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Biaxial Flow-Induced Alignment of Silicate Layers in Polypropylene/Clay Nanocomposite Foam

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Received June 27, 2001*; Revised Manuscript Received July 17, 2001*

ABSTRACT

Via batch process in an autoclave, we conducted foam processing on polypropylene (PP)/clay nanocomposite (PPCN) by using supercritical CO_2 as foaming agent under 10 MPa at 134.7 °C. Through transmission electron microscopy observation, the biaxial flow-induced alignment of clay particles along the cell boundary was identified. Such aligning behavior of clay particles helps cells to withstand the stretching force from breaking the so thin cell wall and to improve the modulus of the foam.

In the preceding paper,[1] we reported rheological properties of an intercalated polypropylene (PP)/clay nanocomposite (PPCN). In the PPCN containing 4 wt % clay (PPCN4), under uniaxial elongation, the PPCN4 exhibited high viscosity and a tendency of strong strain-induced hardening, which originated from the perpendicular alignment of the silicate layers to the stretching direction. The strain-induced hardening behavior is an indispensable characteristic for foam processing due to its capacity to withstand the stretching force experienced during the latter stages of bubble growth.[2] To evaluate the performance potential of the PPCNs for foam application, we conducted the foam processing of PPCNs with the expectation that they would provide advanced foams with excellent properties, meeting our demands.[3] A main objective of this paper is to investigate the alignment feature of the dispersed silicate layers with nanometer dimensions in the cell wall under biaxial flow of the material during foam processing. We also discuss here the dispersed clay structure−property relationships of the PPCN foams.

The material examined in this study was the PPCN4, where the PP chains modified by 0.2% maleic anhydride (MA) (PP−MA) were intercalated in the silicate galleries (intercalating sites).[1,4] The PPCN4 was pressed into a sheet with ∼1.5 mm thickness under pressure of ∼1 MPa in a hot press for 3 min at 180 °C (above melting temperature T_m of the PPCN4 (= 143 °C)) and annealed at 80 °C for 1 h to crystallize isothermally before being subjected to foam processing. The foam processing was conducted on PPCN4 and PP−MA without clay in an autoclave (Taiatsu Techno Corporation) at 134.7 °C (just below T_m) by using supercritical CO_2 under the pressure of 10 MPa. The details of the foam processing have been described elsewhere.[3] The structures of cells and dispersed clay particles in cell walls were investigated by using scanning electron microscope (SEM) (JSM-5310LV, JEOL) and transmission electron microscope (TEM) (H-7100, Hitachi Co.), respectively.

Figure 1 shows the typical results of SEM images of the fracture surfaces of the PPCN4 and PP−MA without clay. Both foams exhibit the polygon closed-cell structures having pentagonal and hexagonal faces, which express the most energetically stable state of polygon cells. Such foam structure was obtained probably because PP−MA and PPCN4 foams belong to the polymeric foams having high gas-phase volume (>0.74).[2] From SEM results, we quantitatively obtained the morphological parameters of the cells and summarized these in Table 1. The function for determining cell density N_c is defined as[2]

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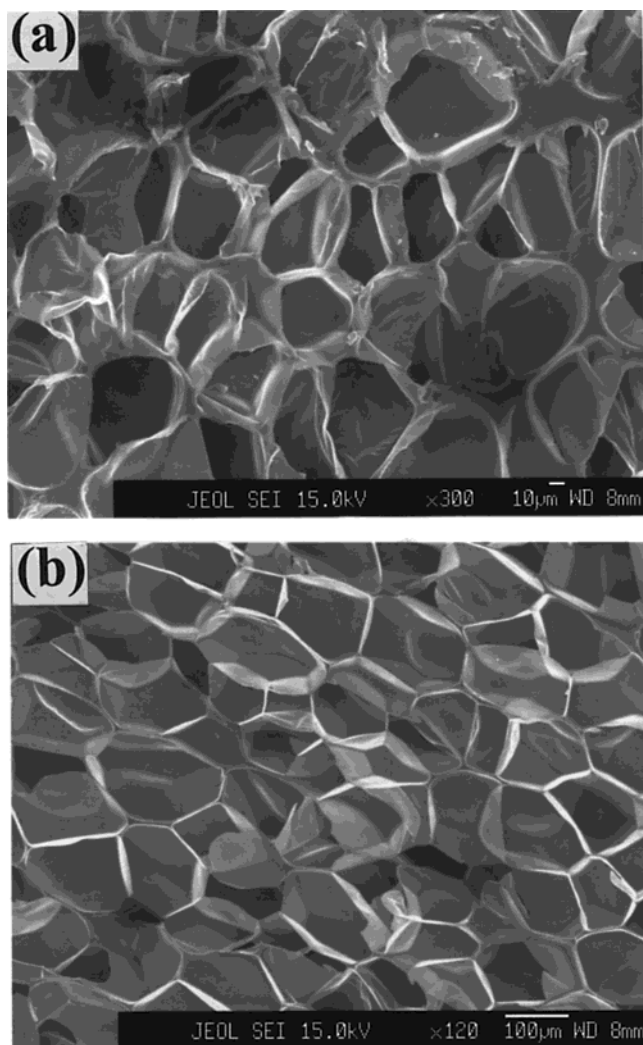[§] Toyota Central R&D Labs.

Figure 1. SEM micrographs for (a) PPCN4 and (b) PP-MA foamed at 134.7 °C.

Table 1: Morphological Parameters and Compression Modulus of PP−MA and PPCN Foams

foam	ρ_f/g·cm^{-3}	d/μm	$N_c \times 10^{-6}$/ cell·cm^{-3}	δ/μm	K'^a/MPa
PP-MA	0.06	155.3	2.49	5.6	0.44
PPCN2	0.06	133.0	3.94	4.6	1.72
PPCN4	0.12	93.4	9.64	11.9	1.95
PPCN7.5	0.13	33.9	220	2.7	2.80

^{a} At 25 °C.

$$N_c \cong \frac{1 - \dfrac{\rho_f}{\rho_p}}{10^{-4}\,d^3} \tag{1}$$

The mean wall thickness δ is given by[2]

$$\delta = d\left(\frac{1}{\sqrt{1 - \dfrac{\rho_f}{\rho_p}}} - 1\right) \tag{2}$$

where ρ_p, ρ_f, and d are the density of the polymer (pre-

foamed materials), the density of the foam (post-foamed samples) in g/cm^3, and the mean cell size in mm, respectively.

Obviously, the PPCN4 foam shows smaller d and larger N_c compared to PP−MA foam, suggesting that the dispersed clay particles act as nucleating sites for cell formation and lower d with increasing clay content.[23] The δ of the PPCN4 foam becomes twice the value compared to that of the PP−MA foam. The final ρ_f is controlled by the competitive process in the cell nucleation, its growth, and coalescence. The cell nucleation, in the heterogeneous nucleation system such as PPCN4 foam, took place in the boundary between the matrix PP−MA and the dispersed clay particles. The cell growth and coalescence are strongly affected by the modulus and the loss modulus ($\cong$ viscosity component) of the materials during processing. Even though the foam processing in this study was conducted at the temperature just below T_m,[2] due to the supercritical CO$_2$ dissolved into the matrix PP−MA, we should take into account not only clay effect on N_c and the moduli but also the strain-induced hardening on the formed thick cell wall in the foam processing in order to understand the above feature based 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 breakage at high temperature; therefore, the strain-induced hardening led to the high cell wall thickness in the PPCN4 foam.

To confirm our consideration for the strain-induced hardening and the feature of the alignment of the dispersed clay particles under biaxial flow in the foam processing, we conducted the TEM observation of the cell wall in the PPCN4 foam. Figure 2 shows TEM micrograph on the structure of one cell wall (a) and the junction of three cell walls (b) for PPCN4 foamed at 134.7 °C. Interestingly, in Figure 2a, 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 (vs cell boundary) calculated statistically from the TEM photograph is about 5 ± 3.6°, indicating that the planer orientation of the dispersed clay particles to the cell boundary occurred. In our previous paper,[1] for the PPCN4 melt, we showed the perpendicular alignment of the clay particles to the stretching or elongating direction, which was the main reason for causing the strain-induced hardening in the uniaxial elongational viscosity.

In this foam processing, apparently, the similar structure is formed with probably a different mechanism. Due to the biaxial flow of material during foam process, the clay particles probably either turned their face (marked with the arrows (A) in Figure 2a) or fixed face orientation (marked with the arrows (B) in Figure 2a) and aligned along the flow direction of materials, i.e., 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 so thin cell wall; in other words, to improve the strength of the foam in mechanical properties. The clay particles seem to act as a secondary cloth layer to
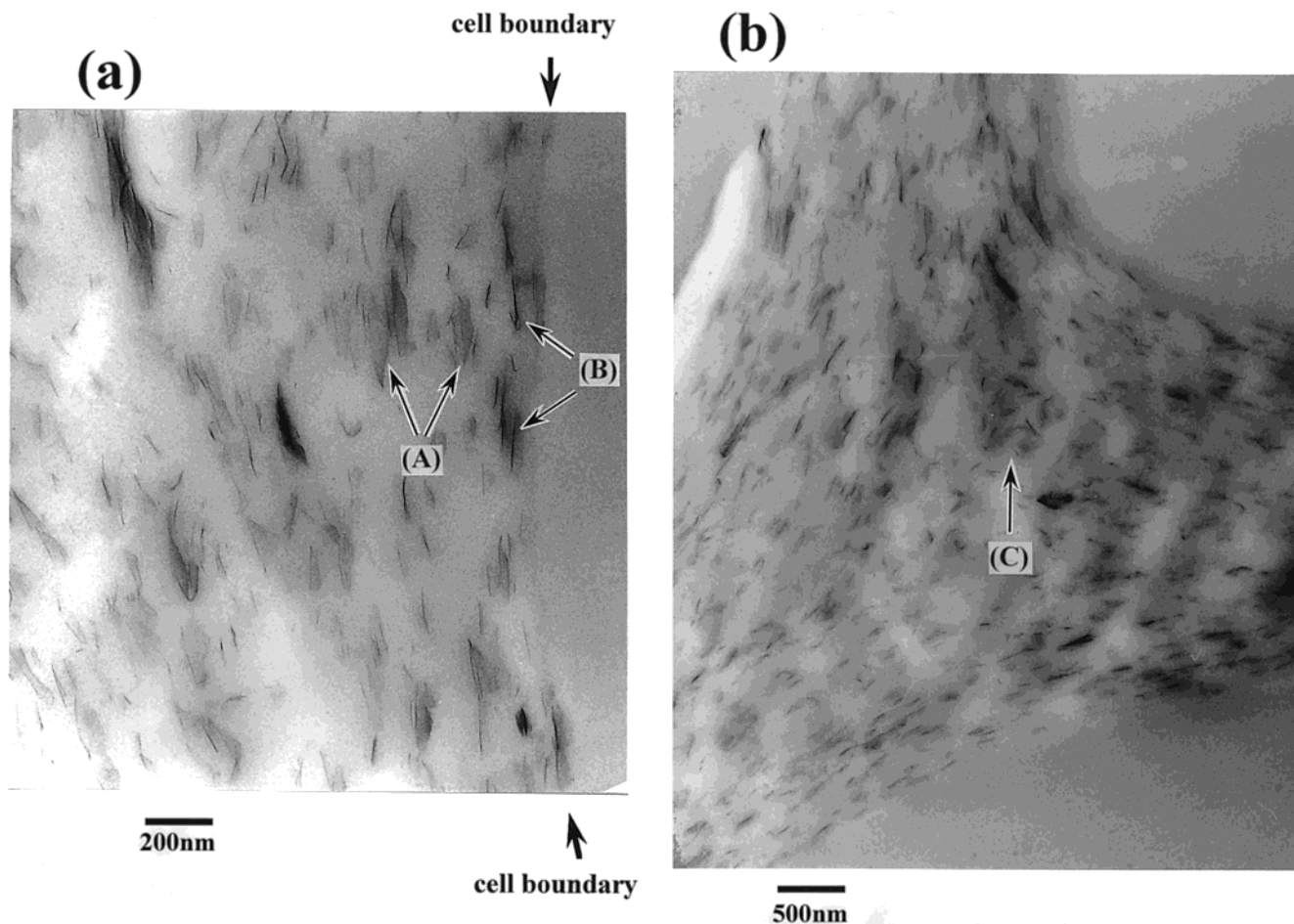
Figure 2. TEM micrographs for PPCN4 foamed at 134.7 °C: (a) one cell wall and (b) junction of three contacting cells.

protect the cells from being destroyed by external forces. Here, a question arises: How much improvement of mechanical properties does such unique alignment represent? To elucidate this, we measured the compression modulus K' of the foams of $3 \times 3 \times 1.5$ mm^3 size by using a thermal mechanical analyzer (TMA4020S, MAC Science Co.) in the compression mode at a constant frequency ω of 6.28 rad/s with heating rate of 5 °C/min. The results are summarized in Table 1. For comparison, we also show the data of other PPCNs with clay content of 2 and 7.5 wt % (PPCN2 and PPCN7.5) foamed at 134.7 °C. The K' of the PPCN foams appear higher than that of PP−MA foam even though at same ρ_f level. This may create the improvement of mechanical properties for polymeric foams through polymeric nanocomposites.

In Figure 2b, in addition to the alignment of clay particles, we can observe a random dispersion of clay in the central area of the junction (marked with the arrow (C) in Figure 2b). Such behavior of clay particles presumably reflects the effect of the stagnation flow region of material under the growth of three contacting cells.

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NL010051+