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Full Paper: The measurement of rheological properties of any polymeric material under molten state is crucial to gain fundamental understanding of the processability of that material. In the case of polymer/layered silicate nanocomposites, the measurements of rheological properties are not only important to understand the knowledge of the processability of these materials, but is also helpful to find out the strength of polymer-layered silicate interactions and the structure-property relationship in nanocomposites. This is because rheological behaviors are strongly influenced by their nanoscale structure and interfacial characteristics. In order to get this knowledge in the case of polylactide/montmorillonite nanocomposites, we have studied melt rheological properties of these materials in detail. On the basis of rheological data, we have conducted foam processing of pure polylactide and one representative nanocomposite by a newly developed pressure cell technique using carbon dioxide as a physical-blowing agent.



The time variation of the elongational viscosity of one of the intercalated polylactide/montmorillonite nanocomposites.

# New Polylactide/Layered Silicate Nanocomposites, 6<sup>a</sup>

# Melt Rheology and Foam Processing

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# Introduction

Throughout the world today, the development of biodegradable polymeric materials with excellent materials properties is a subject of great research challenge in materials science. One of the most promising candidates in this direction is polylactide (PLA) because it is made from renewable agricultural products and is readily biodegradable.<sup>[1,2]</sup> PLA is a linear aliphatic thermoplastic polyester, produced by the ring-opening polymerization of lactide.<sup>[3,4]</sup> Lactide is a cyclic dimer prepared by the controlled depolymerization of lactic acid, which in turn is obtained by the fermentation of corn, sugar beat, etc.<sup>[1,5]</sup> PLA has good mechanical properties, thermal plasticity, fabric produces no nitrogen oxide gases and only one-third the combustible heat generated by polyolefins, it does not damage the incinerator and thus, provides significant energy savings.<sup>[7]</sup> Thus PLA is a promising polymer for various end-use

ability, and biocompatibility.<sup>[6]</sup> Even when burned it

applications and, currently, there is increasing interest in using PLA for disposable degradable plastic articles.<sup>[8]</sup> However, some of the other properties, such as heatdeflection temperature, flexural and gas barrier properties, and melt-viscosity for further processing, are frequently not good enough for a wide-range of applications.<sup>[9]</sup> On the other hand, the preparation of nanocomposites with organically modified layered silicates (OMLS) has already proven to be an effective way to improve these properties significantly.<sup>[10]</sup>

<sup>&</sup>lt;sup>a</sup> Part 5, cf. ref.<sup>[14a]</sup>

In a series of our recent publications,<sup>[11-14]</sup> we have reported on the preparation, characterization, materials properties, and biodegradability of various PLA/OMLS nanocomposites. The present study is concerned with the detailed melt rheological behavior of a series of PLA/ montmorillonite (MMT) nanocomposites, because the measurements of rheological properties of any polymeric material are very important to gain the fundamental understanding of the nature of processability for these materials, which is the final goal of any polymeric material. Aside from these, on the basis of viscoelastic behaviors under molten state we can easily find out the structureproperty relationship and PLA-OMLS interfacial interactions in these materials. Finally, on the basis of obtained rheological behaviors, we have conducted foam processing of pure PLA and one representative nanocomposite by a newly developed pressure cell technique using supercritical carbon dioxide  $(CO_2)$  as a physical-blowing agent.

# **Experimental Part**

#### Materials

PLA ( $T_g = 60 \degree C$ ,  $T_m = 168 \degree C$ ) with a D-lactide content of 1.1– 1.7% was supplied by Unitika Co. Ltd., and was used after being dried under vacuum at 70 °C. The organically modified MMT ( $C_{18}$ -MMT) used in this study as an OMLS was supplied by Nanocor Inc., and was synthesized by replacing Na<sup>+</sup> in MMT of a cation-exchange capacity of 110 mequiv  $\cdot$  100 g<sup>-1</sup> with octadecylammonium cation ( $C_{18}$ ) by an ion-exchange reaction.

#### Nanocomposite Preparation

For nanocomposite preparation,  $C_{18}$ -MMT powder and PLA pellets were first dry-mixed by shaking them in a bag. The mixture was then melt-extruded by using a twin-screw extruder (S-1 KRC, Kurimoto Ltd.) operated at 190 °C to yield very light gray coloured nanocomposite strands. Henceforth, the product nanocomposites were abbreviated as PLACNs. PLACNs with three different amounts of  $C_{18}$ -MMT of 3 (MMT = 2 wt.-%), 5 (MMT = 3 wt.-%), and 7 (MMT = 4.8 wt.-%) wt.-% were correspondingly abbreviated as PLACN3, PLACN5, and PLACN7, respectively. The extruded strands were pelletized and dried under vacuum at 60 °C for 48 h to remove water. The dried PLACNs pellets were then converted into sheets with a thickness of 0.7 to 2 mm by pressing with ca. 1.5 MPa at 190 °C for 3 min for various characterizations.

#### Characterization Methods

### Wide-Angle X-Ray Diffraction (WAXD)

WAXD experiments were performed for  $C_{18}$ -MMT powder and various PLACN sheets (annealed at 110 °C for 1.5 h) using a Maxlabo X-ray diffractometer (MAC Science Co., 3 kW,

#### Transmission Electron Microscopy (TEM)

The structure of the nanocomposites was investigated by means of a high-resolution TEM (H-7100, Hitachi Co.), operated at an accelerating voltage of 100 kV. The ultra-thin sections (the edge of the sample sheets) with a thickness of 100 nm were microtomed at -80 °C using a Reichert Ultra cut cryo-ultramicrotome without staining. The direction of the compression mold relative to the TEM sample surface was perpendicular.

#### Gel Permeation Chromatography (GPC)

The number-average  $(\overline{M}_n)$  and weight-average  $(\overline{M}_w)$  molecular weights of the PLA matrix (before and after nanocomposite preparation) were determined by means of GPC (LC-VP, Shimadzu Co.), using polystyrene standards for calibration and chloroform as a carrier solvent at 40 °C with the flow rate of 0.5 mL  $\cdot$  min<sup>-1</sup>. For the measurement of GPC we first dissolved PLA or PLACNs in chloroform and then diluted with tetrahydrofuran (THF). GPC results are summarized in Table 1. From Table 1 we can see that there is almost no degradation of the PLA matrix after nanocomposite preparation with C<sub>18</sub>-MMT.

#### Melt Rheology

Melt rheological measurements were conducted on Rheometric Dynamic Analyzer (RDAII) instrument with a torque transducer capable of measurements over the range of 0.2-200 g  $\cdot$  cm<sup>-1</sup>. Dynamic oscillatory shear measurements of polymeric materials are generally performed by applying a time dependent strain of  $\gamma(t) = \gamma_0 \sin(\omega t)$  and measuring the resultant shear stress  $\sigma(t) = \gamma_0 [G'(\omega) \sin(\omega t) + G''(\omega)]$  $\cos(\omega t)$ ], where  $G'(\omega)$  and  $G''(\omega)$  are the storage and loss moduli, respectively. Measurements were conducted by using a set of 25-mm diameter parallel plates with a sample thickness of ca. 1.5 mm and in the temperature range of 175–205 °C.<sup>b</sup> The strain amplitude was fixed to 5% to obtain reasonable signal intensities even at elevated temperature or low  $\omega$  to avoid the non-linear response. For each PLACN investigated, the limits of linear viscoelasticity were determined by performing strain sweeps at a series of fixed frequencies. The master curves were generated using the principle of timetemperature superposition and shifted to a common reference temperature ( $T_{ref}$ ) of 175 °C, which was chosen as the most representative of a typical processing temperature of PLA.

Steady-shear viscosity measurements were conducted at  $175 \,^{\circ}C$  using a 25-mm diameter cone and plate geometry with a

<sup>&</sup>lt;sup>9</sup> The degradation of intercalated octdecylammonium salt was checked by thermogravimetric analysis. There is no degradation up to 210 °C, however, after 272 °C there is a 5% weight loss.

Table 1. GPC results of pure PLA before and after nanocomposites preparation.

Sample	$\overline{M}_{ m w}~ imes~10^{-3}$	${\overline{M}_{ m w}}/{\overline{M}_{ m n}}$
	$g \cdot mol^{-1}$	
PLA	180	1.6
PLACN3	178	1.8
PLACN5	185	1.8
PLACN7	177	1.7

cone angle of 0.1 rad. The steady-shear viscosity data reported in this paper were obtained both as a function of shear rate ( $\dot{\gamma}$ ) and time.

#### Elongational Flow Rheology

A uniaxial elongation test at constant Hencky strain rate  $(\dot{e}_0)$  in the melt state was conducted with our recently developed elongational flow optorheometry, such as Meissner's new elongational rheometer (commercialized as RME from Rheometric Scientific). The detailed instrumentation is described elsewhere.<sup>[15]</sup>

On each run of the elongation test, samples of  $60 \times 7 \times 1 \text{ mm}^3$  size were annealed at a predetermined temperature (just above the  $T_{\rm m}$ ) for 3 min before starting the run in the rheometer, and uniaxial elongation experiments were conducted at various  $\dot{\epsilon}_0$  ranging from 0.01 to 1 s<sup>-1</sup>.

#### Foam Processing (Pressure Cell Technique)

Crystallized pure PLA (degree of crystallinity,  $\chi_c = 36\%$ ) and PLACN3 ( $\chi_c = 49\%$ ) sheets were cut into 2 cm × 2 cm pieces and placed in an autoclave connected to a CO<sub>2</sub> cylinder. The samples were then saturated with CO<sub>2</sub> at elevated temperature (140 °C, below the melting point of PLA) and pressure (ca. 10 MPa). Samples were then kept under this condition for 2 h. Subsequently, the CO<sub>2</sub> was quickly released from the autoclave (within 1 s). After removing the CO<sub>2</sub>-saturated pure PLA and PLACN3 sheets from the autoclave, the samples were immersed in a silicon oil bath maintained at the desired temperature (165 °C) for a fixed time (30 s, known as foaming time). The foamed samples were next quenched in an ethanol/water (1:1) mixture, washed in ethanol for at least 30 min, and dried under vacuum at 30 °C for 48 h to remove traces of ethanol and water.

The cellular morphologies of the foamed samples were investigated using a JEOL JSM-5310LV scanning electron microscope (SEM). The samples were freeze-fractured in liquid nitrogen and sputter coated with gold at an argon pressure of 0.1 Torr for 15 min at a current of 15 mA.

The mass density of both pre-foamed ( $\rho_p$ ) and post-foamed ( $\rho_f$ ) samples in g  $\cdot$  cm<sup>-3</sup> were estimated by using the method of buoyancy. The cell size (*d*) was obtained by measuring the maximum diameter of each cell perpendicular to the skin. To determine the cell-size distribution, the sizes of at least 75 cells in the core part of the cross section of the fractured-foam sample were measured. The cell densities ( $N_c$ ) and mean cell-wall thickness ( $\delta$ ) were determined by using the following

equations, respectively.<sup>[16]</sup>

$$N_{\rm c} \approx \frac{1 - \rho_{\rm f}/\rho_{\rm p}}{10^{-4}d^3} \text{ and } \delta = d\left(\frac{1}{\sqrt{1 - \rho_{\rm f}/\rho_{\rm p}}} - 1\right)$$
 (1)

# **Results and Discussions**

#### Nanocomposite Structure

Figure 1a represents the WAXD patterns of  $C_{18}$ -MMT powder and three PLACNs in the range of  $2\theta = 1-10^{\circ}$ . The mean interlayer spacing of the (001) plane ( $d_{(001)}$ ) for the  $C_{18}$ -MMT powder measured by WAXD measurements is 2.31 nm ( $2\theta \approx 3.82^{\circ}$ ). In the case of PLACN3, a small peak is observed at  $2\theta \approx 2.85^{\circ}$  ( $\approx 3.1$  nm), corresponding to the (001) plane of the silicate layers dispersed in the PLA matrix. With increasing  $C_{18}$ -MMT content, this peak becomes stronger and shifted to a higher diffraction angle



Figure 1. a) WAXD patterns for pure  $C_{18}$ -MMT powder and corresponding PLACNs. The asterisks indicate the (001) peak for  $C_{18}$ -MMT dispersed in the PLA matrix. Data were vertically shifted in order to make a clear presentation. b) TEM bright-field image of PLACN5. Dark entities are the cross section of the intercalated and stacked  $C_{18}$ -MMT layers.

Table 2. Form factors of various PLACNs.

Method of analysis		PLACN3	PLACN5	PLACN7
TEM	d <sub>MMT</sub> /nm L <sub>MMT</sub> /nm L <sub>MMT</sub> /d <sub>MMT</sub>	$38 \pm 17.25$ $448 \pm 200$ 12 $255 \pm 137$	$39 \pm 17$ $485 \pm 192$ 12.5 $229 \pm 121$	$40 \pm 18$ $512 \pm 201$ 13 $192 \pm 92$
WAXD	$d_{(001)}/\text{nm}$ $d_{\text{MMT}}/d_{(001)}$	3.1 12.2	3.01 13	2.89 14

at  $2\theta \approx 3.05^{\circ}$  ( $\approx 2.89$  nm) for PLACN7, accompanied by the appearance of another peak at  $2\theta \approx 5.6^{\circ}$ . After calculation, it was confirmed that this peak was because of a (002) plane  $(d_{(002)})$  of the intercalated and stacked silicate layers dispersed in the PLA matrix. In each PLACN, polymer chains were intercalated in the silicate galleries, and the coherent order of the silicate layers is much higher with increasing MMT content. So from the WAXD analyses, we can conclude that the ordered intercalated nanocomposites were formed with PLACNs, although the interlayer spacing increased significantly compared to that of C<sub>18</sub>-MMT.<sup>[11a]</sup>

The internal structure of the nanocomposites in the nanometer scale was directly observed via TEM imaging. TEM allows a qualitative understanding of the internal structure through direct visualization. Figure 1b shows the TEM bright-field image of PLACN5, in which dark entities are the cross section of the intercalated  $C_{18}$ -MMT layers.<sup>c</sup> From the TEM image, we observed stacked and flocculated silicate layers, which are randomly distributed in the PLA matrix.

Table 2 summarizes the form factors of various PLACNs obtained from WAXD patterns and TEM observations, i.e., average length ( $L_{MMT}$ ), thickness ( $d_{MMT}$ ) of the dispersed stacked and intercalated silicate layers, and the correlation length ( $\xi_{MMT}$ ) between them.

# Melt Rheology

#### Dynamic Oscillatory Shear Measurements

Generally, the rheology of polymer melts depends strongly on the temperature at which the measurement is carried out. It is well known that for thermo-rheologically simple materials, bi-logarithmic plots of the isotherms of the  $G'(\omega)$ ,  $G''(\omega)$ , and complex viscosity  $(|\eta^*|(\omega))$  can be superimposed by horizontal shifts  $\log(a_T)$ , along the  $\log(\omega)$ axis, and vertical shifts given by  $\log(b_T)$  such that:<sup>[17]</sup>

$$b_{\mathrm{T}}G'(a_{\mathrm{T}}\omega, T_{\mathrm{ref}}) = b_{\mathrm{T}}G'(\omega, T)$$
  

$$b_{\mathrm{T}}G''(a_{\mathrm{T}}\omega, T_{\mathrm{ref}}) = b_{\mathrm{T}}G''(\omega, T)$$
  

$$(b_{\mathrm{T}}/a_{\mathrm{T}})|\eta^*|(a_{\mathrm{T}}\omega, T_{\mathrm{ref}}) = |\eta^*|(\omega, T)$$



Figure 2. Reduced frequency dependence of storage modulus,  $G'(\omega)$  and loss modulus,  $G''(\omega)$  of PLA and various PLACNs.

where  $T_{ref}$  is the reference temperature. All isotherms measured for pure PLA and for various PLACNs can be superimposed in this way.

In the case of polymer samples, it is expected that at the temperatures and frequencies at which the rheological measurements were carried out, they should exhibit characteristic homopolymer-like terminal flow behavior, expressed by the power-laws  $G'(\omega) \propto \omega^2$  and  $G''(\omega) \propto \omega$ .

The master curves for  $G'(\omega)$  and  $G''(\omega)$  of pure PLA and various PLACNs with different weight percentages of  $C_{18}$ -MMT loading are presented in Figure 2. At high frequencies ( $a_T \cdot \omega > 10$ ), the viscoelastic behaviors of all PLACNs are the same. On the other hand, at low frequencies ( $a_T \cdot \omega < 10$ ), both moduli exhibit weak frequency dependence with increasing  $C_{18}$ -MMT content, such that there are gradual changes of behavior from liquid-like  $[G'(\omega) \propto \omega^2$  and  $G''(\omega) \propto \omega$ ] to solid-like with increasing  $C_{18}$ -MMT content.

The terminal regions slope of the master curves for  $G'(\omega)$ and  $G''(\omega)$  are presented in Table 3. The slope of  $G'(\omega)$  and  $G''(\omega)$  in the terminal region of the master curves of PLA matrix is 1.85 and 1, respectively, and these values are in the range expected for polydisperse polymers.<sup>[18]</sup> On the other hand, the slopes of  $G'(\omega)$  and  $G''(\omega)$  are considerably lower for all PLACNs compared to those of pure PLA. In fact, for PLACNs with high C<sub>18</sub>-MMT content,  $G'(\omega)$  becomes

<sup>&</sup>lt;sup>c</sup> Since the silicate layers are composed of heavier elements (AL, Si, O, etc.) than the intercalated and surrounding matrix (C, H, N, etc.), they appear darker in the bright-field image.

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Table 3. Terminal regions slopes of  $G'(\omega)$  and  $G''(\omega)$ .

Sample	$G'(\omega)$	$G''(\omega)$
PLA	1.85	1
PLACN3	0.25	0.5
PLACN5	0.18	0.4
PLACN7	0.1	0.3

nearly independent at low  $a_{\rm T} \cdot \omega$  and exceeds  $G''(\omega)$ , which is characteristic of materials exhibiting a pseudo-solid-like behavior.

As seen in Table 2,  $\xi_{MMT}$  values of PLACNs are smaller than that of  $L_{\text{MMT}}$  suggesting the formation of a 'spatiallylinked structure'. According to this structure, the individual stacked silicate layers are incapable of freely rotating (only translational motion is available), and hence, the relaxations of the structure by imposing small  $\omega$  are prevented almost completely with high MMT content.<sup>[19a]</sup> This type of prevented relaxation arising from the high geometric constraints or physical jamming of the stacked and intercalated MMT layers led to the presence of pseudo-solidlike behavior as observed in the cases of the PLACNs. The formation of this type of 'spatially-linked structure' in the PLACNs with high C18-MMT content under molten state is also confirmed by the lower slope values and the higher absolute values of the dynamic moduli in the case of the PLACNs.<sup>[19a]</sup>

Figure 3 represents the C<sub>18</sub>-MMT content dependent (wt.-%) flow activation energy  $(E_a)$  of pure PLA and various nanocomposites obtained from an Arrhenius fit<sup>[11a,20]</sup> of master curves. There is a significant increase of  $E_a$  for PLA/ C<sub>18</sub>-MMT3 compared to that of pure PLA followed by a much slower increase with increasing C<sub>18</sub>-MMT content. This behavior may be because of the dispersion of intercalated and stacked C18-MMT silicate layers in the PLA matrix.



Figure 3. Flow activation energy as a function of  $C_{18}$ -MMT content.



Figure 4. Reduced frequency dependence of complex viscosity

 $(|\eta^*|(\omega))$  of PLA and various PLACNs.

The dynamic complex viscosity  $[|\eta^*|(\omega)]$  master curves for the pure PLA and various PLACNs, based on linear dynamic oscillatory shear measurements, are presented in Figure 4. From Figure 4, we can see at low  $a_{\rm T} \cdot \omega$  region  $(< 10 \text{ rad} \cdot \text{s}^{-1})$ , pure PLA exhibits almost Newtonian behavior while all PLACNs show a very strong shearthinning tendency. On the other hand, the  $\overline{M}_{w}$  and PDI of pure PLA and various PLACNs are almost the same, thus the high viscosity of PLACNs can be explained by the flow restrictions of polymer chains in the molten state arising from the presence of MMT particles.

We believe this behavior comes from the nature of the layered silicate particles, which are dispersed in the PLA matrix. In our previous study<sup>[21]</sup> on lyophilized smectic clay-toluene suspensions, we observed this type of shear thinning feature of the clay particles in the rapid shear flow. Such a feature is strongly dependent on the shear rate in the dynamic measurements, because of the formation of the shear-induced alignment of the dispersed clay particles.<sup>[22]</sup>

#### Steady Shear Measurements

The steady shear rheological behavior of pure PLA and a series of intercalated PLACNs are shown in Figure 5. The shear viscosity of PLACNs is enhanced considerably at all shear rates with time, and at a fixed shear rate increases monotonically with increasing MMT content. On the other hand, all intercalated PLACNs exhibit strong rheopexy behavior, and this behavior becomes prominent at low shear rate ( $\dot{\gamma} = 0.001 \text{ s}^{-1}$ ), while pure PLA exhibits a time independent viscosity at all shear rates. With increasing shear rates, the shear viscosity attains a plateau after a certain time (indicated with the arrows in Figure 5), and the time require to attaining this plateau decreases with increasing shear rates. The possible reason for this type of behavior may be because of the planer alignment of the MMT particles towards the flow direction under shear. When shear rate is



Figure 5. Steady shear viscosity of PLA and various PLACNs as a function of time.

very slow (0.001 s<sup>-1</sup>), MMT particles take a longer time to attain complete planer alignment along the flow direction, and this measurement time (1000 s) is too short to attain such alignment. For this reason, nanocomposites show strong rheopexy behavior. On the other hand, under slightly lower shear rates (0.005 s<sup>-1</sup> or 0.01 s<sup>-1</sup>) this measurement time is enough to attain such alignment, and hence, nanocomposites show time-independent shear viscosity after a certain time.

In Figure 6, we show the shear rate dependence of viscosity for pure PLA and various PLACNs measured at 175 °C. While the pure PLA exhibits almost Newtonian behavior at all shear rates, the PLACNs exhibited non-



Figure 6. Steady shear viscosity of PLA and various PLACNs as a function of shear rate.

Newtonian behavior. At very low shear rates, the shear viscosity of the PLACNs initially exhibit some shear-thickening behavior and this corresponds to the rheopexy as observed at very low shear rates (see Figure 5). Subsequently, all PLACNs show a very strong shear-thinning behavior at all measured shear rates and this behavior is analogous to the results obtained in the case of oscillatory shear measurements (see Figure 4). Additionally, at very high shear rates, the steady shear viscosities of PLACNs are comparable to that of pure PLA. These observations suggest that the silicate layers are strongly oriented towards the flow direction (there may be perpendicular alignment of the silicate layers towards the stretching direction) at high shear rates, and that the pure polymer dominates shear-thinning behavior at high shear rates.<sup>[21]</sup>

Like the other polymer/OMLS systems,<sup>[19,23]</sup> the data for PLACNs also exhibit significant deviation from the Cox-Merz relation,<sup>[24]</sup> while pure PLA nicely obeys the empirical Cox-Merz relation, which requires that for  $\dot{\gamma} = \omega$ the viscoelastic data should obey the relationship  $\eta(\dot{\gamma}) =$  $|\eta^*|(\omega)$ . There are two possible reasons for the deviation of the Cox-Merz relation in the case of nanocomposites: First of all this rule is only applicable for homogeneous systems like homopolymer melts, but nanocomposites are heterogeneous systems. For this reason this relation is nicely obeyed in the case of pure PLA. Secondly, the structure formation is different when nanocomposites are subjected to dynamic oscillatory shear and steady shear measurements.<sup>[19a]</sup>

# Elongational Flow Behavior

Figure 7a shows double-logarithmic plots of transient elongational viscosity ( $\eta_{\rm E}$ ) against time (*t*) observed for PLACN5 at 170 °C with different Hencky strain rates ( $\dot{\epsilon}_0$ )



Figure 7. a) Time variation of elongational viscosity for PLACN5 melt at 170  $^\circ C.$  b) Strain rate dependence of up-rising Hencky strain.

ranging from 0.01 to  $1 \text{ s}^{-1}$ . We see in Figure 7a a very strong tendency to strain-induced hardening for the PLACN5 melt. In the early stage,  $\eta_{\rm E}$  gradually increases with t but is almost independent of  $\dot{\epsilon}_0$ , which we generally call the *linear region* of the viscosity curve. After a certain time,  $t_{\eta_F}$ , which we call the *up-rising* time (marked with the upward arrows in the Figure), is strongly dependent on  $\dot{\epsilon}_0$ , we see rapid upward deviation of  $\eta_{\rm E}$  from the curves of the linear region. On the other hand, we have tried to measure the elongational viscosity of pure PLA but we were unable to do that accurately. We believe the very low shear viscosity of pure PLA is the main reason for this, because the minimum viscosity range of our instrument is greater than  $10^4$  Pa  $\cdot$  s. However, we have confirmed that neither strain-induced hardening in elongation nor rheopexy in shear flow (see Figure 5 and Figure 6) took place in the case of pure PLA having the same molecular weights and polydispersity with that of PLACN3.

Like polypropylene/OMLS systems, the extended Trouton rule,  $3\eta_0(\dot{\gamma};t) \approx \eta_E(\dot{\epsilon}_0;t)$ , does not hold for PLACN5 melt, as opposed to the melt of pure polymers.<sup>[22]</sup> These results indicate that in the case of PLACN5, the flow induced internal structural changes also occur in elongation flow,<sup>[24]</sup> but the changes are quite different from shear flow. The strong rheopexy observed in shear measurements for PLACN5 at a very slow shear rate reflects the fact that the shear-induced structural change involved a process with an extremely long relaxation time.

As to the elongation-induced structure development, we show in Figure 7b the Hencky strain rate dependence of the up-rising Hencky strain  $(\varepsilon_{\eta_E}) = \dot{\varepsilon}_0 \times t_{\eta_E}$  taken for PLACN5 at 170 °C. The  $\varepsilon_{\eta_E}$  values increase systematically with  $\dot{\varepsilon}_0$ . The lower the value of  $\dot{\varepsilon}_0$ , the smaller is the value of  $\varepsilon_{\eta_E}$ . This tendency probably corresponds to the rheopexy of PLACN5 under slow shear flow.

#### Foam Processing and Cellular Structure

In the preceding sections, we have reported on melt rheological properties of pure PLA and various PLACNs in detail. Dynamic measurements indicated the formation of 'spatially linked structure' in the case of PLACN melts, and during shear measurements we observed very strong rheopexy behavior under very slow shear field. Under uniaxial elongational flow, PLACN5 exhibited very high viscosity and a tendency of strong strain-induced hardening, which may originate from the perpendicular alignment of the MMT layers towards the stretching direction.<sup>[22]</sup> This strain-induced hardening behavior is an indispensable characteristic for foam processing because of its capacity to withstand the stretching force experienced during the latter stages of bubble growth. To evaluate the performance potential of the biodegradable PLACNs toward foam application, we have conducted the foam processing of one representative nanocomposite PLACN5, using a newly developed pressure cell technique, with the expectation that it would provide advanced biodegradable foam with excellent properties, meeting our demand.

Figure 8 shows the typical results of SEM images of the freeze-fractured surfaces of pure PLA and PLACN5 foams. We noted here that homogeneous cells with close-cell structure were formed in the case of the PLACN5 foam, while the pure PLA foam shows non-uniform cell structure having large cell size ( $\approx 230 \,\mu$ m). In addition, the PLACN5 foam shows a smaller cell size (*d*) and larger cell density ( $N_c$ ) compared to that of pure PLA foam, suggesting that the dispersed silicate particles act as nucleating sites for cell formation.

In the case of the PLACN5 foam, we have calculated the distribution function of cell size from SEM images and the results are presented in Figure 9. The PLACN5 foam nicely obeys a Gaussian distribution. From the SEM image, we



### PLACN5

Figure 8. SEM image of the freeze-fractured surface of pure PLA and PLACN5 foams.

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have quantitatively calculated various morphological parameters such as d,  $\delta$ ,  $N_c$  etc. for PLACN5 foam, and the values are, 2.59 µm, 0.66 µm, and  $3.6 \times 10^{11}$  cell  $\cdot$  cm<sup>-3</sup>, respectively.



Figure 9. Cell size distribution of PLACN5 foam. Average values of *d* in  $\mu$ m and variances  $\sigma_d^2$  in  $\mu$ m<sup>2</sup> in the Gaussian fit through the data are 2.59 and 0.551, respectively.

These results indicate that the presence of the MMT particles play a vital role in controlling the size of the cell during foaming. On the other hand, the very high value of  $N_c$  in the case of the PLACN5 foam indicates that the final  $\rho_f$  is controlled by the competitive process in the cell nucleation, its growth, and coalescence. The cell nucleation, in the case of the nanocomposite system, took place in the boundary between the matrix polymer and the dispersed MMT particles. For this reason, the cell growth and coalescence are strongly affected by the storage and loss modulus ( $\approx$  viscosity component) of the materials during processing.

Even though the foam processing in this study was conducted just below the  $T_{\rm m}$  of the matrix but in the presence of supercritical CO<sub>2</sub> the material became soft. For this reason, we have to take into account not only the effect of the MMT particles on  $N_{\rm c}$  and the moduli but also the strain-induced hardening on the formed thick cell wall during foam processing in order to understand the above features on the nanocomposite foam. Such strain-induced hardening behavior is probably strong enough to increase the extensional viscosity under biaxial flow and to protect the cell from the breakage at high temperature; therefore, the strain-induced hardening led to the formation of homogeneous micro-cellular foam in the case of PLACN5 without the loss of mechanical properties.

# Conclusions

In this article we have reported the detailed melt rheological properties of a series of  $C_{18}$ -MMT-based nanocomposites of polylactide. The viscoelastic measurements under molten state indicated the presence of pseudo-solid-like behavior in nanocomposites, and are more prominent with high MMT content. We have established that this behavior caused by the formation of a mesoscopic structure of randomly oriented intercalated and stacked  $C_{18}$ -MMT layers in the PLA matrix. In the case of steady shear measurements, we observed very strong rheopexy behavior in the case of PLACNs under a very slow shear field.

Under uniaxial elongational flow, the nanocomposites exhibited very high viscosity and a tendency to strong strain-induced hardening, which we believe originated from the perpendicular alignment of the MMT layers towards the stretching direction. On the basis of these rheological data, we have conducted foam processing of one representative nanocomposite using a newly developed pressure cell technique using carbon dioxide as a physical-blowing agent. The nanocomposite foam shows homogeneous close-cell structure having a cell size in the micrometer region (2.59  $\mu$ m).

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