

Structure Orientation and Micromechanical Characterization of Platelet-Reinforced Polyethylene Nanocomposites

Y. Fan,¹ Y. C. Lu,² J. Lou,³ C. C. Tang,¹ D. M. Shinozaki³

¹School of Materials Science and Engineering, Hebei University of Technology, Tianjin, China 300132

²Department of Mechanical Engineering, University of Kentucky, Lexington, Kentucky 40506-0503

³Department of Mechanical and Materials Engineering, the University of Western Ontario, London, Ontario, Canada N6A 5B9

Correspondence to: Y. Fan (E-mail: yfan@hebut.edu.cn)

ABSTRACT: Clay reinforced polyethylene nanocomposites were prepared by melt mixing followed by transfer molding. The microstructure of the composites was characterized using Fourier transform infrared spectrometer and X-ray diffraction. Results revealed the relative degree of particle orientation as a function of depth in the transferred molded materials. The particles were mostly oriented at the surface layers and randomly distributed at the core region. The anisotropy in mechanical properties due to clay orientations was characterized through novel dynamic microindentation test and analyzed by finite element simulation. When loaded in the flow direction (direction of clay orientations), the composites exhibited higher modulus at the surface than at the core; while loaded normal to the flow direction, the composites exhibited lower modulus at the surface than at the core. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: nanocomposites; clays; orientation; indentation

Received 11 January 2012; accepted 2 May 2012; published online

DOI: 10.1002/app.38018

INTRODUCTION

The processing and mechanical properties of polymer composites with nanometer size reinforcements have been extensively studied. Of particular interest has been the thermoplastic matrices reinforced with the nanoclay (montmorillonite) particles.^{1–7} For melt mixed composites, the nanoclay particles are initially in the form of multilayers made of hard silicate monolayers separated by relatively soft interlayers (dimethyl, dehydrogenated tallow quaternary ammonium). The stacks of particles intercalate or exfoliate during processing to form plate-like particles. The exfoliation of the clay particles is often incomplete, so the final composites are typically consisted of nanoplatelets mixed with multilayer particles imbedded within the polymer matrix.

The microstructure of the nanocomposites is affected by the thermomechanical processing history. For conventional fiber reinforced polymer composites, the flow induced fiber orientation has been reported and the resultant composites display a shear rate dependent skin-core structure.^{8,9} This inhomogeneous structure is caused by the differential shear rates within the mold. The fibers are oriented parallel to the flow direction in the melt near the mold wall where the shear rates are high, and relatively unoriented in the low shear rate regions away from the mold walls. The similar skin-core structure has been

reported for the platelet reinforced polymer composites.^{10–16} The nanoclay platelets have a typical diameter of several hundreds nanometers and a thickness of only a few nanometers. Such high aspect ratios make the platelet particles behave like the conventional fibers. The mechanism for the platelet orientation has been ascribed to the shear gradient of the flow layers in the mold.^{12–14} During molding, the melt near the skin is immediately solidified due to the dramatic temperature difference between the cold molded wall and the hot melt. Consequently, the particles are observed to be highly oriented at the skin but random at the core. The degree of orientation has been further found to depend upon the particle contents. Composites with low or medium clay contents (<3 wt %) tend to exhibit much higher level of orientations.¹² Although the shear-induced orientations in nanocomposites have been extensively studied, the corresponding variation of mechanical properties which is expected to change with microstructure has not been reported.

The development of heterogeneous microstructures in platelet reinforced polymer composites may result in the variation in mechanical properties. Much of the existing work has dealt with some aspects of the methods of preparation and characterization of these materials. There remains only a limited understanding of the relationship between nanostructure, processing, and mechanical properties. The overall objective of the present

paper is to examine the structure orientation and resultant mechanical properties in transfer molded polyethylene-clay nanocomposites. The microstructure of the processed composites will be examined using Fourier transform infrared spectrometer and X-ray diffraction. The resultant mechanical properties will be measured through dynamic microindentation test, a novel technique that has been successfully used to characterize the point-to-point mechanical properties in processed polymers and composites.^{17–20}

EXPERIMENTAL

Materials and Processing

A Dow Chemical high-density polyethylene (HDPE) was used as the matrix. It had a melt mass flow index of 3.2 g/10 min and a density of 0.953 g cm⁻³. The maleated polyethylene (MAPE) was obtained from Aldrich. It was used for compatibilization, with reported characteristics: $M_w = 9300$; $M_w/M_n = 2.1$; $T_m = 99.3^\circ\text{C}$ and a maleated content of 3.0 wt %. The nanoscale reinforcing phase was an organophilic montmorillonite (Southern Clay Cloisite 20A). It had been ion-exchanged with dimethyl dehydrogenated tallow ammonium ions (~65% C18; ~30% C16; ~5% C14) for compatibility. The organic modifier in the clay component represented about 30 wt % of the as-received material.²¹ The specific gravity of the modified clay was ~1.8 g mL⁻¹.

Composites with 5 wt % clay, 5 wt % MAPE, and 90 wt % HDPE were prepared. The materials were first melt mixed in a Brabender laboratory mixer with the mixing speed of ~10 rpm. A measured weight of polyethylene was first introduced into the mixer, then the maleated polyethylene (5 wt %) and Cloisite (5 wt %) were added. The mixer was kept at 160°C for 20 min, using high shear blades. After mixing, the materials from the mixer solidified into irregular shapes. Those materials were labeled as “as-mixed” clay composites.

After mixing, the material was subsequently transfer molded between two hot plate in a manual hydraulic press (Caever, 100 kN capacity) (Figure 1). The hot plates in contact with mold were preheated so the mold surface temperature reached 185°C. Because the thermal conductivity of the mold was limited, the center temperature within the mold, where the polymer was to be placed, was at a somewhat lower temperature. The mold itself was then preheated to 180°C on a separate hot plate, and the mixed material was added. The mold containing the mixture was held at this temperature on the hot plate for a time $3 < t < 5$ min to allow the material to reach temperature. The mold and material were moved to the Carver hot plates, and left for a time $5 < t < 10$ min to equilibrate on the press. The force (F) applied by the Carver press was found to be small, since the melt viscosity was low. The mold and molten sample was removed from the press and air cooled. After cooling to room temperature, the sample was removed from the mold. The rectangular samples prepared through this process had dimensions of $54 \times 24 \times 3.5$ mm³.

Microstructure Characterizations

Fourier transform infrared (FTIR) spectra were recorded on pure polyethylene and clay–polyethylene nanocomposites. Tests

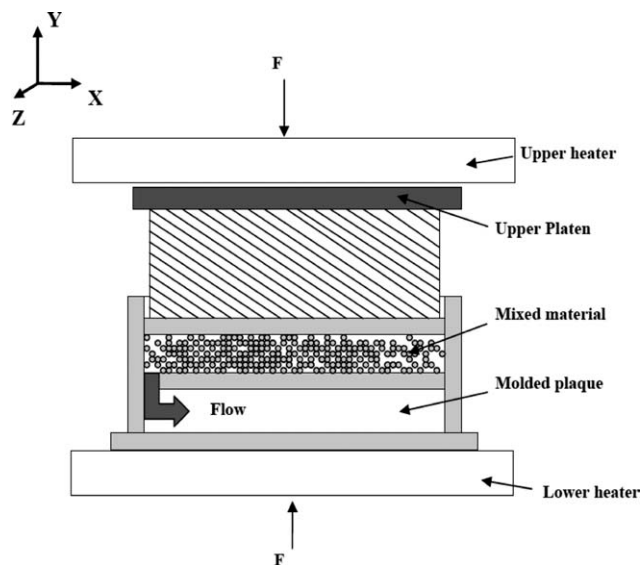


Figure 1. Transfer molding between two hot plates in a manual hydraulic press (Carver, 100 kN capacity).

were conducted using a Nicolet™ 380 spectrometer with a resolution of 4 cm⁻¹ using an accumulation of 32 scans. The spectra were recorded in reflectance mode for the range of 400–2600 cm⁻¹ with polarized light. The background spectra were recorded under the same conditions as the sample. The microstructures of the composites were examined using wide-angle X-ray patterns (WAXD) with Cu K α radiation. Specimens were cut from the surface, interior and center of the transfer molded composites. Specimens from the as-mixed composites were also tested. The as-mixed specimens were prepared by air cooling the materials from the mixer and then cutting them into smaller samples.

Microindentation Testing

The local properties of the transfer molded composites were measured using a custom built indentation apparatus. Small scale, dynamic indentation experiment, similar to the conventional dynamic mechanical analysis (DMA), was conducted. The advantage of the dynamic indentation test is that it allows for extracting the mechanical properties of materials at much smaller penetration depths as compared to conventional indentation tests.^{17–20} A cylindrical flat-ended tip of 80 μm diameter was used. The tip was driven by a piezoelectric driver, which was feed-back controlled through a strain gauge attached to the driver. The driving voltage was dictated by a computer-controlled DC power supply which set the tip position, and a function generator connected in series, which generated an oscillatory tip displacement for dynamic mechanical tests. The lock-in amplifier served two functions. The first was to provide the system with a displacement in a sinusoidal wave. The second function of the lock-in amplifier was to pick out the resultant load from the total load cell and the swift angle (δ). The oscillation frequency used was 2 Hz. The applied displacement amplitude was equal to 36 nm (rms amplitude).

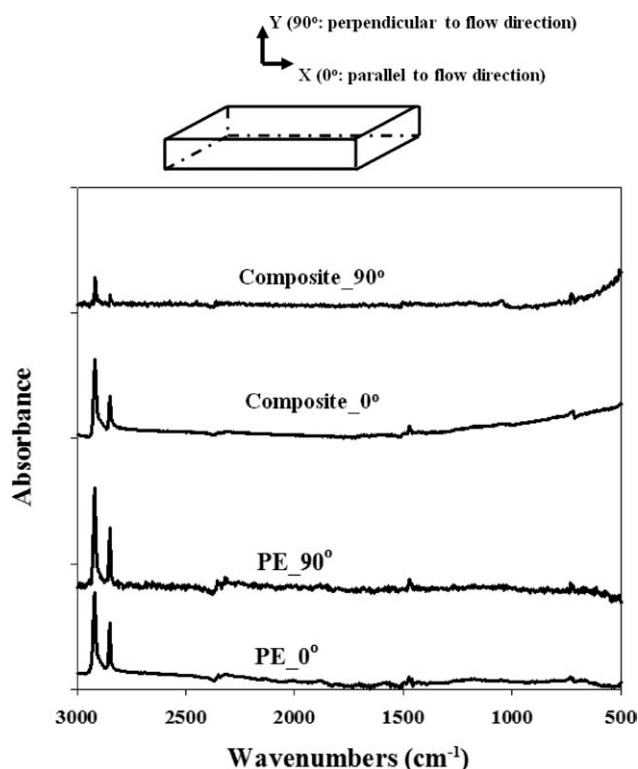


Figure 2. FTIR polarized SR spectra for pure HDPE and 5 wt % clay composites with the incident radiations being parallel (0°) and perpendicular (90°) to the flow direction, respectively.

RESULTS AND DISCUSSION

Microstructure Orientations

The chemical characteristics and the surface orientations of the neat polyethylene and platelet-reinforced polyethylene nanocomposites were first characterized by FTIR, which is an effective way to evaluate the degree of orientation.^{15,22} In the present FTIR tests, the spectra were collected in reflectance mode. The incident radiations were taken on specimens at: (1) parallel to the flow direction (0°) and (2) perpendicular to the flow direction (90°). Figure 2 shows the spectra of pure polyethylene and

Table I. Infrared Band Assignments of Polyethylene Resin and Platelet Reinforced Polyethylene Nanocomposite

Frequency (cm ⁻¹)	Band assignment
2844	v _s (CH ₂)
2913	v _{as} (CH ₂)
1474	CH ₂ bending due to crystalline phase
1464	CH ₂ bending due to crystalline and amorphous phases
730	CH ₂ rocking due to crystalline phase
720	CH ₂ rocking due to crystalline and amorphous phases
1050	Si—O—Si stretching
520	Al—O stretching
464	Si—O bending

transfer molded platelet polyethylene composite skins. Table I lists the frequencies and the vibration assignments of the neat polyethylene and the nanocomposites.

It is interesting to see that the spectra for pure HDPE specimen are similar when tested at different directions (parallel or perpendicular to the mold flow direction). However, the spectra for the molded platelet composite show difference when tested at different directions. In the present study, the dichroic ratios are used to characterize the orientation of transfer molded samples of matrix and composites. The dichroic ratio is defined as:

$$D = A_{\parallel}/A_{\perp} \quad (1)$$

where A_{\parallel} and A_{\perp} are absorption determined with the incident radiation being polarized parallel and perpendicular, respectively to the shear direction. If the dichroic ratio of absorption bands equals to ~ 1 , it means that no apparent orientation occurs to the relative structure. The dichroic ratios for pure polyethylene and clay-polyethylene nanocomposites show big difference. In the 5 wt % clay composite, the dichroic ratios of 3.31 and 3.06 for the 2923/2851 cm⁻¹ band of CH₂ stretching and the dichroic ratios of 0.20 and 2.11 for the 720/730 cm⁻¹ band of CH₂ rocking indicate that polyethylene lamellae are highly oriented. In pure HDPE, the dichroic ratios of 2923/2851 cm⁻¹ band and 720/730 cm⁻¹ band are close to 1. This implies that polyethylene lamellae are highly oriented on 5 wt % clay transfer molded plaque skin, while no obvious polyethylene orientation exists in plain HDPE.

The microstructure and orientations of the platelet reinforced composites were further examined with the X-ray diffractometer. The starting injection molded plaque had a thickness of about 3.5 mm. The interior layer was exposed by grinding away the specimen surface layer of 0.5 mm. The core layer was deeper by about 1.75 mm. Figure 3 shows the X-ray diffractometer

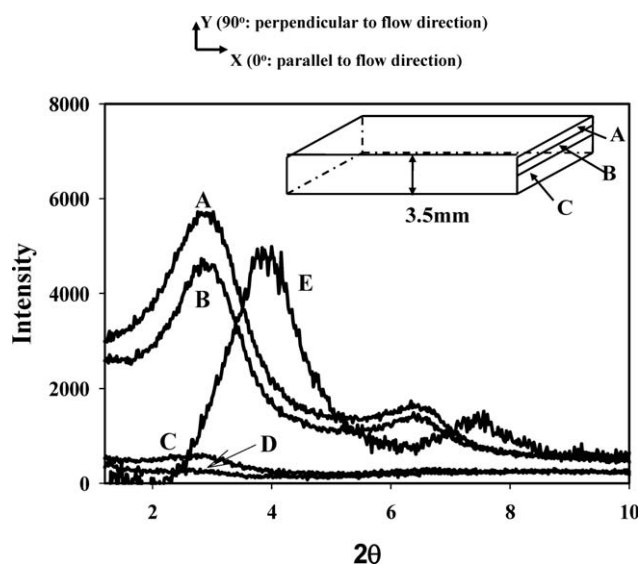


Figure 3. WAXD showing orientation gradient in the transfer molded composites. (A) Skin, (B) interior, (C) core regions cut from the transfer molded 5 wt % clay composites, (D) the as-mixed of 5 wt % clay composite, and (E) the Cloisite 20A clay.

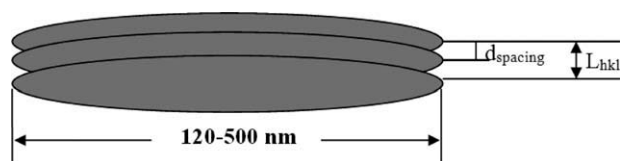


Figure 4. Sketch of the intercalated platelet particle.

traces on specimens cut from the molded sample at different depths: (A) $d = 0$ mm, (B) $d = 0.5$ mm, and (C) $d = 1.75$ mm, and (D) as-mixed of 5 wt % clay composite.

The introduction of Cloisite 20A into polyethylene matrix shifts clay peak from $2\theta = 3.65^\circ$ to $2\theta' = 2.92^\circ$ (sample E in Figure 3). According to Bragg's law ($n\lambda = 2d\sin\theta$), the (001) plane d -spacing expands from 24.2 to 30.2 Å for Cloisite 20A.

A careful examination of the X-ray diffraction peaks at lower angles reveals some useful details about the microstructure of the dispersed clay phases. Tactoids of clay are plate-like in shape, and consist of a periodic structure of silicate layers separated by organic interlayers. Analysis of the diffraction peak can then yield useful information about the structure in the dispersed nanoclay platelets^{21,23,24}:

$$\text{spacing between platelet layers : } d_{\text{spacing}} = \frac{\lambda}{2\sin\theta} \quad (2)$$

$$\text{platelet thickness : } L_{\text{hkl}} = \frac{k\lambda}{\beta_{\text{hkl}}\cos\theta} \quad (3)$$

$$\text{number of platelets in one tactoid : } N = \frac{L_{\text{hkl}} - d_s}{d_{\text{spacing}}} \quad (4)$$

where λ is the wave length and θ the Bragg angle of the particular reflection (2θ is the scattering angle). k is the crystallite shape factor, β_{hkl} the reflection width at the half-maximum intensity, and d_s the thickness of each clay platelet layer. Based on the X-ray diffraction results (Figure 3), the following information are obtained for the 5 wt % clay composites: $L_{\text{hkl}} = 7.16$ nm, $d_{\text{spacing}} = 3.02$ nm, $d_s = 1$ nm and $N = 3$. The individual clay tactoid structure can be sketched as shown in Figure 4.

The X-ray diffraction scans can also reveal the microstructure of the dispersed clay phases with depth into the molded sample (Figure 3). Although hard X-rays penetrate quite thick sections of polymers, the small Bragg's angle and the instrument geometry result in relatively thin layers near the surface of each specimen effectively scattering into the measured diffraction peak.²⁵ The thickness of the layer from which the diffraction information is obtained depends on the depth to which the incident beam can penetrate at these shallow angles of incidence. The diffraction scans of Figure 3 thus reveal the relative degree of orientation as a function of depth from the mold wall in the sample.

As shown in Figure 3, the lower angle peak associated earlier with the modified tactoids (2.92°) is clearly much larger near skin regions (A). Toward the center of the molded sample (B) (further away from the surface), the peak diminishes and is almost undetectable at the sample center (C) which is similar to that of the as-mixed 5 wt % clay composite (D). The peak size

depends on the scattering efficiency of the periodic structure, which depends on: (1) the relative properties of the silicate and the interlayer, (2) the volume fraction of tactoids, and (3) the degree of orientation of the particles. Assuming (1) and (2) do not vary across the thickness of a molded sample, the variation in tactoid peak size can be explained in terms of average orientation of the tactoids, which was also proposed by Wallace.²⁶ Results indicate that the tactoids at the skin layer of the composite are mostly oriented parallel to the flow direction while the tactoids at the core are mostly randomly distributed.

Micromechanical Characterizations

The X-ray results have clearly indicated a variation in the degree of orientation of the tactoids at various regions of the composite. It is thus expected that the mechanical properties of the composites would vary accordingly. The local mechanical properties of the composites were examined using novel dynamic indentation test. Small scale dynamic mechanical analysis (DMA) was conducted with a flat-ended indenter (diameter = 80 μm). Compared with the common used sharp indenters (Berkovich indenter, conical indenter), the flat indenter is more suitable for measuring crystalline polymers and composites, in which local properties are affected by microstructure.^{17–20} For example, semi-crystalline polyethylene (PE) has spherulites with typical dimensions >5 μm . With flat cylindrical indenters with diameters $\gg 5$ μm , the measurements represent averages over many spherulites.

The contact problem between two elastic bodies has been solved by Sneddon.²⁷ When the two bodies are in contact, the normal separation between the two surfaces is described by the arbitrary function $f(x)$, where x is the dimensionless coordinate $x = r/a$, and a the radius of the contact area (Figure 5). The load (p) required to achieve a displacement (h) is given by

$$p = \pi E_r a \int_0^1 \chi(t) dt \quad (5)$$

where $\chi(t)$ is defined by

$$\chi(t) = \frac{2}{\pi} \left[h - t \int_0^t \frac{f'(x) dx}{\sqrt{t^2 - x^2}} \right].$$

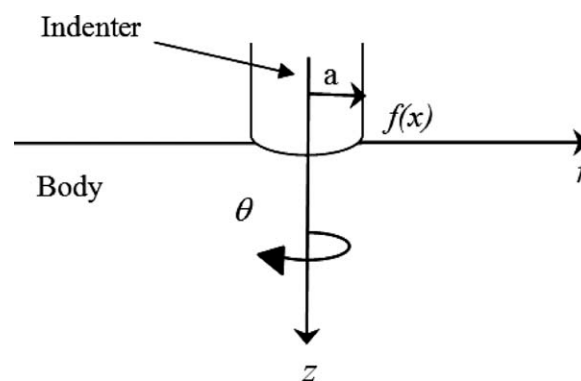


Figure 5. Contact geometry between a flat indenter and specimen.

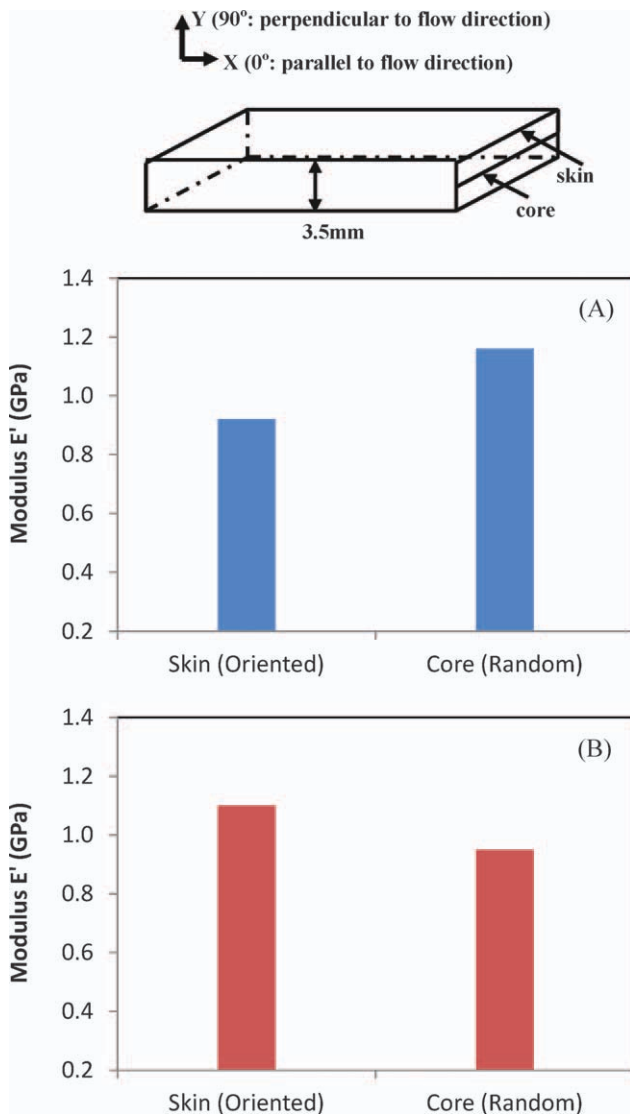


Figure 6. Modulus of the transfer molded 5 wt % clay composite obtained from dynamic indentation tests. (A) Loading normal to the flow direction and (B) Loading parallel to the flow direction. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

For a flat-ended, cylindrical indenter, the separation function $f(x)$ becomes zero. Reorganizing eq. (5) yields to the modulus of the indented material

$$E_r = \frac{P}{h} \frac{1}{2a} \quad (6)$$

To measure the localized mechanical properties, the depth (h) of the indentation has to be kept at small. In this experiment, a small displacement of sinusoidal form ($h = 36$ nm, amplitude) was applied to the indenter tip and the resultant load (P) and phase shift (δ) were measured simultaneously. Using eq. (7), the storage modulus (E') was calculated and used to evaluate the mechanical responses of the composites as a result of structure changes.

$$E' = \frac{P \cos \delta}{h \ 2a} \quad (7)$$

where P and h become the amplitudes of load and displacement functions, respectively.

The platelet composite was first tested from “top-on” direction (the indentation direction is perpendicular to the flow direction). To measure the properties at the core region, the specimen surfaces were removed progressively from both sides. Although the tested samples had the same composition, a difference in mechanical properties was found for the composite plaque at different regions. The modulus is 0.92 GPa for the skin as compared to 1.16 GPa for the core [Figure 6(a)]. The platelet composite was then tested from “end-on” direction (the indentation direction is parallel to the flow direction). The modulus is 1.1 GPa for the skin as compared to 0.95 GPa for the core [Figure 6(b)]. The results indicate that the molded platelet composites exhibit heterogeneity in both structure and mechanical properties. The mechanical responses depend highly upon the local orientations of the platelet particles. When loaded in the flow direction, the surfaces of the composites are stiffer than the core; while loaded normal in the flow direction, the surfaces of composites become softer than the core.

The mechanical properties of the transfer-molded composites were further examined to compare with those from the as-mixed composites and the polyethylene matrix alone. Plaques with a range of thicknesses (3.5 mm, 1.2 mm, and 0.6 mm) were transfer molded and then examined with the micro-indenter (Figure 7). The polyethylene matrix material shows relatively low and isotropic modulus when tested from two directions. The as-mixed 5 wt % clay composite shows isotropic modulus which is higher than matrix modulus.

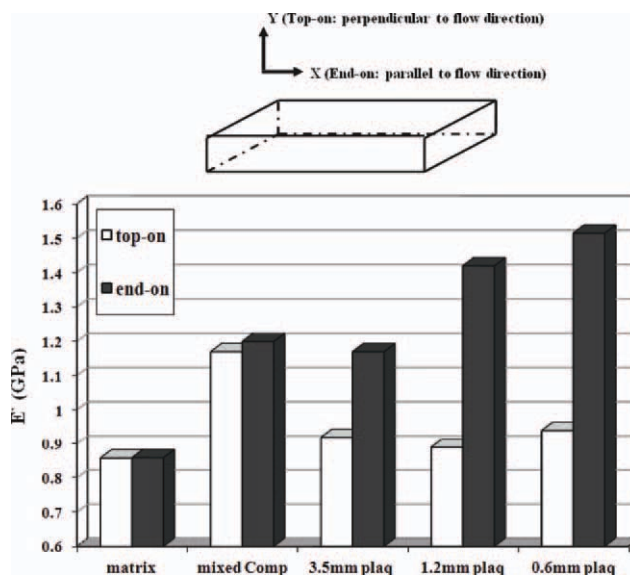


Figure 7. Microindentation testing for HDPE matrix, as-mixed 5 wt % clay composite, and transfer molded 5 wt % clay composites with various thicknesses.

The surfaces of the transfer molded composites show anisotropic properties. Moduli tested from the top-on direction (the indentation direction is perpendicular to the flow direction) are lower compared with modulus tested from the end-on direction (the indentation direction is parallel to the flow direction) for all three materials. Thinner plaques (1.2 mm and 0.6 mm) seem to have relatively uniform and high orientation as shown by wide angle X-ray diffraction and thus shows higher moduli. All these observations manifest that the preferred orientation of the clay particles, which develops during the transfer molding process, affects the mechanical properties of the materials.

The effect of structure orientation on mechanical responses of the platelet reinforced polyethylene composites was further examined through finite element simulation (using the general purpose finite element software ABAQUS²⁸). Composite with a clay content of 5 wt % was simulated (Figure 8), based upon the tactoid characteristics calculated from X-ray diffractions (Figure 4). The calculation for the homogeneous matrix material was conducted first and compared with experiment (tensile test) (Figure 7). Results show that the finite element prediction fits reasonably with the experiment. The analyses were then conducted on platelet reinforced composites: one for the surface skin and the other for the core region (Figure 9). The individually exfoliated plate-like particles were assumed to be isotropic, but the shape of the particle introduced an orientation-dependent effect. For a fully exfoliated composite, the modulus of the matrix (E_m) is ~ 0.9 GPa, the modulus of the clay (single layer) is $\sim E_p = 170$ GPa,^{29,30} and the ratio (E_p/E_m) is thus ~ 200 . For incompletely exfoliated particles, E_p would be much smaller due to the softening effect caused by the soft interlayers. The composite specimens were loaded in directions of parallel and perpendicular to flow directions, respectively. It was interesting to observe that different phenomena appeared when pulled from axial or normal direction (Figure 9). When the specimen was

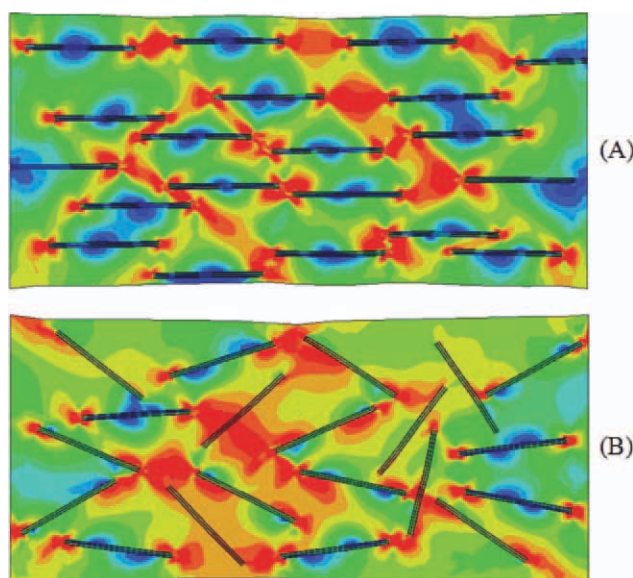


Figure 8. Finite element models of platelet reinforced nanocomposite: (A) Oriented surface layer and (B) Random core region. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

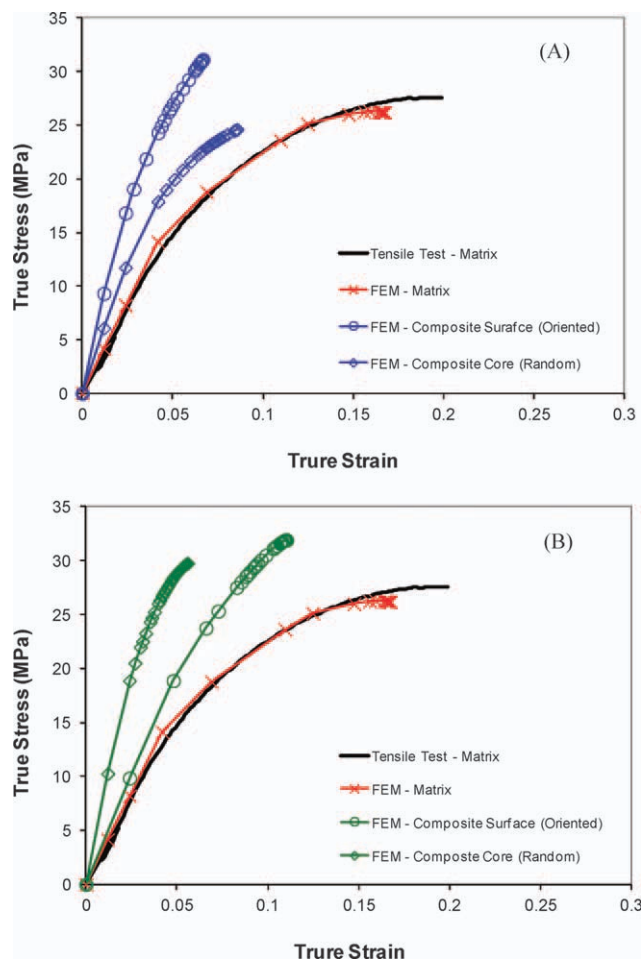


Figure 9. Stress–strain responses of platelet reinforced nanocomposite: (A) loading direction in parallel to the flow direction, (B) loading direction in perpendicular to the flow direction. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

loaded from axial direction [Figure 9(a)], the oriented skin has a higher measured modulus than the random core. When the specimen was loaded from normal direction [Figure 9(b)], the oriented skin had a lower modulus than the random core. The results are consistent with experimental measurements shown in Figure 6(a, b).

CONCLUSIONS

The anisotropy of microstructure and mechanical properties in transfer molded platelet reinforced polyethylene nanocomposites was examined. FTIR and X-ray diffraction were used to characterize the structure and orientations of the platelet particles of the molded plaques. Results showed that the particles at the surface layers were mostly oriented parallel to the direction of melt flow, while the particles at the core were randomly distributed. The effect of clay orientations on mechanical properties was examined through novel dynamic microindentation test and analyzed finite element simulation. The spatial variation of the properties was correlated with the distribution of nanocomposite particles, and the orientation of the particles with respect to the loading directions. It is clear from this work that the

anisotropy of particle properties resulted from melt processing can contribute to significant local anisotropy in properties.

REFERENCES

- Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J. Appl. Polym. Sci.* **1993**, *8*, 1185.
- Kawasumi, M.; Hasegawa, N.; Kato, M.; Usuki, A.; Okada, A. *Macromolecules* **1997**, *30*, 6333.
- Vaia, R. A.; Vasudevan, S.; Krawiec, W.; Scanlon, S. G.; Giannelis, E. P. *Adv. Mater.* **1995**, *7*, 154.
- Giannelis, E. P. *Adv. Mater.* **1996**, *8*, 29.
- Choi, M. H.; Chung, I. J.; Lee, J. D. *Chem. Mater.* **2000**, *12*, 29777.
- Perrin-Sarazin, F.; Ton-That, M. T.; Bureau, M. N.; Denault, J. *Polymer* **2005**, *46*, 11624.
- Fan, Y.; Lou, J.; Shinozaki, D. M. *J. Appl. Polym. Sci.* **2007**, *103*, 204.
- Coyle, D. J.; Blake, J. W.; Macosko, C. W. *AIChE J.* **1987**, *33*, 1168.
- Lee, S. W.; Young, J. R.; Hyun, J. C. *Mater. Res. Innov.* **2002**, *6*, 189.
- Rendon, S.; Burghardt, W. R.; New, A.; Bubeck, R. A.; Thomas, L. S. *Polymer* **2004**, *45*, 5341.
- Xie, S.; Zhang, S.; Liu, H.; Chen, G.; Feng, M.; Qin, H.; Wang, F.; Yang, M. *Polymer* **2005**, *46*, 5417.
- Wang, K.; Zhao, P.; Yang, H.; Liang, S.; Zhang, Q.; Du, D.; Fu, Q.; Yu, Z.; Chen, E. *Polymer* **2006**, *47*, 7103.
- Lele, A.; Mackley, M.; Galgali, G.; Ramesh, C. J. *Rheol.* **2002**, *46*, 1091.
- Ren, J. X.; Silva, A. S.; Krishnamoorti, R. *Macromolecules* **2003**, *33*, 3739.
- Gorrasi, G.; Di Lieto, R.; Patimo, G.; De Pasquale, S.; Sorrentino, A. *Polymer* **2011**, *52*, 1124.
- Yang, J.; Wang, K.; Deng, H.; Chen, F.; Fu, Q. *Polymer* **2010**, *51*, 774.
- Lu, Y.; Shinozaki, D. M. *Polym. Eng. Sci.* **1997**, *37*, 1815.
- Lu, Y. C.; Tandon, G. P.; Jones, D. C.; Schoeppner, G. A. *Mech. Time-Depend Mater.* **2009**, *13*, 245.
- Lo, J. C. W.; Lu, Y. C.; Shinozaki, D. M. *Mater. Sci. Eng. A*, **2005**, *409*, 76.
- Lu, Y. C.; Shinozaki, D. M. *Exp. Mech.* **2010**, *50*, 71.
- Koo, C. M.; Ham, H. T.; Kim, S. O.; Wang, K. H.; Chung, I. J. *Macromolecules* **2002**, *35*, 5116.
- Ward, I. M.; Coates, P. D.; Dumoulin, M. M., Eds. *Characterization of Orientation in Solid Phase Processing of Polymers*; Carl Hanser Verlag: Munich, **2000**.
- Roover, B. D.; Sclavons, M.; Carlier, V.; Devaux, J.; Legras, R.; Momtaz, A. J. *Polym. Sci.* **1995**, *33*, 829.
- Zhang, F.; Kabeya, H.; Kitagawa, R.; Hirotsu, T.; Yamashita, M.; Otsuki, T. *Chem. Mater.* **1999**, *11*, 1952.
- Klug, H. P.; Alexander, L. E. *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*; Wiley: NY, USA, **1974**; p 618.
- Wallace, A. I. *The Effects of Processing and Orientation on Partially Exfoliated Polypropylene Nanocomposites*; University of Western Ontario: London Ont., **2004**.
- Sneddon, I. N. *Proc. Cambridge Phil. Soc.* **1946**, *42*, 29.
- ABAQUS, 2008, *ABAQUS Users' Manual*, Hibbit, Karlson and Sorenson, Pawtucket, RI. .
- Sheng, N.; Boyce, M. C.; Parks, D. M.; Rutledge, G. C.; Abes, J. I.; Cohen, R. E. *Polymer* **2004**, *45*, 487.
- Okamoto, M.; Nam, P. H.; Maiti, P.; Kotaka, T.; Hasegawa, N.; Usuki, A. *Nano Lett.* **2001**, *1*, 295.