Nanostructure Development and Foam Processing in Polymer/Layered Silicate Nanocomposites

M. Okamoto

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6.1 Introduction

A decade of research has shown that nanostructured materials have the potential to significantly impact growth at every level of the world economy in the twenty-first century. This new class of materials is now being introduced in structural applications including gas barrier films, flame retardant products, and other load-bearing applications.

Of particular interest are recently developed nanocomposites consisting of a polymer and layered silicate, which often exhibit remarkably improved properties when compared with polymer or conventional composites (both micro- and macro-composites). In polymer/layered silicate nanocomposites, a nylon 6/layered silicate hybrid reported by Toyota Central Research & Development Co. Inc. (TCRD) was successfully prepared by in-situ polymerization of \( \varepsilon \)-caprolactam in a dispersion of montomorillonite (MMT). The silicate can be dispersed in liquid monomer or a solution of monomer. It has also been possible to melt-mix polymers with layered silicates, avoiding the use of organic solvents. This method permits the use of conventional processing techniques such as injection molding and extrusion. The extensive literature on nanocomposite research are covered in recent reviews.\(^1,3,4\)

Continued progress in nanoscale controlling, as well as an improved understanding of the physico-chemical phenomena at the nanometer scale, have contributed to the rapid development of novel nanocomposites. This chapter presents current research on polymer/layered silicate nanocomposites (PLSNCs) with the primary focus on nanostructure development and foam processing operations.

Development of nanocomposite foams is one of the latest evolutionary technologies of the polymeric foam following a pioneering effort by Okamoto and his colleagues.\(^5,6\) They prepared polypropylene (PP)/layered silicate, poly(l-lactide) (PLA)/layered silicate and polycarbonate (PC)/layered silicate nanocomposites foams in a batch process using supercritical \( \text{CO}_2 \) as a physical foaming agent.\(^6,8\)

To innovate on the material properties of nanocomposite foams, one needs to pin down the morphological correlation between the dispersed silicate particles with nanometer dimensions in the bulk and the formed closed-cellular structure after foaming. This chapter is devoted to the study of evaluation of the performance potential of PLSNCs in foam application.
6.2 Nanostructure Development

6.2.1 Melt Intercalation

Since the possibility of direct melt intercalation was first demonstrated, melt intercalation has become a preparation of the intercalated polymer/layered silicate nanocomposites (PLSNCs). This process involves annealing, statically or under shear, a mixture of the polymer and organically modified layered fillers (OMLFs) above the softening point of the polymer. During annealing, the polymer chains diffuse from the bulk polymer melt into the nanogalleries between the layered fillers.

In order to understand the thermodynamic issue associated with the nanocomposite formation, Vaia et al. have applied a mean-field statistical lattice model and found conclusions based on the mean field theory agreed with the experimental results. The entropy loss associated with confinement of a polymer melt is not prohibited to nanocomposite formation because an entropy gain associated with the layer separation balances the entropy loss of polymer intercalation, resulting in a net entropy change near to zero. Thus, from the theoretical model, the outcome of nanocomposite formation via polymer melt intercalation depends on energetic factors, which may be determined from the surface energies of the polymer and OMLF.

Nevertheless, we have often faced the problem where the nanocomposite shows fine and homogeneous distribution of the nanoparticles in the polymer matrix (e.g. poly(l-lactide)) without a clear peak shift of the mean interlayer spacing of the (001) plane, as revealed by wide-angle X-ray diffraction (WAXD) analysis. Furthermore we sometimes encounter a decrease in interlayer spacing compared with that of pristine OMLF, despite very fine dispersion of the silicate particles. For this reason, information on the structure of the surfactant (intercalant)–polymer interface is necessary to understand the intercalation kinetics that can predict final nanocomposite morphology and overall material properties.

6.2.2 Interlayer Structure of OMLFs and Intercalation

6.2.2.1 Nanofillers

In characterizing layered silicate, including layered titanate (HTO), the surface charge density is particularly important because it determines the interlayer structure of intercalants as well as cation exchange capacity (CEC). Lagaly proposed a method consisting of total elemental analysis and the dimension of the unit cell:

\[
\text{surface charge} \left( \frac{e^-}{\text{nm}^2} \right) = \frac{\xi}{ab}
\]  

(6.1)
where $\xi$ is the layer charge (1.07 for HTO, 0.66 for synthetic fluorine hectorite (syn-FH), and 0.33 for montmorillonite (MMT); $a$ and $b$ are cell parameters of HTO ($a = 3.782$ Å, $b = 2.978$ Å), syn-FH ($a = 5.24$ Å, $b = 9.08$ Å), and MMT ($a = 5.18$ Å, $b = 9.00$ Å). For syn-FH, however, about 30% of the interlayer Na$^+$ ions are not replaced quantitatively by intercalants due to the non-activity for ion-exchange reactions. For HTO, only 27% of interlayer H$^+$ (H$_3$O$^+$) is active for ion-exchange reactions. The remaining part is the non-active site in the HTO. Thus the incomplete replacement of the interlayer ions is ascribed to the intrinsic chemical reactivity. The characteristic parameters of three nanofillers are summarized in Table 6.1.

### Table 6.1

<table>
<thead>
<tr>
<th>Parameters</th>
<th>HTO</th>
<th>syn-FH</th>
<th>MMT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>$H_{1.07}Ti_{1.73}O_{3.95}·0.5H_2O$</td>
<td>$Na_{0.66}Mg_{2.6}Si_7O_{10}(F)_2$</td>
<td>$Na_{0.33}(Al_{1.67}Mg_{0.33})Si_7O_{19}(OH)_2$</td>
</tr>
<tr>
<td>Particle size (nm)</td>
<td>~100–200</td>
<td>~100–200</td>
<td>~100–200</td>
</tr>
<tr>
<td>BET area (m$^2$/g)</td>
<td>~2400</td>
<td>~800</td>
<td>~700</td>
</tr>
<tr>
<td>CEC$^+$ (meq/100 g)</td>
<td>~200 (660)</td>
<td>~120 (170)</td>
<td>~90 (90)</td>
</tr>
<tr>
<td>$\xi$ (charge/nm$^2$)</td>
<td>1.26</td>
<td>0.971</td>
<td>0.708</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>2.40</td>
<td>2.50</td>
<td>2.50</td>
</tr>
<tr>
<td>Refractive index ($n_20^\prime$)</td>
<td>2.3</td>
<td>1.55</td>
<td>1.55</td>
</tr>
<tr>
<td>pH</td>
<td>4–6</td>
<td>9–11</td>
<td>7.5–10</td>
</tr>
</tbody>
</table>

$^a$ Methylene blue adsorption method. The values in the parenthesis are calculated from chemical formula of nanofillers.

(a) Octadecyl ammonium \([\text{C}_{18}\text{H}_3\text{N}^+]\)

(b) Octadecyl trimethyl ammonium \([\text{C}_{18}(\text{CH}_3)_3\text{N}^+]\)

(c) Dioctadecyldimethyl ammonium \([2\text{C}_{18}(\text{CH}_3)_2\text{N}^+]\)

(d) \(N\)-(coco alkyl)-\(N,N\)-[bis(2-hydroxyethyl)]-\(N\)-methyl ammonium \([q\text{C}_{14}(\text{OH})]\)

FIGURE 6.1 Molecular dimensions of intercalants: (a) octadecylammonium \((\text{C}_{18}\text{H}_3\text{N}^+))\); (b) octadecyltrimethylammonium \((\text{C}_{18}(\text{CH}_3)_3\text{N}^+))\); (c) dioctadecyldimethylammonium \((2\text{C}_{18}(\text{CH}_3)_2\text{N}^+))\); and (d) \(N\)-(coco alkyl)-\(N,N\)-[bis(2-hydroxyethyl)]-\(N\)-methyl ammonium cations \((q\text{C}_{14}(\text{OH}))\). (From: Yoshida, O. and Okamoto, M. Macromolecular Rapid Communications 27 (2006): 751. © 2006 Wiley-VCH.)

layer arrangement like flat-lying chains\(^{13}\) in each gallery space of the nano-fillers. All of the intercalants are oriented with some inclination to the host layer in the interlayer space to form an interdigitated layer. This is suggested by the paraffin-type layer structure proposed by Lagaly, especially in the case of highly surface-charged clay minerals.\(^{13}\)
Wide-angle X-ray diffraction (WAXD) patterns for three OMLF powders are presented in Figure 6.2. The mean interlayer spacing of the (001) plane ($d_{(001)}$) for the HTO intercalated with qC$_{14}$(OH) (HTO-qC$_{14}$(OH)) obtained by WAXD measurements is 2.264 nm (diffraction angle, $2\theta \cong 3.90^\circ$). The appearances of small peaks observed at $2\theta \cong 7.78^\circ$, $11.78^\circ$ and $15.74^\circ$ confirmed that these reflections were due to (002) up to (004) plane of HTO-qC$_{14}$(OH). HTO-qC$_{14}$(OH) showed a surprisingly well-ordered suprastructure, as demonstrated by WAXD with diffraction maxima up to the fourth order, due to the high surface charge density of the HTO layers. On the other hand, syn-FH and MMT, which have low surface charge density compared with that of HTO, show a less-ordered interlayer structure; that is, the coherent order of the silicate layers is much lower in each syn-FH and MMT intercalated with surfactants.

From WAXD results, we can discuss the interlayer opening that is estimated after subtraction of the layer thickness value of 0.374 nm for HTO, 0.98 nm for syn-FH, and 0.96 nm for MMT. This is an important point for the following discussion of the interlayer structure. The illustration of a model of interlayer structure of the \( \text{qC}_{14} \text{(OH)} \) in the gallery space of the HTO is shown in Figure 6.3. For nanofillers with high surface charge density, the intercalants can adopt a configuration with orientation where the alkyl chains are tilted under the effect of van der Waals forces, which decreases the chain–chain distance. For this reason, the angle \( \alpha \) should be directly related to the packing density of the alkyl chains. The value of \( \alpha \) decreases until close contact between the chains is attained, giving an increase in the degree of the crystallinity of the intercalants in the nanogalleries. To estimate the tilt angle \( \alpha \), we combined the molecular dimension, interlayer spacing, and loading amount of intercalant in the layers, which was calculated from thermogravimetry analysis (TGA). The characteristic parameters are summarized in Tables 6.2 and 6.3. Note that HTO exhibits a large layer opening accompanied with large values of \( \alpha \) and endothermic heat flow (\( \Delta H \)) owing to the melting of the intercalants in the galleries when compared with those of syn-FH and MMT. This indicates that HTO leads to a highly interdigitated layer structure and the interlayer

\[
\begin{align*}
\text{HTO-qC}_{14} \text{(OH)} \\
\text{Ti-O} & \quad \text{OH} \\
\text{N}^+ \text{CH}_3 & \quad \text{OH} \\
\text{CH}_3 \quad \text{N}^+ \text{CH}_3 & \quad \text{OH} \\
\text{CH}_3 \quad \text{N}^+ \text{HO} & \quad \text{CH}_3 \quad \text{N}^+ \text{HO} \\
\end{align*}
\]

**FIGURE 6.3** Illustration of a model of interlayer structure of intercalant \( \text{N}-(\text{cocoalkyl})-\text{N},\text{N}-(\text{bis[2-hydroxyethyl]}))-\text{N}-\text{methyl ammonium cation (qC}_{14}(\text{OH})) \) in gallery space of layer titanate (HTO). The average distance between exchange sites is 0.888 nm, calculated by surface charge density of 1.26 e/\( \text{nm}^2 \). For \( \text{qC}_{14}(\text{OH}) \), obtained molecular length, thickness and width are 2.09 nm, 0.881 nm, and 0.374 nm, respectively (see Figure 6.1). The tilt angle \( \alpha \) of the intercalants can be estimated by the combination of the interlayer spacing, molecular dimensions, and loading amount of intercalants when the alkyl chains adopt an all-trans conformation. (From: Yoshida, O. and Okamoto, M. *Macromolecular Rapid Communications* 27 (2006): 751. © 2006 Wiley-VCH.)
opening becomes more uniform compared with MMT and syn-FH (possessing lower surface charge density).

From this fact, we can observe well-defined diffraction peaks up to the (004) plane (see Figure 6.2). The entropic contribution of the intercalants, which leads to the entropy gain associated with the layer expansion after intercalation of the polymer chains, may not be significant because of the interdigitated layer structure.

### 6.2.2.3 Correlation of Intercalant Structure and Interlayer Opening

For the interdigitated layer structure in MMT, alkyl chain length (i.e. C18H37, CH3 and (CH2)2OH in the amine structure) changes the interlayer opening. That is, when we compare different intercalants having the same long alkyl chain (i.e. C18H3N+ and C18(CH3)3N+), three methyl (CH3) substituents instead of hydrogen (H) disturb the contact with silicate surfaces. The value of $\alpha$ decreases until close contact between the ammonium cations

### TABLE 6.2

<table>
<thead>
<tr>
<th></th>
<th>HTO-qC14(OH)</th>
<th>syn-FH-qC14(OH)</th>
<th>MMT-qC14(OH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer opening (nm)</td>
<td>1.889</td>
<td>1.083</td>
<td>0.895</td>
</tr>
<tr>
<td>Tilt angle $\alpha$ (°)</td>
<td>64.4</td>
<td>31.1</td>
<td>25.3</td>
</tr>
<tr>
<td>Organic content (wt%)</td>
<td>39.6</td>
<td>30.4</td>
<td>32.5</td>
</tr>
<tr>
<td>$T_m$ (°C)</td>
<td>108.3</td>
<td>111.3</td>
<td>97.7</td>
</tr>
<tr>
<td>$\Delta H$ (J/g)</td>
<td>214.5</td>
<td>141.2</td>
<td>138.6</td>
</tr>
</tbody>
</table>

$^a$ The melting and heat flow of qC14(OH)Cl− are 35.8°C and 69.8 J/g, respectively.


### TABLE 6.3

<table>
<thead>
<tr>
<th></th>
<th>C14H3N+</th>
<th>C14(CH3)3N+</th>
<th>2C14(CH3)2N+</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer opening (nm)</td>
<td>1.350</td>
<td>1.011</td>
<td>1.540</td>
</tr>
<tr>
<td>Tilt angle $\alpha$ (°)</td>
<td>33.2</td>
<td>22.9</td>
<td>40.1</td>
</tr>
<tr>
<td>Organic content (wt%)</td>
<td>35.5</td>
<td>29.5</td>
<td>39.8</td>
</tr>
<tr>
<td>$T_m$ (°C)</td>
<td>69.9</td>
<td>69.5</td>
<td>44.0</td>
</tr>
<tr>
<td>$\Delta H$ (J/g)</td>
<td>177.7</td>
<td>189.6</td>
<td>129.7</td>
</tr>
</tbody>
</table>

$^a$ The melting and heat flow of C14H3N+, C14(CH3)3N+, and 2C14(CH3)2N+ are 83.8°C and 95.6 J/g; 103.5°C and 161.2 J/g; and 37.0°C and 54.6 J/g, respectively.

and silicate surfaces is attained, giving a decrease in the interlayer opening (\(d_{(001)}\)) (see Table 6.3 and Figure 6.2).

In cases where the intercalant has two long alkyl chains (i.e. \(2\text{C}_{18}(\text{CH}_3)\text{N}^+\)), the packing density of the alkyl chains is reduced and sterically limited in the nanogalleries. Consequently, MMT-\(2\text{C}_{18}(\text{CH}_3)\text{N}^+\) exhibits large interlayer opening accompanied by low crystallinity of the intercalant (\(\Delta H \sim 130\) J/g) compared with MMT-\(\text{C}_{18}\text{H}_3\text{N}^+\) and MMT-\(\text{C}_{18}(\text{CH}_3)\text{N}^+\). Accordingly, we observe a disordered diffraction peak of (001) plane of MMT-\(2\text{C}_{18}(\text{CH}_3)\text{N}^+\) in the WAXD analysis (see figure 1 in Reference 17). We have to pay attention to the molecular size of the substituents instead of H attached to the nitrogen for the better understanding of the interdigitated layer structure and direct polymer melt intercalation. This feature has been observed in the results of OMLFs intercalated with various intercalants (such as octadecyl di-methylbenzylammonium, \(n\)-hexadecyl tri-\(n\)-butyl phosphonium, \(n\)-hexadecyl tri-phenyl phosphonium cations).18

### 6.2.2.4 Nanocomposite Structure

Figure 6.4 shows the results of TEM bright field images of PLA-based nanocomposites, in which dark entities are the cross-section of intercalated MMT layers. The organically modified MMT content in all nanocomposites was 4 weight-percentage. From the TEM images, it becomes clear that there are some intercalated and stacked silicate layers in the nanocomposites. Yoshida et al. estimated the form factors obtained from TEM images; that is, average value of the particle length (\(L\)), of the dispersed particles, and the correlation length (\(\xi\)) between them.19 From the WAXD patterns, the crystallite size (\(D\)) of intercalated stacked silicate layers of each nanocomposite was calculated using the Scherrer equation. The calculated value of \(D\) (\(=\)thickness of the dispersed particles) and other parameters for each nanocomposite are presented in Table 6.4.

For PLA/MMT-\(\text{C}_{18}(\text{CH}_3)\text{N}^+\) and MMT content in all nanocomposites was 4 weight-percentage. From the TEM images, it becomes clear that there are some intercalated and stacked silicate layers in the nanocomposites. Yoshida et al. estimated the form factors obtained from TEM images; that is, average value of the particle length (\(L\)), of the dispersed particles, and the correlation length (\(\xi\)) between them.19 From the WAXD patterns, the crystallite size (\(D\)) of intercalated stacked silicate layers of each nanocomposite was calculated using the Scherrer equation. The calculated value of \(D\) (\(=\)thickness of the dispersed particles) and other parameters for each nanocomposite are presented in Table 6.4.

For PLA/MMT-\(\text{C}_{18}(\text{CH}_3)\text{N}^+\) and MMT-\(\text{C}_{18}\text{H}_3\text{N}^+\) in the WAXD analysis (see figure 1 in Reference 17). We have to pay attention to the molecular size of the substituents instead of H attached to the nitrogen for the better understanding of the interdigitated layer structure and direct polymer melt intercalation. This feature has been observed in the results of OMLFs intercalated with various intercalants (such as octadecyl di-methylbenzylammonium, \(n\)-hexadecyl tri-\(n\)-butyl phosphonium, \(n\)-hexadecyl tri-phenyl phosphonium cations).18

Although the (initial) interlayer opening of MMT-\(\text{C}_{18}(\text{CH}_3)\text{N}^+\) at 1.011 nm is smaller than MMT-\(\text{C}_{18}\text{H}_3\text{N}^+\) at 1.350 nm and MMT-\(2\text{C}_{18}(\text{CH}_3)\text{N}^+\) at 1.540 nm, the intercalation of the PLA in these different OMLFs gives almost the same basal spacing after preparation of the nanocomposites. Note that the existence of a sharp Bragg peak in PLA-based nanocomposites
FIGURE 6.4 Bright filed TEM images of PLA-based nanocomposites prepared with: (a) MMT-C₆H₁₃N⁺; (b) MMT-C₆(CH₃)₂N⁺; and (c) MMT-2C₆(CH₃)₂N⁺. The dark entities are the cross-section and/or face of intercalated-and-stacked silicate layers and the bright areas are the matrix. (From: Yoshida, O. and Okamoto, M. Macromolecular Rapid Communications 27 (2006): 751. © 2006 Wiley-VCH.)
after melt extrusion clearly indicates that the dispersed silicate layers still retain an ordered structure after melt extrusion.

In Table 6.4 they summarized the layer expansion after preparation (=opening) of three nanocomposites, or after subtraction of the initial layer opening. For the same MMT with different intercalants (e.g. comparison between MMT-C_{18}(CH_{3})_{3}N\(^{+}\) and MMT-2C_{18}(CH_{3})_{2}N\(^{+}\)), the layer expansion of the former (0.879 nm) exhibits a large value compared with that of the latter (0.45 nm) in PLA-based nanocomposites. In other words, the smaller interlayer opening caused by the configuration with a small tilt angle (\(\alpha = 22.9^\circ\) for C_{18}(CH_{3})_{3}N\(^{+}\)) promotes a large amount of intercalation of the polymer chains. Accordingly, PLA/MMT-C_{18}(CH_{3})_{3}N\(^{+}\) exhibits finer dispersion of the nanofillers compared with PLA/MMT-2C_{18}(CH_{3})_{2}N\(^{+}\) and PLA/MMT-C_{18}H_{3}N\(^{+}\) as discussed previously (see Figure 6.4).

A more interesting feature is the absolute value of \(\Delta\) opening, According to the molecular modeling, the width and thickness of the PLA are 0.76 nm and 0.58 nm (see Figure 6.5). This may suggest that the polymer chains could not penetrate into galleries in the case of MMT-2C_{18}(CH_{3})_{2}N\(^{+}\) when we compare the apparent interlayer expansion (=\(\Delta\) opening).

Now it is necessary to understand the meaning of the interlayer expansion in the intercalated nanocomposites. As discussed previously, we have to take the interdigitated layer structure into consideration. This structure may suggest that a different orientation angle could be adopted when the polymer chains penetrate into the galleries, giving a decrease in basal spacing after intercalation. At the same time, this structure apparently provides a balance between the polymer penetration and different orientation angle of the intercalants; that is, we have to pay attention to the polymer chain intercalation into the galleries from the result of the change of the basal spacing as revealed by WAXD. Presumably the penetration of the polymer chain is prevented or reduced by the steric limitation of the

**TABLE 6.4**
Form Factors of Three Nanocomposites Obtained from WAXD and TEM Observations

<table>
<thead>
<tr>
<th>Nano-composites</th>
<th>PLA/MMT-C_{18}H_{3}N(^{+})</th>
<th>PLA/MMT-C_{18}(CH_{3})_{3}N(^{+})</th>
<th>PLA/MMT-2C_{18}(CH_{3})_{2}N(^{+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d_{001}) (nm)</td>
<td>3.03</td>
<td>2.85</td>
<td>2.95</td>
</tr>
<tr>
<td>(\Delta) opening (nm)</td>
<td>0.72</td>
<td>0.879</td>
<td>0.45</td>
</tr>
<tr>
<td>Final layer opening (nm)</td>
<td>2.07</td>
<td>1.89</td>
<td>1.99</td>
</tr>
<tr>
<td>(D) (nm)</td>
<td>20.9</td>
<td>10.73</td>
<td>14.71</td>
</tr>
<tr>
<td>((D/d_{001}) + 1)</td>
<td>7.9</td>
<td>4.8</td>
<td>6.0</td>
</tr>
<tr>
<td>(L) (nm)</td>
<td>450 ± 200</td>
<td>200 ± 25</td>
<td>655 ± 121</td>
</tr>
<tr>
<td>(\xi) (nm)</td>
<td>260 ± 140</td>
<td>80 ± 20</td>
<td>300 ± 52</td>
</tr>
</tbody>
</table>

configuration with a large value of $\alpha$ (e.g. $\alpha = 40.1^\circ$ for MMT-2C$_{18}$(CH$_3$)$_2$N$^+$). Accordingly, we sometimes observe small interlayer expansion and encounter a decrease in the interlayer spacing after melt intercalation. As seen in Table 6.4, the initial interlayer opening depends on the interlayer expansion ($=\Delta$ opening) after melt intercalation. The smaller initial opening leads to the larger interlayer expansion, and gives almost same final interlayer opening. This feature has been observed in the results of other nanocomposites prepared by different OMLFs intercalated with different surfactants.\textsuperscript{20} From this result, the entropic contribution of the intercalants, which leads to the entropy gain associated with layer expansion after intercalation of the small molecules and/or polymer chains, may not be significant owing to the interdigitated layer structure. Presumably the penetration takes place by pressure drop within the nanogalleries, nanocapillary action, generated by the two platelets.

As reported in the literature,\textsuperscript{18} the pressure drop ($\Delta p$) in the nanogalleries, which makes the polymer penetration more difficult, should be discussed. The estimated pressure difference ($\sim 24$ MPa) is much larger than the shear stress ($\sim 0.1$ MPa) during melt compounding.\textsuperscript{18} This suggests that shear stress has little effect on the delamination (exfoliation) of the layer. This reasoning is consistent with the intercalated structure reported by so many nanocomposite researchers, who can prepare only intercalated (not exfoliated) nanocomposites via the simple melt extrusion technique.\textsuperscript{1} A novel compounding process is currently in progress. Solid-state shear processing may be an innovative technique to delaminate the layered fillers.\textsuperscript{21}

Compared to OMLFs, the nanocomposite structure is difficult to model using atomic scale molecular dynamics (MD) because the intercalated polymer chain conformation is complex and is rarely in an equilibrium state. However, Pricl et al.\textsuperscript{22} explored and characterized the atomic scale
structure to predict binding energies and basal spacing of PLSNCs based on polypropylene (PP) and maleated (MA) PP (PP-MA), MMT, and different alkylammonium ions as intercalants (see Figure 6.6). From a global interpretation of all of these MD simulation results, they concluded that intercalants with a smaller volume are more effective for clay modification as they improve the thermodynamics of the system by increasing the binding energy. On the other hand, intercalants with longer tails are more effective for intercalation and exfoliation processes, as they lead to higher
basal spacing. Additional information is necessary to predict a more reasonable nanostructure of PLSNCs. Some literature related to the confined polymer chains within the silicate galleries by using coarse-grained MD simulation has been published.\textsuperscript{23–26}

### 6.3 Flow-Induced Structure Development

Rheological behavior, especially elongational and shear flow behavior in the molten state of PLSNCs, has not been well studied, although such knowledge should be indispensable in relation to their performance in processing operations. One objective of this chapter is to focus on a profound understanding of PLSNCs for their innovations in practical material production. For this purpose, it is indispensable to illuminate the nanostructure as well as rheological properties of PLSNCs to assess appropriate processing conditions for designing and controlling their hierarchical nanostructure, which must be closely related to their material performance.

#### 6.3.1 Elongational Flow and Strain-Induced Hardening

Okamoto et al.\textsuperscript{27} first conducted an elongation test of PP-based nanocomposites (PPCN4) under molten state at constant Hencky strain rate, $\dot{\varepsilon}_0$, using an elongation flow opto-rheometry, and attempted to control the alignment of the dispersed MMT layers with nanometer dimensions of intercalated PPCNs under uniaxial elongational flow.

Figure 6.7 shows double logarithmic plots of transient elongational viscosity $\eta_\varepsilon(\dot{\varepsilon}_0,t)$ against time $t$ observed for a nylon 6/OMLS system (N6CN3.7: MMT = 3.7 weight-percentage) and PPCN4 (MMT = 4 weight-percentage) with different Hencky strain rates, $\dot{\varepsilon}_0$, ranging from 0.001 s\textsuperscript{−1} to 1.0 s\textsuperscript{−1}.

The solid curve represents time development of three-fold shear viscosity, $3\eta_\dot{\gamma}(\dot{\gamma},t)$, at 225°C with a constant shear rate $\dot{\gamma} = 0.001$ s\textsuperscript{−1}. In $\eta_\varepsilon(\dot{\varepsilon}_0,t)$ at any $\dot{\varepsilon}_0$ N6CN3.7 melt shows a weak tendency of strain-induced hardening compared with that of PPCN4 melt. A strong behavior of strain-induced hardening for PPCN4 melt was originated from the perpendicular alignment of the silicate layers to the stretching direction as reported by Okamoto et al.\textsuperscript{28}

From TEM observation,\textsuperscript{29} the N6CN3.7 forms a fine dispersion of the silicate layers of about 100 nm in $L_{\text{clay}}$, 3 nm thickness in $d_{\text{clay}}$ and $\xi_{\text{clay}}$ of about 20–30 nm between them. The $\xi_{\text{clay}}$ value is one order of magnitude lower than the value of $L_{\text{clay}}$ suggesting the formation of a spatially linked-like structure of the dispersed clay particles in the nylon 6 matrix. For N6CN3.7 melt, the silicate layers are densely dispersed into the matrix and hence
difficult to align under elongational flow. Under flow fields, the silicate layers might translationally move, but not rotationally in such a way that the loss energy becomes minimum. This tendency was also observed in PPCN7.5 melt having higher content of MMT (weight-percentage).30

One can observe two features for the shear viscosity curve. First, the extended Trouton rule, \( \eta_0(\dot{\gamma}; t) = \eta_0(\dot{\gamma}_0;t) \), does not hold for both N6CN3.7 and PPCN4 melts, as opposed to the melt of ordinary homo-polymers. The latter, \( \eta_0(\dot{\gamma}_0;t) \), is more than 10 times larger than the former, \( 3\eta_0(\dot{\gamma}; t) \). Second, again unlike ordinary polymer melts, \( 3\eta_0(\dot{\gamma}; t) \) of N6CN3.7 melt increases continuously with \( t \), never showing a tendency of reaching a steady state within the time span (600 s or longer) examined here. This time-dependent thickening behavior may be called anti-thixotropy or rheopexy. Under slow shear flow (\( \dot{\gamma} = 0.001 \) s\(^{-1}\)), \( 3\eta_0(\dot{\gamma}; t) \) of N6CN3.7 exhibits a much stronger rheopexy behavior with almost two orders of magnitude higher than that.

**FIGURE 6.7** Time variation of elongational viscosity \( \eta_0(\dot{\gamma}; t) \) for: (a) N6CN3.7 melt at 225°C; and (b) PPCN4 at 150°C. The solid line shows three times the shear viscosity, \( 3\eta_0(\dot{\gamma}; t) \), taken at a low shear rate \( \dot{\gamma} = 0.001 \) s\(^{-1}\) on a cone-plate rheometer. (From Okamoto, M. “Polymer/Layered Silicate Nanocomposites.” Rapra Review Report No. 163, Rapra Technology Ltd, London, 2003. 166 pp. © 2003 Rapra Technology Ltd.)
of PPCN4. This reflects a fact that the shear-induced structural change involved a process with an extremely long relaxation time as well as for other PLSNCs having rheopexy behavior, especially under the weak shear field.

In uniaxial elongational flow (converging low) for a PPCN4, the formation of a ‘house-of-cards’ structure is found by TEM analysis. The perpendicular (but not parallel) alignment of disk-like MMT clay particles with large anisotropy toward the flow direction might sound unlikely but this could be the case, especially under an elongational flow field in which the extentional flow rate is the square of the converging flow rate along the thickness direction, if the assumption of affine deformation without volume change is valid. Obviously under such conditions, the energy dissipation rate due to viscous resistance between the disk surface and the matrix polymer is minimal when the disks are aligned perpendicular to the flow direction.

Some 20 years ago, van Olphen pointed out that the electrostatic attraction between the layers of natural clay in aqueous suspension arises from higher polar forces in the medium. The intriguing features such as yield stress thixotropy and/or rheopexy exhibited in aqueous suspensions of natural clay minerals may be taken as a reference to the present PLSNCs.

6.4 Foam Processing

Flow-induced internal structural change occurs in both shear and elongational flow, but differs in each case, as noted from the above results on $\eta(\dot{\varepsilon}, \dot{\gamma})$ and $3\eta(\dot{\gamma}; t)$ (see Figure 6.7). Thus, with the rheological features of the PLSNCs and the characteristics of each processing operation, tactics should be selected accordingly for a particular nanocomposite for the enhancement of its mechanical properties.

For example, the strong strain-induced hardening in $\eta(\dot{\varepsilon}, \dot{\gamma})$ is requisite for withstanding the stretching force during the processing, while the rheopexy in $3\eta(\dot{\gamma}; t)$ suggests that for such PLSNC a promising technology is the processing in confined space (such as injection molding) where shear force is crucial.

6.4.1 Foam Processing of PP-Based Nanocomposites

PPCNs have already been shown to exhibit a tendency toward strong strain-induced hardening. On the basis of this result, the first successful nanocomposite foam, processed by using supercritical (sc)-CO$_2$ as a physical foaming agent, appeared through a pioneering effort by Okamoto et al.

A small amount of nanofillers in the polymer matrix serve as nucleation
sites to facilitate the bubble nucleation during foaming. Novel nanocomposite foams based on the combination of new nanofillers and sc-CO$_2$ led to a new class of materials. The process consists of four stages: (1) saturation of CO$_2$ in the sample at desired temperature; (2) cell nucleation when the release of CO$_2$ pressure started (supersaturated CO$_2$); (3) cell growth to an equilibrium size during the release of CO$_2$; and (4) stabilization of cell via cooling of the foamed sample. The autoclave setup used in their study is shown in Figure 6.8. Figure 6.9 represents the scanning electron microscopy (SEM) images of PP-MA and various PPCNs foams conducted at various temperatures under a pressure of 10 MPa. From the SEM images it can be clearly observed that, apart from PPCN4 (MMT = 4 weight-percentage) and PPCN7.5 foams prepared at 130.6°C, all exhibit neatly closed-cell structures with cells having 12- or 14-hedron shapes. The formed cells show their faces mostly in pentagons or hexagons, which express the most energetically stable state of polygon cells. They also calculated the distribution function of cell sizes from SEM images as shown in Figure 6.10. From the distribution curve it is clearly seen that PPCN7.5 exhibited a bimodal distribution of cell size, whereas the other samples neatly follow a Gaussian distribution. Another interesting observation from Figure 6.10 is the width of the distribution peaks—the polydispersity of the cell size became narrower with the addition of clay into the matrix (PPCN2 and
PPCN4). This behavior may be due to the heterogenous clay sites possibly acting for cell nucleation and their uniform dispersion in the matrix, which, if present, leads to the high homogeneity in cell size. On the other hand, the cell size of prepared foam gradually decreases with increasing clay content in the PPCNs. This behavior is due to the intrinsically high viscosity of the materials with increasing clay loading, which were subjected to foam processing. In contrast, the cell density of the foams behaved in the opposite way. The characteristic parameters of pre- and post-formed samples are listed in Table 6.5. The function for determining cell density \( N_c \) in cells/cm\(^3\) is defined in the following equation:\(^6\)

\[
N_c = 10^4 \frac{3[1-(\rho_f/\rho_p)]}{4\pi d^3} \tag{6.2}
\]

On the other hand, the mean cell wall thickness \( \delta \) in \( \mu m \) was estimated by the following equation:\(^6\)

\[
\delta = d(1/\sqrt[3]{1 - (\rho_f/\rho_p)} - 1) \tag{6.3}
\]

Figure 6.11 shows the TEM images on the structure of the mono-cell wall (a) and the junction of three cell walls (b) for PPCN4 foamed at 134.7°C. In Figure 6.11a, the dispersed clay particles in the cell wall align along
the interface between the solid and gas phase. In other words, the clay particles arrange along the boundary of cells. The orientation angle of the dispersed clay particles (versus cell boundary), calculated statistically from TEM photographs, is about $5 \pm 3.6^\circ$, indicating that plane orientation of the dispersed clay particles to the cell boundary occurred. In a previous paper for PPCN4 melt, the perpendicular alignment of the clay particles to stretching or elongating direction was shown, which was the main reason for causing the strain-induced hardening in the uniaxial elongational viscosity.

In this foam processing, apparently, a similar structure is formed, probably by a different mechanism. Due to the biaxial flow of material during foam process, the clay particles probably either turned their face (marked

FIGURE 6.10 Typical example for cell size distribution of foamed PP-MA and PPCNs in experiment at 134.7°C. Average values of $d$ in $\mu m$ and variances $\sigma^2$ in $\mu m^2$ in the Gaussian fit through the data are: 122.1 and 12.1 for PP-MA foam; 95.1 and 9.8 for PPCN2 foam; and 64.4 and 3.1 for PPCN4 foam. (From Nam, P. H., Okamoto, M., Maiti, P., et al. Polymer Engineering Science 42 (2002): 1907. © 2002 Society of Plastic Engineers. With permission.)
with the arrows (A) in Figure 6.11a or fixed face orientation (marked with the arrows (B) in Figure 6.11a) and aligned along the flow direction of materials; that is, along the cell boundary. The interesting point here is that such aligning behavior of the clay particles may help cells to withstand the stretching force from breaking the thin cell wall; in other words, to improve the strength of foam in mechanical properties. The clay particles seem to act as a secondary cloth layer to protect the cells from being destroyed by external forces. How do such unique alignments represent an improvement in mechanical properties?

The compression modulus $K$ of the foams are shown in Table 6.6. The $K$ of the PPCN foams appears higher than that of PP-MA foam even though they have the same $\rho_f$ level. This may create the improvement of mechanical properties for polymeric foams through polymeric nanocomposites.
In Figure 6.11b, besides the alignment of clay particles, we can observe a random dispersion of clay in the central area of the junction (marked with the arrow in Figure 6.11b). Such behavior of clay particles presumably reflects the effect of stagnation flow region of material under the growth of three contacting cells.

Figure 6.12 shows the stress–strain curves and the strain recovery behavior of the PP-based nanocomposite (PPCN) foams in the compression mode at a constant strain rate of 5% min⁻¹. The nanocomposite foams exhibit high modulus compared to neat PP-g-MA foam. The residual strain is 17%.

### TABLE 6.6
Morphological parameters and compression modulus of PP and PPCN foams

<table>
<thead>
<tr>
<th>Foam Samples</th>
<th>$\rho_f$ (g.cm⁻³)</th>
<th>$d$ (µm)</th>
<th>$N_c \times 10^{-*}$ (Cell.cm⁻³)</th>
<th>$\delta$ (µm)</th>
<th>$K^*$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-MA</td>
<td>0.06</td>
<td>155.3</td>
<td>2.49</td>
<td>5.6</td>
<td>0.44</td>
</tr>
<tr>
<td>PPCN2</td>
<td>0.06</td>
<td>133.0</td>
<td>3.94</td>
<td>4.6</td>
<td>1.72</td>
</tr>
<tr>
<td>PPCN4</td>
<td>0.12</td>
<td>93.4</td>
<td>9.64</td>
<td>11.9</td>
<td>1.95</td>
</tr>
<tr>
<td>PPCN7.5</td>
<td>0.13</td>
<td>33.9</td>
<td>220</td>
<td>2.7</td>
<td>2.80</td>
</tr>
</tbody>
</table>

* At 25°C.

for PPCN2 (MMT = 2 weight-percentage) as well as neat PP foam, providing the excellent strain recovery and the energy dissipation mechanism, probably with the ‘house-of-cards’ structure formation in the cell wall, which enhances the mechanical properties of the nanocomposites like a spruce wood which is close to right-handed helix (see Figure 6.13).

6.4.2 In-Situ Observation of Foaming

To understand the complex mechanism of physical foaming, Taki et al. studied the dynamic behavior of bubble nucleation and growth in the batch foaming of PP-based nanocomposites. Employing image-processing techniques, the bubble nucleation and growth rate for different nanocomposites are analyzed from the series micrographs. Together with the solubility and diffusivity of CO$_2$ into the PP matrix, the mechanism of nanocomposite foaming is investigated.

Figure 6.14 shows a schematic diagram of the visual observation apparatus for batch physical foaming. It consists of a high-pressure cell, a gas supply line and a pump with a gas cylinder. The high-pressure cell is made of stainless steel and has two sapphire windows on the walls. The C-shape stainless steel is used for a spacer. A signal processing board (DITECT, Japan; HAS-PCI) is installed so as to record a series of micrographs onto an online computer.

Figure 6.15 shows the series of micrographs of PP-MA (upper) and PPCN7.5 (lower) foaming at 150°C under a pressure of 13 MPa. The
FIGURE 6.13 X-Ray microdiffraction experiment with a 2-μm-thick section of spruce wood embedded in resin. Note the asymmetry of the patterns in the enlargement (far left) which can be used to determine the local orientation of cellulose fibrils in the cell wall (arrows). The arrows are plotted in the right image with the convention that they represent the projection of a vector parallel to the fibrils onto the plane of the cross-section. The picture clearly shows that all cells are right-handed helices. (From Fratzl, P. Current Opinion in Colloid Interface Science 8 (2003): 32. © 2003 Elsevier Science.)

The dynamic behavior of bubble nucleation and growth in the very early stages of foaming can be seen in Figure 6.16. The bubble nucleation rate and the final density of bubbles were highest at PPCN7.5 foaming. Although a distinct difference in bubble nucleation rate as well as in the final bubble density could not be observed between PPCN2 and PPMA foaming, the nucleation rate and the final bubble density increased as the weight fraction of clay increased. Furthermore, the induction time became shorter as the clay content increased.

The bubble growth rate is quantified by measuring temporal change in cross-sectional area of each bubble. Figure 6.17 shows the representative growth rate of the bubbles born at the designated time in PP-MA and nano-composite foaming. Since the change in cross-sectional area of bubbles can be approximated by a linear function of time as mentioned above, the bubble growth observed by micrographs is a mass transfer-controlled process. Therefore, it can be said that the clay content changes the mass transfer rate of CO₂ from the matrix polymer to the bubbles. The clay particles decrease the diffusivity of CO₂ while keeping the solubility of CO₂ in the matrix polymer the same. Owing to the clay-induced diffusivity depression, the

increase in clay content depresses the mass transfer of CO₂ from the matrix polymer to the bubbles. As a result, the bubble growth rate is decreased.

### 6.4.3 PLA-Based Nanocomposite Foaming

Figure 6.18 shows the typical results of SEM images of the fracture surfaces of the PLA/MMT-ODA and neat PLA without clay foamed at a temperature range of 100–140°C under the different isobaric saturation conditions (14, 21, and 28 MPa). All foams exhibit the neat closed-cell structure. We noted here that homogeneous cells were formed in the case of nanocomposite foams, while neat PLA foams show rather non-uniform cell structure having large cell size. The nanocomposite foams show smaller cell size \( d \) and larger cell density \( N_c \) compared with neat PLA foam, suggesting that the dispersed silicate particles act as nucleating sites for cell formation.

For both foam systems, the calculated distribution function of cell size from SEM images are presented in Figure 6.19. The nanocomposite foams nicely obeyed the Gaussian distribution. In the case of PLA/ODA foamed at 150°C under high pressure of 24 MPa, we can see that the width of the distribution peaks, which indicates the dispersity for cell size, became narrow accompanied by finer dispersion of silicate particles.

Obviously, with decreasing saturation pressure condition (~140°C and 14 MPa), both foams exhibit large cell size due to the low supply of CO₂.

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molecules, which can subsequently form a small population of cell nuclei upon depressurization. The incorporation of nanoclay (OMLS) induces heterogeneous nucleation because of a lower activation energy barrier compared with homogeneous nucleation. However, the competition between homogeneous and heterogeneous nucleation is no longer discernible.

6.4.4 Foaming Temperature Dependence of Cellular Structure

The dependence of the foam density ($\rho$) at the $T_f$ under different CO$_2$ pressures are shown in Figure 6.20. Throughout the whole CO$_2$ pressure range, the mass density of PLA/MMT-ODA foams remains at a constant value at low foaming temperature ($T_f$) range and abruptly decreases beyond a certain $T_f$ and then attains a minimum constant value up to 150°C again. From the above results, it can be said that such behavior of mass density is due to the competition between cell nucleation and cell growth. At the low $T_f$ range (~110°C), in which a large supply of CO$_2$ molecules are provided, the cell nucleation is dominant, while at the high $T_f$ (~140°C), cell growth and the coalescence of cells are prominent due to low viscosity of the systems compared with the low $T_f$ range (~110°C). This behavior clearly appears in the plots of the cell size ($\equiv 2d$), the cell density ($N_c$), and the mean cell wall thickness ($\delta$) versus $T_f$ under various pressure conditions, respectively. As seen in Figure 6.21, with increasing $T_f$ all nanocomposite foams show an increasing tendency of $2d$ and/or $\delta$ and attain a maximum.

![Figure 6.19](image-url)
On the other hand, the temperature dependence of $N_c$ shows opposite behavior compared with the tendency of $2d$ due to cell growth and coalescence. Both $2d$ and $N_c$ affect the mass density of the foams.

Using $T_g$ depressions (corresponding to $\Delta T_g$), reconstructed plots of $\rho_f$ versus $T_f + \Delta T_g$ were drawn from the data of Figure 6.20. The results are shown in Figure 6.22. All of the data, including neat PLA and PLA/MMT-SBE, neatly conform to a reduced curve with $\rho_f \approx 1.0 \pm 0.1$ g/cm$^3$ at $T_f + \Delta T_g < 140 \pm 4^\circ$C (nanocellular region), whereas $\rho_f$ values approach around $0.3 \pm 0.15$ g/cm$^3$ as reduced temperature ($T_f + \Delta T_g$) increased well above 150°C (microcellular region). The critical temperature is thus $140 \pm 4^\circ$C, above which cell growth prevails. Below the critical temperature, cell nucleation dominates and cell growth is suppressed due to the high modulus and viscosity as revealed by the temperature dependence of stage, $G'(\omega)$, and loss, $G''(\omega)$, moduli ($G' = 162$ MPa and viscosity component $G''/\omega = 2$ MPa s at 140°C). Figure 6.23 shows temperature-reduced plots of $2d$, $N_c$ and $\delta$ versus $T_f + \Delta T_g$. All data nicely conform to a reduced curve such as in Figure 6.22. Interestingly, when both $T_g$ and $T_m$ depressions were used to conduct superposition, it was recognized that the reduced curve is neatly constructed but there is no significant difference in comparison with the case of $T_f + \Delta T_g$. This indicates that $T_g$ depression is important in optimizing foam processing conditions but $T_m$ depression may be not a significant factor for processing because the $T_f$ range is still below $T_m$ after CO$_2$ saturation.

In Figure 6.24, the relationship between $2d$ and $N_c$, and $\delta$ and $2d$ in this study are shown. The relationship neatly obeys Equations 6.2 and 6.3 but

**FIGURE 6.20** Foaming temperature dependence of mass density for PLA/MMT-ODA foamed under different CO$_2$ pressure conditions. (From Ema, Y., Ikeya, M., and Okamoto, M. *Polymer* 47 (2006): 5350. © 2006, Elsevier Science.)
the deviation occurs beyond the value of $N_c \sim 10^{12}$ cell/cm$^3$ for panel (a) and below $2d \sim 1$ μm for panel (b). The downward and upward deviations indicate that the heterogeneous cell distribution mechanism due to the rigid crystalline phases in the PLA matrix is caused by a high degree of crystallinity (~49 weight-percentage) under the low foaming temperature range (~100°C). As seen in Figure 6.25, the PLACN foams exhibit a heterogeneous cell distribution. The PLA foam reduces the value of $N_c$ accompanied by a large value of $\delta$ compared with that of PLACN foams. In the case of PLACN foams, the controlled structure of the PLACN foams is from microcellular ($2d \equiv 30$ μm and $N_c \equiv 3.0 \times 10^7$ cells/cm$^3$) to nanocellular ($2d \equiv 200$ nm and $N_c \equiv 2.0 \times 10^{13}$ cells/cm$^3$).

FIGURE 6.21  Foaming temperature dependence of: (a) cell size; (b) cell density; and (c) mean cell wall thickness under different CO$_2$ pressure conditions. (From Ema, Y., Ikeya, M., and Okamoto, M. Polymer 47 (2006): 5350. © 2006, Elsevier Science.)
6.4.5 CO\textsubscript{2} Pressure Dependence

At high pressure, both homogeneous and heterogeneous nucleation mechanisms may appear to be of comparable significance. All systems demonstrate that \(N_c\) increases systematically with increasing CO\textsubscript{2} pressure in the low \(T_f\) region (~100–120°C). For PLA/MMT-ODA foams, the system suggests that the heterogeneous nucleation is favored in high-pressure conditions. The cell nucleation in the heterogeneous nucleation system such as PLA/MMT-ODA foams took place in the boundary between the matrix and the dispersed nanoclay particles. Accordingly, the cell size decreased without individual cell coalescence for PLA/MMT-ODA and neat PLA systems, as seen in Figure 6.25. To clearly investigate whether the addition of internal surfaces of the dispersed nanoclay may hinder CO\textsubscript{2} diffusion by creating a more tortuous diffusive pathway,\textsuperscript{19} characterization of the interfacial tension between bubble and matrix was conducted using the modified classical nucleation theory.\textsuperscript{36}

According to the theory proposed by Suh and Colton, the rate of nucleation of cells per unit volume \((N)\) can be written as

\[
N = N_0 \exp \left[ \frac{-16\pi y^3 S(\theta)}{3(k_B T)(\Delta P_{CO_2})} \right] 
\]  

(6.4)
where C is the concentration of CO$_2$ and/or the concentration of heterogeneous nucleation sites, $f$ is the collision frequency of CO$_2$, $\gamma$ is the interfacial tension between bubble and matrix, $S(\theta)$ is the energy reduction factor for the heterogeneous nucleation (i.e. PLA/MMT-ODA), $\Delta P_{CO2}$ is the magnitude of the pressure quench during depressurization, $k_B$ is the Boltzmann constant, and $T$ is absolute temperature.

The theoretical cell density is given by

$$N_{\text{theor}} = \int_0^1 \dot{N} \, dt \quad \text{(6.5)}$$
where \( t \) is the foaming time that takes approximately 3 s. Assuming no effect of the coalescence of cell on the value of \( N_c \), we estimate the interfacial tension of the systems calculated using Equations 6.4 and 6.5; that is, the slope of the plots (\( N_c \) versus \( 1/\Delta P_{CO_2} \)). The characteristic parameters of two systems are shown in Table 6.7. The interfacial tension of PLA/MMT-ODA and neat PLA are 6.65 mJ/m\(^2\) and 7.43 mJ/m\(^2\) at 110°C, respectively. These estimated \( \gamma \) values are in good agreement with that of the other poly(methyl methacrylate) (PMMA)-CO\(_2\) system (\( \sim 10 \) mJ/m\(^2\)). The PLA/MMT-ODA system has a low value compared to that of neat PLA. This trend reflects the relative importance of heterogeneous nucleation, which
FIGURE 6.25  SEM images of the fracture surfaces of: (a) neat PLA; (b) PLA/MMT-ODA; and (c) PLA/MMT-SBE foamed at 100°C under 28 MPa. (From Ema, Y., Ikeya, M., and Okamoto, M. Polymer 47 (2006): 5350. © 2006, Elsevier Science.)
dominates over the homogeneous one in the event that the amount of CO₂ available for bubble nucleation is limited because of a lower activation energy barrier, as mentioned previously. That is, in the heterogeneous nucleation (PLA/MMT-ODA), we have to take the reduction of the critical energy into consideration because of the inclusion of nucleants, which is a function of the PLA-gas-nanoclay contact angle (θ) and the relative curvature (W) of the nucleant surface to the critical radius of the nucleated phase. In the case of W ≥ 10, the energy reduction factor S(θ) can be expressed:

\[
S(\theta) = \frac{1}{4} (2 + \cos \theta)(1 - \cos \theta)^2
\]

In the case of homogeneous nucleation S(θ) is unity (θ = 180°). The obtained values of the contact angle are 107.3° at 110°C and 85.3° at 120°C. The estimated reduction factor (S(θ) = 0.4–0.7) was not so small when we compared with the other nanofillers (e.g. carbon nanofibers, S(θ) = 0.006). However, experimentally, nanoclay particles lead to an increase in Nc.

For PLA/MMT-SBE foams prepared under condition with low Tf (~100–110°C) and high pressure (~28 MPa), the nanocomposite foams exhibit no significant difference in Nc, compared with PLA/MMT-ODA foams. This reasoning is consistent with the large value of W in both systems.

### 6.4.6 TEM Observation

To confirm the heterogeneous nucleation and the nanocellular features of foam processing, Okamoto et al. conducted TEM observation of the cell wall in the PLA/MMT-ODA foam.

Figure 6.26 shows a TEM micrograph for the structure of the cell wall foamed at 100°C under 28 MPa. Interestingly, the grown cells having a diameter of ~200 nm are localized along the dispersed nanoclay particles in the cell wall. In other words, the dispersed nanoclay particles act as nucleating sites for cell formation and the cell growth occurs on the surfaces of the clays; that is, the cellular structure has an oval-faced morphology.
rather than spherical cellular structures for high $T_f$ conditions (~140°C). In Figure 6.26, in addition to the nanocellular structure formation, we can observe a lamellar pattern beside the nanoclay particles. This behavior appears to arise from the formation of the $\alpha$-phase of the PLA crystal in the presence of nanoclay particles. This is a unique observation of the epitaxial crystallization of PLA grown up from clay surfaces due to the nucleation effect of the dispersed nanoclays.

### 6.4.7 Polycarbonate (PC)-Based Nanocomposite Foams

Figure 6.27 shows the typical results of SEM images of the fracture surfaces of the PC/SMA blend (matrix) and PC-based nanocomposites foamed at 140°C under different isobaric saturation condition (10, 18, and 24 MPa). PC/SMA foams exhibit polygon closed-cell structures having pentagonal and hexagonal faces, which express the most energetically stable state of polygon cells. Obviously, under low saturation CO$_2$ pressure (~10 MPa),
both PC/SMA/MAE1 and PC/SMA/MAE2.5 foams exhibit larger cell size compared with PC/SMA, indicating that dispersed clay particles hinder CO₂ diffusion by creating a maze or a more tortuous path. However, high CO₂ pressure (~24 MPa) provides a large supply of CO₂ molecules, which can subsequently form a large population of cell nuclei upon depressurization. The incorporation of nanoclay hinders CO₂ diffusion and simultaneously induces heterogeneous nucleation because of a lower activation energy barrier compared with homogeneous nucleation.

In Figure 6.28, the relationship between $d$ and $N_c$, and $\gamma$ and $d$ are plotted. Equations 6.2 and 6.3 lead to these relations but some deviation occurs in each system. For example, PC/SMA/MAE2.5 (syn-FH-C₁₈TM) (MMT = 1 weight-percentage) exhibits a smaller value of $N_c$ under the same $d$ value when compared with PC/SMA and PC/SMA/MAE1. For the relationship between $\delta$ and $N_c$, PC/SMA/MAE2.5 (MMT = 2.5 weight-percentage) shows a large value of $\delta$ compared with PC/SMA/MAE1. These deviations indicate that the heterogeneous cell distribution mechanism due to the rigid matrix phases in PC/SMA is caused by high MAE loading (MMT = 2.5–5.0 weight-percentage) as seen in Figure 6.28. As well as PLA-based nanocomposite foams, in Table 6.8, the interfacial tension and energy reduction factor of systems are summarized.

The interfacial tension of PC/SMA/MAE1 (including energy reduction factor $S(\theta)$) and PC/SMA ($S(\theta) = 1$) are 9.7 mJ/m² and 10.9 mJ/m² at 14 MPa, respectively. These estimated values of $\gamma$ are of the same order of magnitude compared with the PLA system (5–7 mJ/m²). The interfacial tension slightly decreases with an increase in clay content under the same
CO₂ pressure conditions, indicating heterogeneous cell nucleation occurs easily with increasing clay content. The estimated reduction factor \( S(\theta) = 0.3–0.8 \) is the same order compared with the foaming of PLA-based nanocomposites. The TEM micrograph of the structure of the cell wall foamed at 160°C is shown in Figure 6.29. The grown cells are localized along the dispersed nano clay particles in the cell wall.

**6.4.8 Mechanical Properties of Nanocomposite Foams**

Figure 6.30 shows the relationship of relative modulus \((K_f/K_p)\) against relative density \((\rho_f/\rho_p)\) of neat PLA and nanocomposite foams, taken in the parallel (a) and perpendicular (b) directions to the flow, respectively.
TABLE 6.8
Interfacial Tension \([\gamma S(\theta)^{1/3}]\) Including Energy Reduction Factor \([S(\theta)]\) of Systems

<table>
<thead>
<tr>
<th>Systems</th>
<th>(\gamma S(\theta)^{1/3}) (mJ/m(^2))</th>
<th>(S(\theta))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC/SMA-CO(_2)</td>
<td>10.7</td>
<td>1.0</td>
</tr>
<tr>
<td>PC/SMA/MAE1-CO(_2)</td>
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<td>0.53</td>
</tr>
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<td>1.0</td>
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<tr>
<td>PC/SMA/MAE1-CO(_2)</td>
<td>(P_{CO_2} = 10) MPa</td>
<td>9.7</td>
</tr>
<tr>
<td>PC/SMA/MAE2.5-CO(_2)</td>
<td>(P_{CO_2} = 14) MPa</td>
<td>9.9</td>
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<tr>
<td>PC/SMA-CO(_2)</td>
<td></td>
<td>13.6</td>
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<tr>
<td>PC/SMA/MAE1-CO(_2)</td>
<td>(P_{CO_2} = 18) MPa</td>
<td>10.2</td>
</tr>
<tr>
<td>PC/SMA/MAE2.5-CO(_2)</td>
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<tr>
<td>PC/SMA/MAE1-CO(_2)</td>
<td>(P_{CO_2} = 22) MPa</td>
<td>12.4</td>
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<td>PC/SMA/MAE2.5-CO(_2)</td>
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To clarify whether the modulus enhancement of the nanocomposite foams was reasonable, we applied the following Equation 6.7 proposed previously by Kumar\textsuperscript{43} to estimate relative moduli with various foam densities:

\[
\frac{K_f}{K_p} = \frac{\rho_f}{\rho_p} \frac{1 + \left( \frac{\rho_f}{\rho_p} \right)^4}{1 + \left( \frac{\rho_f}{\rho_p} \right)^4 - \left( \frac{\rho_f}{\rho_p} \right)^4}
\]  

where \( K_f \) and \( K_p \) are the modulus of pre-foamed and post-foamed samples, respectively. The solid line in the figure represents the fit with Equation 6.7.

**FIGURE 6.30** The relation of relative modulus \((K_f/K_p)\) against relative density \((\rho_f/\rho_p)\) of neat PLA and PLA-based nanocomposite foams, taken in directions parallel (a) and perpendicular (b) to the flow.
The neat PLA foams do not show any difference between the two moduli (a) and (b). On the other hand, for PLACN foams, the relative moduli exhibit a large value compared with the theoretical one. The dispersed clay particles in the cell wall align along the thickness direction of the sample. In other word, the clay particles arrange owing to the biaxial flow of material during foaming. The clay particles seem to act as a secondary cloth layer to protect the cells from being destroyed by external forces. In the directions perpendicular to the flow, the relative modulus of PLA/MMT-ODA and PLA/MMT-SBE foams appear higher than the predicted value even at the same relative mass density in the range 0.7–0.85 (see Figure 6.30a). This upward deviation suggests that the small cell size with large cell density enhances the material property as predicted by Weaire. This may create the improvement of mechanical properties for polymeric foams through polymeric nanocomposites. More detailed surveys on various types of nanocomposite foaming can be also be found in the literatures.

6.4.9 Porous Ceramic Materials Via Nanocomposite

A new route for the preparation of porous ceramic material from thermosetting epoxy/clay nanocomposite was first demonstrated by Brown et al. This route offers attractive potential for diversification and application of the PLFNCs. Okamoto and coworkers have reported the results on the novel porous ceramic material via burning of the PLA/MMT system (PLACN). The PLACN contained 3.0 weight-percentage inorganic clay. The SEM image of the fracture surface of porous ceramic material prepared from simple burning of the PLACN in a furnace of up to 950°C is shown in Figure 6.31. After complete burning, as seen in the figure, the PLACN becomes a white mass with a porous structure. The bright lines in the SEM image correspond to the edge of the stacked silicate layers. In the porous ceramic material, the silicate layers form a house-of-cards structure, which consist of the large plates having a length of ~1000 nm and thickness of ~30–60 nm. This implies that the further stacked platelet structure is formed during burning. The material exhibits the open-cell type structure having a 100–1000 nm diameter void, a BET surface area of 31 m² g⁻¹ and a low density of porous material of 0.187 g ml⁻¹ estimated by the buoyancy method. The BET surface area value of MMT (780 m²/g) and that of the porous ceramic material (31 m²/g), suggests about 25 MMT plates stacked together. When MMT is heated above 700°C (but below 960°C) all OH groups are first eliminated from the structure and thus MMT is decomposed into that of a non-hydrated aluminosilicate. This transformation radically disturbs the crystalline network of the MMT, and the resulting diffraction pattern is indeed often typical of an amorphous (or non-crystalline) phase. The estimated rough value of the compression modulus (K) is of the order of ~1.2 MPa, which is five orders of magnitude lower than the bulk modulus of MMT.
In the stress–strain curve, the linear deformation behavior is nicely described in the early stage of the deformation; that is, the deformation of the material closely resembles that of ordinary polymeric foams. This open-cell type porous ceramic material consisting of the house-of-cards structure is expected to provide strain recovery and an excellent energy dissipation mechanism after unloading in the elastic region up to 8% strain, probably each plate bend like leaf spring. This porous ceramic material is a new material possessing elastic feature and is very lightweight. This new route for the preparation of porous ceramic material via burning of nanocomposites can be expected to pave the way for a much broader range of applications of the PLSNCs. This porous ceramic material provides an excellent insulator flame retardant property for PLFNCs. The flame behavior must be derived from the morphological control of the shielding properties of the graphitic/clay created during polymer ablation.

6.5 Conclusions and Future Prospects

Development of nanocomposite foams is one of the latest evolutionary technologies of polymeric foams. The nanocomposite foams offer attractive potential for diversification and application of conventional polymeric
materials. Some of them are already commercially available and applied in industrial products through Unitika Ltd., Japan, and open a new dimension for plastics and composite foams. The major impact will be at least a decade away.

References
