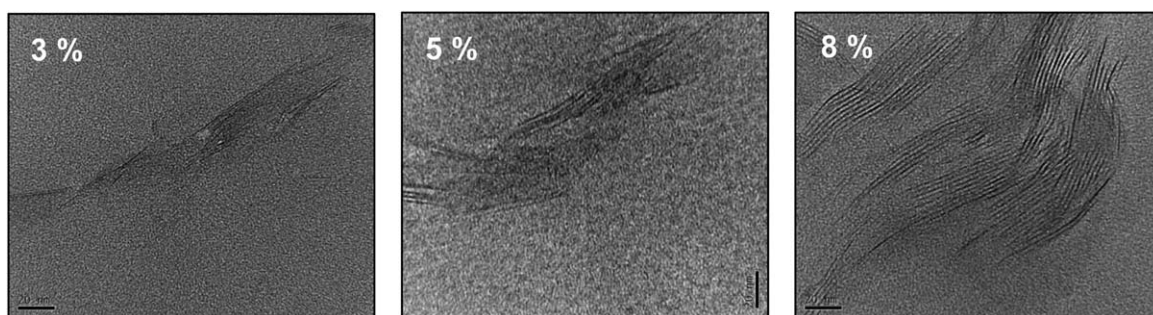

Figure 2. TEM images of PC/clay nanocomposite diffusers with different nanoclay contents.
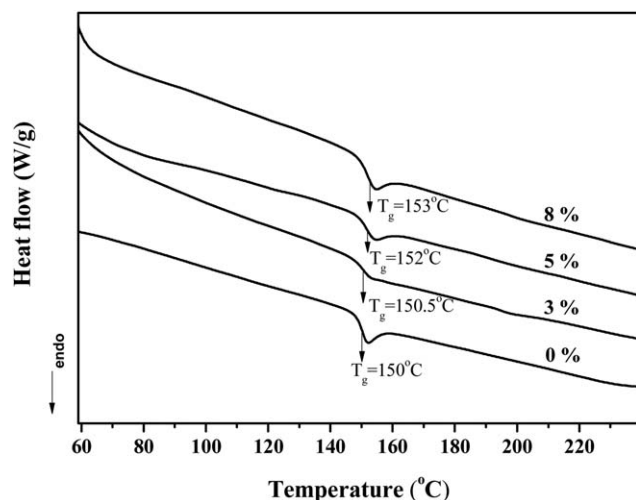
Figure 3. DSC heating thermograms of PC/clay nanocomposites with different nanoclay contents.

with various clay loadings as a function of temperature in the range of 45 to 175°C. All of nanocomposite diffusers showed significantly improved storage moduli in the temperature range below 150°C exhibiting glassy solid state, compared to the PC diffuser without nanoclay. Particularly, 5 wt % nanoclay incorporated nanocomposite showed remarkably improved storage modulus by around 53%, as compared to PC without nanoclay. However, incorporation of nanoclay at more than 5 wt % slightly increased the storage modulus of the nanocomposite, which may be due to poor clay dispersion with excess clay loading. In addition, tan δ (E''/E' ratio, E': storage modulus, E'':loss modulus), which has generally been used to obtain the glass transition behavior occurring in the amorphous phase, was determined from DMA, and is presented in Figure 4(b). As revealed in the previous DSC results, when incorporated with nanoclay, the peak temperature in the tan δ curves shifted toward higher temperature, indicating an increase in the glass transition temperature. It has also been reported that the thermo-mechanical properties of the optical diffuser used for a BLU system can be enhanced by incorporating the micro-sized inorganic fillers such as glass fiber and porous silica particle into polymer resin.[14,15]

The flexural deformation test for the prepared nanocomposite diffuser sheets was performed to investigate the effect of nanoclay incorporation into PC resin on mechanical reinforcement of the resin. Figure 5 shows the flexural properties of nanocomposite diffusers with various clay loadings. The flexural modulus and flexural strength were increased with increasing nanoclay loading. When incorporated with 5 wt % nanoclay, the flexural modulus and flexural strength were improved by 21.9% and 16.6%, respectively, in comparison with those of the PC without nanoclay. This improvement in flexural modulus and strength is mainly due to the prominent reinforcing effect of dispersed inorganic nanoclay platelets with high stiffness as well as high aspect ratio.[26] Additionally, it can be inferred that the increased physical interaction between nanoclay platelets and PC matrix phases contributes to the improvement in the mechanical performance. However, the nanocomposite diffuser loaded with 8 wt % nanoclay showed deterioration in the flexural strength,
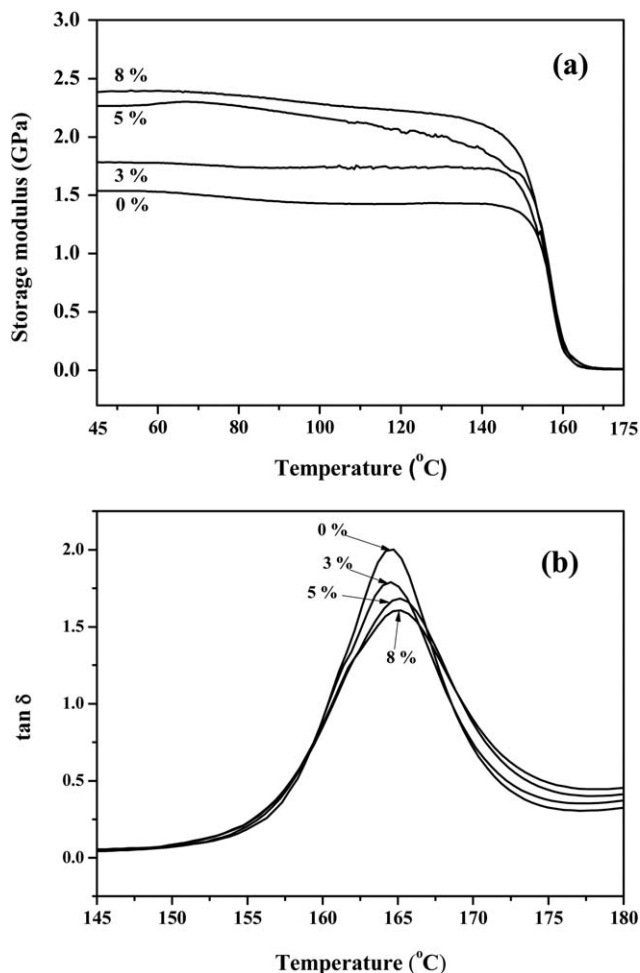

Figure 4. Thermo-mechanical properties as a function of temperature for the nanocomposite diffusers with different nanoclay loadings: (a) storage modulus, (b) tan δ.

which may be ascribed to distribution of a number of stacked clusters with larger domain size in the resultant nanocomposite, as confirmed in previous TEM observation.
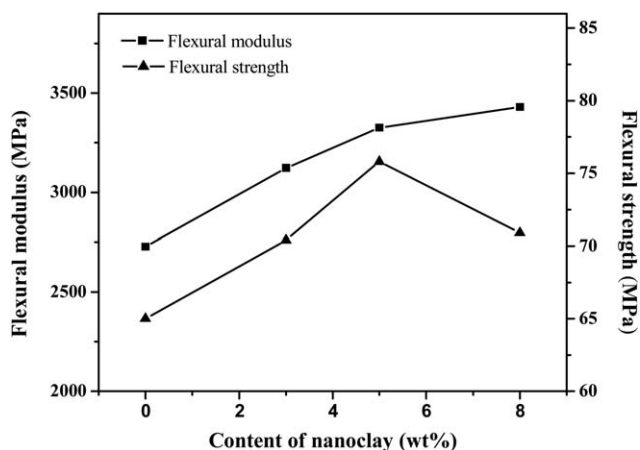

Figure 5. Flexural properties of nanocomposite diffusers as a function of nanoclay content.
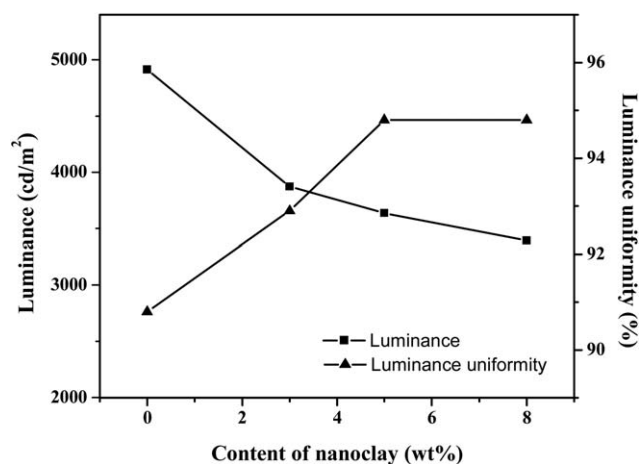
Figure 6. Optical properties of absolute luminance and luminance uniformity for the nanocomposite diffusers with various nanoclay loadings.

Figure 6 displays the measured optical properties of luminance and luminance uniformity for the nanocomposite diffusers with various nanoclay loadings. The luminance was shown to reduce with increasing loading of nanoclay, which is primarily due to an increase in light scattering. The luminance was noticeably reduced by 21% up to 3 wt % loading of nanoclay, and it gradually decreased above 3 wt % loading. It has generally been recognized that the low level of scattering and diffusion of the light rays emerging from the LED chips can induce inhomogeneous distribution of brightness across the whole display front panel, leading to deterioration of the LCD quality. Therefore,

luminance uniformity (U_{lum}) is also an important measure of evaluating optical performance for the diffuser, and can be quantitatively determined from the following equation:

$$U_{lum}(\%) = L_{min}/L_{max} \times 100 \qquad (1)$$

where L_{min} and L_{max} are minimum and maximum luminance values, respectively, among the various luminance values measured at nine different locations of the diffuser. As shown in the figure, the luminance uniformity was considerably enhanced from 90.8% for the PC diffuser without nanoclay to 94.8% for the nanocomposite diffuser with 5 wt % nanoclay loading. However, further increase of nanoclay loading above 5 wt % did not improve the luminance uniformity, which is similar to the trend in the previous results of mechanical performance.

The optical test was performed to qualitatively evaluate the luminance uniformity with respect to locations and the optical diffusivity. Figure 7 shows the digital images of nanocomposite diffusers with various clay loadings, below which a number of LED chips used in an actual direct-lit BLU system were positioned at an even interval of distance between them. Such a qualitative optical test has usually been utilized in industrial fields of LCD, and is called as the mura test. The PC diffuser with only 0.5 wt % silicone bead and the nanocomposite diffuser loaded with small amount of 3 wt % nanoclay displayed the shape of the LED chip more distinctly, as seen on the right half area of the digital image, which is due to low level of light scattering and diffusivity, ultimately leading to poor luminance uniformity. On the other hand, incorporation of 5 wt % nanoclay platelets along with silicone beads resulted in remarkable
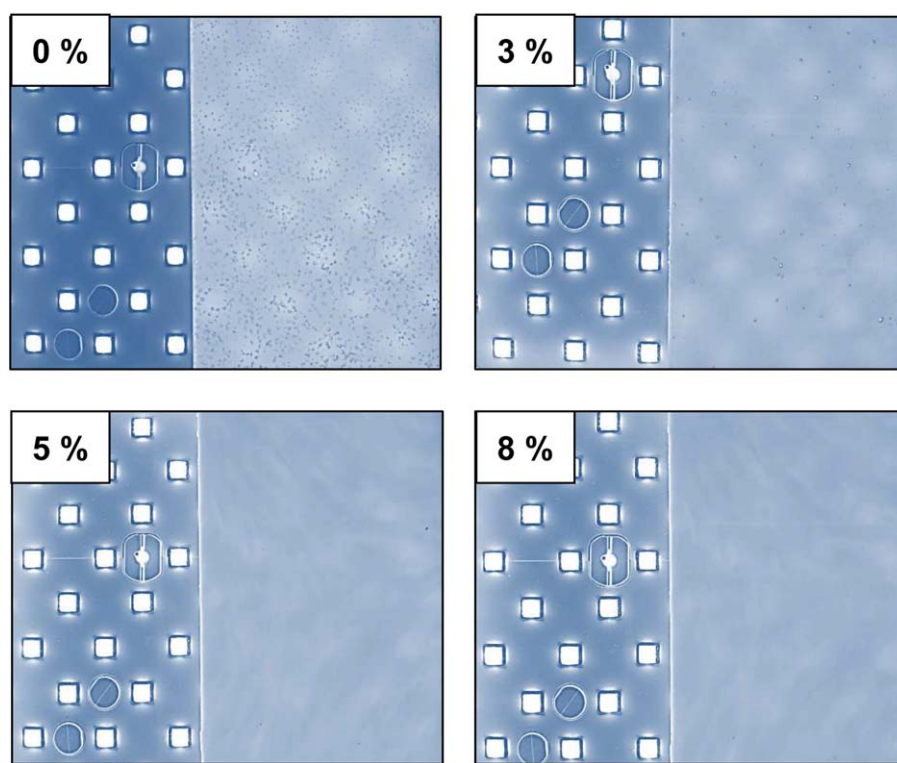

Figure 7. Digital images showing qualitative luminance uniformity of nanocomposite diffusers with various nanoclay loadings. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

improvement in the qualitatively measured luminance uniformity, as shown in the figure.

Figure 8 shows the angular luminance distribution with respect to viewing angle ($-88°\sim+88°$) for the prepared nanocomposite diffusers. In the case of the PC diffuser without nanoclay, non-uniform luminance distribution was observed over the entire range of viewing angles, especially, peak luminance of around 4800 cd/m^2 was detected in the narrow range of $-10°$ to $+10°$. The incorporation of nanoclay platelets could give rise to uniform luminance distribution with a flatter profile with respect to viewing angle, indicating improved luminance uniformity. Moreover, an increase of nanoclay loading widened the viewing angle range, in which uniform luminance distribution was obtained. From these quantitative and qualitative optical tests, the nanoclay platelets with high aspect ratio were revealed to act as efficient co-diffusing agent to induce a high extent of light scattering and diffusion during light transmittance through the diffuser, suggesting the possibility of reducing the amount of the main diffusing agent added in the diffuser.

In this study, we investigated the water absorption behavior of the prepared nanocomposite diffusers, because the warpage of the optical diffusers is significantly dependent on its moisture content and thermal resistance.[13] Vacuum-dried nanocomposite samples were placed in a chamber under 100% relative humidity and room temperature. The water absorption was determined by measuring the weight of samples taken at various time intervals. Figure 9 shows the measured water absorption of the nanocomposite diffusers as a function of storage time in the humid atmosphere. The presence of nanoclay platelets in the PC matrix significantly suppressed the moisture absorption rate, suggesting the feasibility of manufacturing the optical diffusers without warpage. This result probably originates from the increase of tortuous path for penetrating water molecules within the polymer matrix, which results from the dispersion of delaminated nanoclay platelets with high aspect ratio.[27] It should be noted that both nanocomposite diffusers with nanoclay loadings of 5 wt % and 8 wt % exhibited almost the same
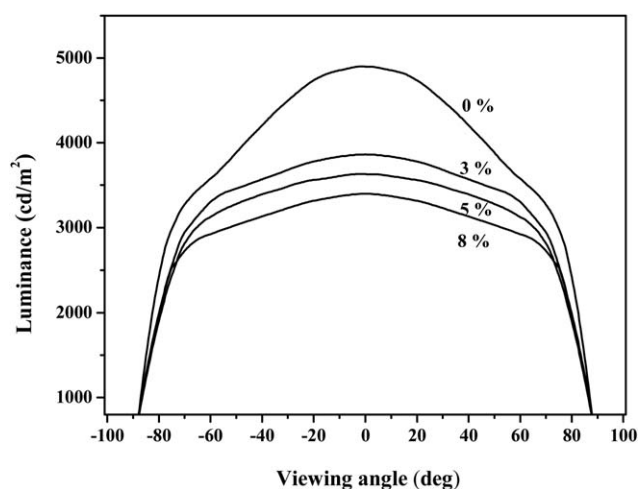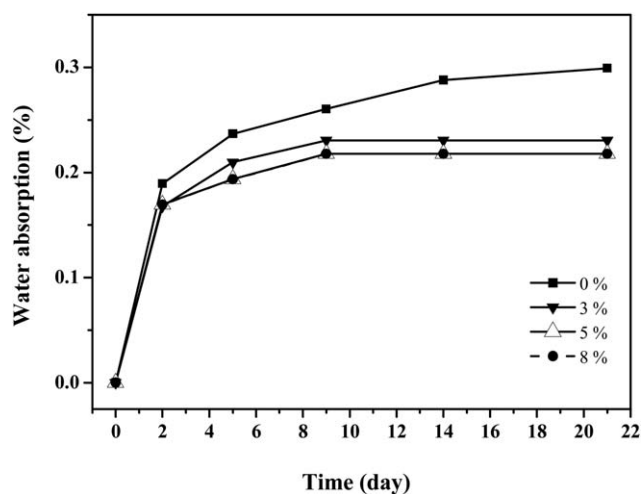

Figure 9. Amount of water absorbed onto nanocomposite diffusers as a function of storage time in the humid atmosphere.

trend in the water absorption behavior, as observed in previous other results.

CONCLUSIONS

The organically modified nanoclays were incorporated into PC resin as reinforcement to prepare nanocomposite optical diffusers with improved performances via a twin-extrusion compounding process. Based on XRD analysis and TEM observation, it was confirmed that the transformation of original nanoclay agglomerates to highly intercalated tactoids or exfoliated nanoclay platelets could be achieved by the high shear stress transfer accompanied by strong physical interaction between PC molecules and hydrophilic C30B nanoclay. The incorporation of nanoclay platelets at an appropriate content resulted in substantial improvement in the physical properties of the nanocomposite diffusers, such as thermal resistance, thermo-mechanical, flexural, and moisture barrier properties. In addition, the nanoclay platelets with high aspect ratio were revealed to be efficient co-diffusing agents as well as reinforcement to prepare the optical diffuser with improved luminance uniformity with respect to both location and viewing angle. However, with an excess loading of nanoclay (above 5 wt %), a slight increase or reduction (in the case of flexural strength) in the properties was observed because of distribution of stacked tactoids with greater domain size.

Figure 8. Angular luminance distributions with respect to viewing angle for the PC/clay diffusers containing various nanoclay contents.

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