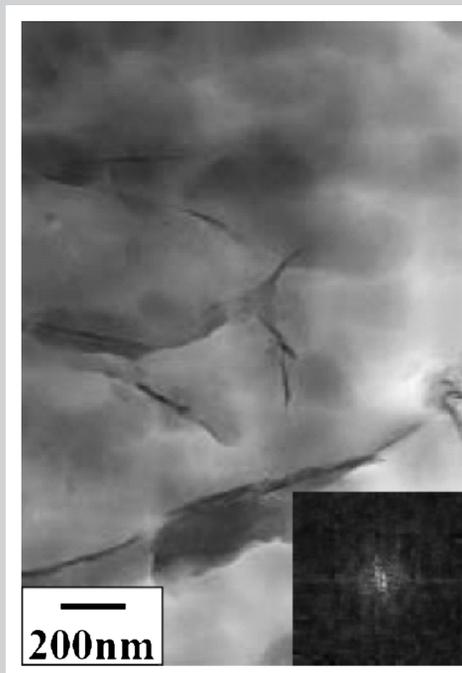


**Summary:** Solid-state processing for the preparation of poly-(*p*-phenylenesulfide) (PPS-) based nano-composites having finely dispersed layered fillers was conducted. The mixture of PPS and organically modified layered filler (OMLF) (95/5 wt./wt.) was subjected to the processing using thermostated hot-press at 150 °C, below  $T_m$  of PPS (i.e., PPS is still at the solid-state), and applying pressures of 33 MPa for 30 s. The mixture exhibited disorder and delaminated layer structure with the thickness of 10–20 nm into the PPS matrix. In contrast, a nano-composite prepared by melt compounding at 300 °C for 3 min showed large stacked silicate layers in the PPS matrix. The processing led to delamination of the silicate layers and attained the discrete dispersion.

TEM bright field image and FFT spectrum of a solid-state processed PPS nano-composite.



## Delamination of Organically Modified Layered Filler via Solid-State Processing

Tomotaka Saito,<sup>1</sup> Masami Okamoto,\*<sup>1</sup> Ryoichi Hiroi,<sup>2</sup> Minoru Yamamoto,<sup>2</sup> Takashi Shirot<sup>2</sup>

<sup>1</sup> Advanced Polymeric Nanostructured Materials Engineering, Graduate School of Engineering, Toyota Technological Institute, Hisakata 2-12-1, Tempaku, Nagoya 468-8511, Japan

<sup>2</sup> Advanced Material Products Group, Research & Technical Center, Otsuka Chemicals Co. Ltd., Kagasuno Kawauchi-Cho 463, Tokushima 771-0193, Japan

Fax: (+81) 052 809 1864; E-mail: okamoto@toyota-ti.ac.jp

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### Introduction

Delamination of stacked layered fillers in polymeric nano-composite is the ultimate target for controlling better overall materials properties.

Since the possibility of direct melt intercalation was first demonstrated by Giannelis et al.,<sup>[1]</sup> a significant amount of work has already been done on various aspects of polymeric nano-composites containing organically modified layered fillers (OMLFs). However, complete exfoliation of OMLFs

in continuous polymer matrix is still a challenging issue because it could not be satisfactorily attained. We know, by now, that the complete exfoliation is not feasible after melt intercalation with appropriate shear. As reported by Yang and Ozisik<sup>[2]</sup> the shear stress does not improve the state of the nano-filler dispersion once a critical morphology was established. That is, the dispersion of the nano-filler in the polymer matrix is governed by a judicious choice of OMLF.

In this regard, we also reported that an optimal interlayer structure on OMLF is most favorable for nano-composite

formation with respect to the number per area and size of surfactant (intercalant) chains.<sup>[3]</sup> The shear stress has little effect on the delamination of the layer as compared with the optimal interlayer structure on OMLF.<sup>[4]</sup> This reasoning is consistent with the intercalated structure reported by so many nano-composite researchers, who prepared intercalated (not exfoliated) nano-composites via simple melt extrusion technique.<sup>[5]</sup> Although the intercalation technology of the polymer melt is developed along with the current industrial process, such as extrusion and injection molding, we have to develop a more innovative compounding process, especially in the preparation of the nano-composites possessing exfoliated layered fillers.

Very recently, Wang et al.<sup>[6]</sup> reported the exfoliation of talc fillers by solid-state shear processing using a pan-type mill, to prepare poly(propylene) (PP)/talc nano-composites. Although the delamination of talc fillers was not achieved in the nano-composite as revealed by transmission electron microscopy (TEM) images, no indication of the layer correlation was observed in wide-angle X-ray diffraction (WAXD). Solid-state shear processing may be an innovative technique to delaminate the layered fillers because the pressure drop ( $\Delta p$ ) within the nano-galleries makes the polymer penetration more difficult.<sup>[3,7]</sup> In this paper, we challenge solid-state processing to delaminate the stacked, layered filler in the polymer matrix. We report a novel method for the nanoscale control of the dispersed layered fillers.

## Experimental Part

OMLF used in this study was synthetic fluorine hectorite (*syn-FH*) intercalated with hexadecyl tributyl phosphonium ( $C_{16}$ TBP) cation. The alkylphosphonium cation as an intercalant has an advantage for the thermal stability than the alkylammonium cation.<sup>[8]</sup> A poly(*p*-phenylenesulfide) (PPS) fine powder ( $M_n = 1.0 \times 10^4 \text{ g} \cdot \text{mol}^{-1}$ ,  $T_m = 285 \text{ }^\circ\text{C}$ ), purchased from Aldrich, was used as a polymer matrix. The homogeneous mixture of PPS and OMLF in the weight ratio 95:5 was prepared. We conducted the solid-state processing using thermostated hot-press (Techno Supply Co.). The mixture was subjected to a hot-press at  $150 \text{ }^\circ\text{C}$ , below the  $T_m$  of PPS powder (i.e., PPS is still at the solid-state), and applying a pressure of 33 MPa for 30 s.<sup>a</sup> Since the melting temperature of the intercalant ( $C_{16}$ TBP) into the nano-galleries was  $85.8 \text{ }^\circ\text{C}$ ,<sup>[7]</sup> we can observe the effect of layer delamination at

<sup>a</sup> The pressure drop (difference)  $\Delta p$  is given by  $\Delta p = \gamma(1/R - 2 \cos \theta/H)$ , where  $\gamma$  is the surface tension of the intercalant,  $R$  is the radius of the disk if we assume all platelets are of identical disk form,  $\theta$  is the contact angle ( $< 90^\circ$ ), and  $H$  is the distance between two disks, corresponding to the interlayer opening. When the value of  $H$  is much smaller than the value of  $R$ , i.e., nano-gallery, the value of  $\Delta p$  become negative, suggesting that the attractive force is generated between two disks. The calculated value of  $\Delta p$  is equal to  $-24 \text{ MPa}$  by assuming  $\theta$  of  $60^\circ$ .<sup>[7]</sup> This value is quite large compared with that of atmospheric pressure ( $\approx 0.1 \text{ MPa}$ ). For these reasons, we observe the limited value of the final interlayer spacing in the nano-composites prepared by melt compounding.

this temperature. Solid-state processing was conducted ten times. The recovered sheet was about 1 mm thick and was kept at room temperature prior to the measurements.

The nano-structure analyses of WAXD and TEM were carried out using the same apparatus as in the previous studies.<sup>[9,10]</sup> To investigate the micro-scale morphology of the nano-composites, we also used a polarizing optical microscope (POM). The recovered sheets were first sandwiched between two pieces of cover glass and placed on a laboratory hot-plate above  $T_m$  of PPS for 30 s. The molten film was then rapidly put on a thermostated hot-stage ( $300 \text{ }^\circ\text{C}$ ) (Linkam RTVMS, Linkam Scientific Instruments, Ltd.) mounted on a POM (Nikon OPTIPHOTO2-POL). For analyzing the features of the micrographs, we carried out fast Fourier transform (FFT) analysis on digitally saved images of POM micrographs using the commercial image analysis software (Ultimage<sup>®</sup>, Graftek, France), which allowed to provide us information equivalent to the scattering analyses.

For comparison, the PPS-based nano-composite preparation was conducted via conventional melt compounding operated at  $300 \text{ }^\circ\text{C}$  for 3 min.<sup>[4]</sup> The extruded samples were dried under vacuum at  $120 \text{ }^\circ\text{C}$  for 6 h to remove water. The dried nano-composite was then converted into sheets with a thickness of 0.7–2 mm by pressing with  $\approx 1.5 \text{ MPa}$  at  $300 \text{ }^\circ\text{C}$  for 1 min using a hot-press.

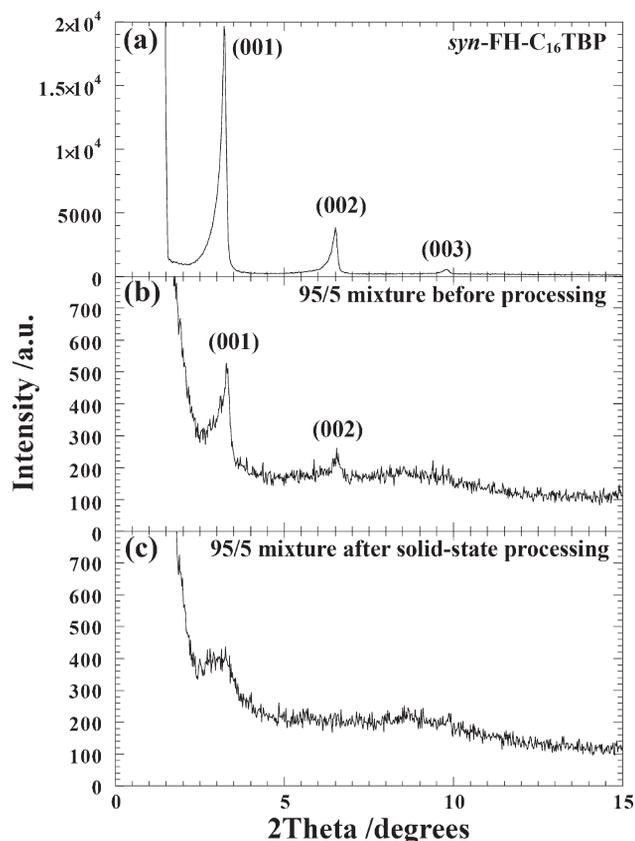


Figure 1. WAXD patterns of (a) *syn-FH-C*<sub>16</sub>TBP, (b) mixture of PPS and *syn-FH-C*<sub>16</sub>TBP (95:5 wt./wt.) before solid-state processing, and (c) processed mixture of PPS and *syn-FH-C*<sub>16</sub>TBP (95:5 wt./wt.).

## Results and Discussion

Wide-angle X-ray diffraction patterns for the typical examples of nano-filler powders are presented in Figure 1(a). The mean interlayer spacing of the (001) plane ( $d_{(001)}$ ) for the *syn*-FH that was modified by C<sub>16</sub>TBP [*syn*-FH-C<sub>16</sub>TBP] obtained by WAXD measurements is 2.741 nm (diffraction angle,  $2\Theta = 3.22^\circ$ ). The appearance of small peaks at  $2\Theta = 7.60^\circ$  and  $11.36^\circ$  confirmed that these reflections are due to the (002) and (003) planes of *syn*-FH-C<sub>16</sub>TBP. *syn*-FH-C<sub>16</sub>TBP exhibits well-ordered layered structure proved by WAXD with diffraction maxima up to the third order. Figure 1(b) shows the result of the mixture of PPS and *syn*-FH-C<sub>16</sub>TBP (95:5 wt./wt.). The intensity of the WAXD peaks decreased sharply due to the diluent effect. In contrast, after solid-state processing with pressure of 33 MPa at 150 °C, the WAXD pattern of the mixture is almost featureless diffraction, exhibiting only a broad and weak reflection, of the layer disorder or collapse of the layer

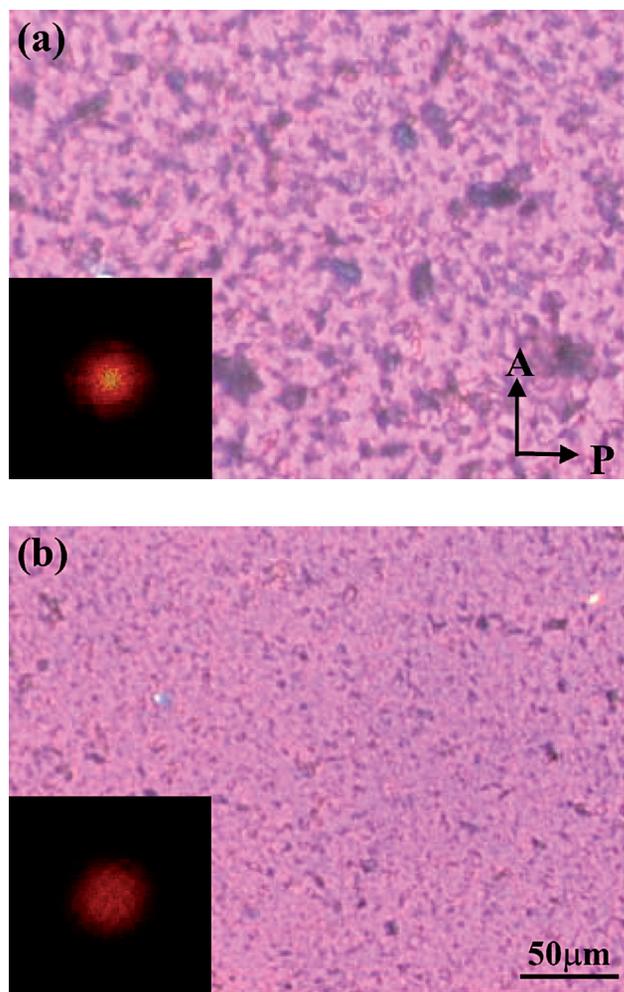


Figure 2. Polarized optical micrographs of (a) a mixture before solid-state processing and (b) a mixture processed at 150 °C under 33 MPa. The inset in each picture is a computed FFT spectrum of the micrograph.

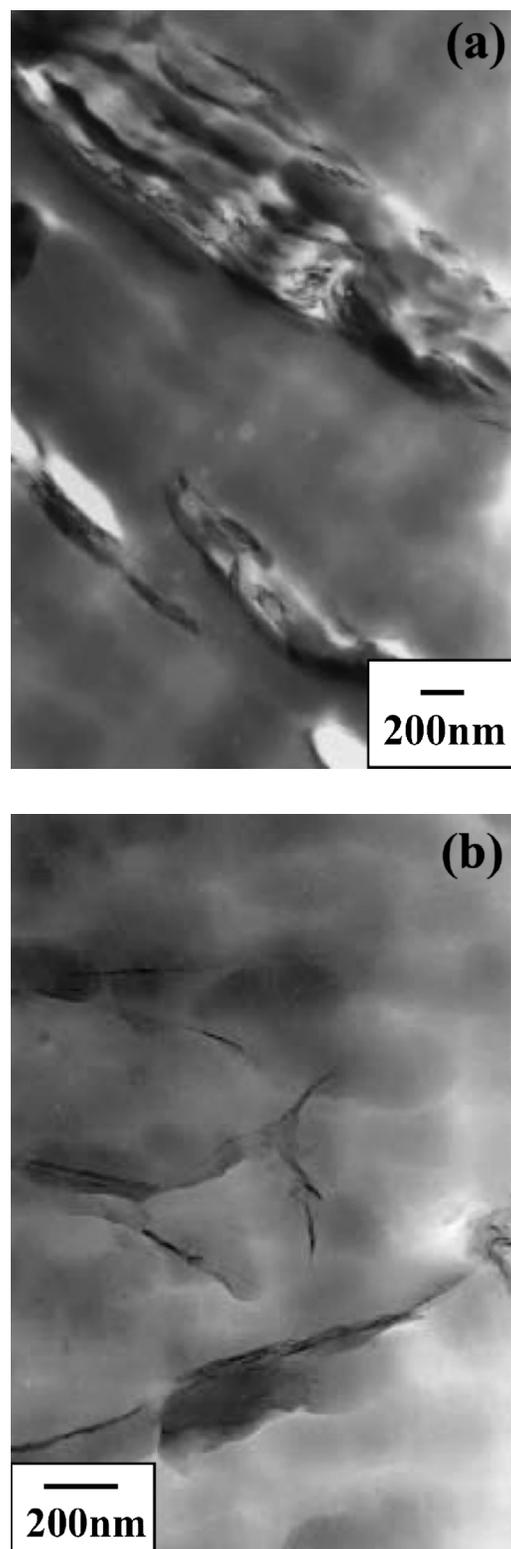


Figure 3. Bright field TEM images of (a) a mixture before solid-state processing and (b) a processed mixture. Both samples are prepared by annealing at 300 °C for 30 s (without shear processing). (c) PPS/*syn*-FH-C<sub>16</sub>TBP prepared by melt compounding with shear (operated at 300 °C for 3 min). The dark entities are the cross-section and/or face of intercalated-and-stacked silicate layers, and the bright areas are the matrix.

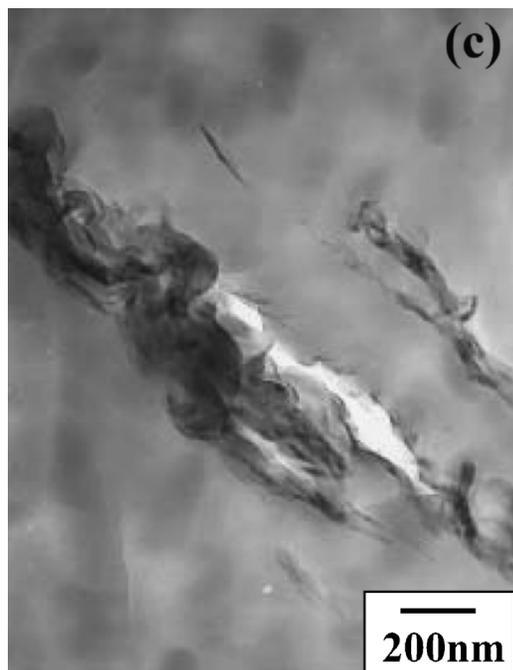


Figure 3. (Continued)

structure. The silicate concentration does not contribute to the featureless diffraction because of the comparison with Figure 1(b). To elucidate the morphologies before and after solid-state processing, we conducted POM observations at 300 °C.

Figure 2 shows the POM photographs with their FFT patterns of the mixtures prepared by annealing at 300 °C for 30 s (without shear processing). It is clear from the POM photographs that stacked and agglomerated structures of layers are evident in the unprocessed mixture [Figure 2(a)], whereas a good dispersion appears in the processed sample [Figure 2(b)]. The FFT pattern shows weak scattering with isotropy (halo) compared with that of the unprocessed mixture. This indicates that the particle size of the dispersed nano-filler becomes small during solid-state processing. The internal structure of the nano-composites in the nanometer scale was directly observed via TEM analyses.

Figure 3 shows the results of TEM bright field images of the mixtures corresponding to the POM experiments, in which dark entities are the cross-section of the layered nano-fillers. The large agglomerated tactoids of about 300 nm thickness are seen in Figure 3(a) (unprocessed sample).

On the other hand, Figure 3(b) shows a disordered and delaminated silicate layer structure with a thickness of 10–20 nm. This is a unique observation of the discrete silicate layers. Figure 3(c) shows the results of TEM bright field images of the nano-composites prepared by melt compounding with shear (operated at 300 °C for 3 min). For PPS/syn-FH-C<sub>16</sub>TBP, we still observe large stacked silicate layers in the nano-composite. Despite shear processing at 300 °C, the nano-composite exhibits some stacked-and-flocculated silicate layers in the PPS matrix.<sup>[4]</sup>

From these facts, the solid-state processing is an extremely effective method to collapse the stacked structure. This processing leads to the layer delamination accompanying the discrete dispersion.

In conclusion, we have described a novel and economic method for the nanoscale control of the dispersed layered fillers via solid-state processing. This processing led to delamination of the silicate layers and attained the discrete dispersion. This approach can be extended to prepare polymeric nano-composites with delamination of the nano-fillers in overcoming the pressure drop within the nanogalleries. The effect of the different temperatures and applying pressures on the delaminating behavior of the nano-fillers will be clarified shortly.<sup>[11]</sup>

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