Supporting information:

Nanoconfinement-Induced Direct Formation of Form I and III Crystals Inside in-situ Formed Poly(butene-1) Nanofibrils

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WAXD results:

The WAXD patterns of the neat Cloisite 15, LDPE and iPB-1 containing 1 phr Cloisite 15 are presented in Figure S1. Cloisite 15 shows three reflections at $2\theta = 2.8$, 5.2 and 7.5° which correspond to (001) plane d-spacing of 31.5, 17 and 11.7 Å, respectively. The LDPE/Cloisite 15 and PB-1/ Cloisite 15 exhibit one reflection at $2\theta = 2.75^{\circ}$. The disappearance of the other two peaks and slightly lower reflection at $2\theta = 2.75^{\circ}$ suggest intercalation of LDPE and PB-1 in the clay galleries. The (001) plane reflection appears at higher reflections of $2\theta = 3.6$, 3.55 and 3.13° corresponding to the d-spacing of 24.5, 24.86 and 28.2 Å for NPEPB5 and NPEPB10 and NPEPB20, respectively. This densification of the clay galleries can be attribute to the interfacial localization of organoclay at LEPE/iPB-1 interface. Due to the limited interfacial area available for organoclay, clay layers jam at the interface and results in a smaller d-spacing when compared with the iPB-1/1 phr organoclay system. However, the interfacial area increases by increase in the iPB-1 content from 5 wt% to 10 and 20 wt% and more interfacial area becomes available for organoclay. Thus, the (001) plane reflection shifts to lower 2 θ suggesting a larger d-spacing.



Figure S1. WAXD pattern of the neat Cloisite 15 (a), LDPE/Cloisite 15 (1 phr) (b) and PB-1/Cloisite 15 (1 phr) (c), NPEPB5 (d), NPEPB10 (e) and NPEPB20 (f).

Interfacial tension measurement:

As it is not possible to directly measure the interfacial tension between solid nanoparticles and polymer melts, an indirect method based on contact angle (CA) measurement is usually employed in the literature to estimate the surface tension of components and then calculate the interfacial tensions using mathematical models. In this study, CA measurements were carried out using the sessile drop technique with the FDS contact angle system OCA Data Physics TBU 90E. 2 μ l of different liquids was placed on films of LDPE and iPB-1 in several positions and imaged after being stable for one minute. For each drop, the average of the right and left angles was used as CA. Then, the surface tensions of polymer components were calculated using contact angle (CA), θ , measurements according to Owens-Wendt equation [1]:

$$\gamma_1(1 + \cos\theta) = 2(\sqrt{\gamma_i^d \gamma_l^d} + \sqrt{\gamma_i^p \gamma_l^p})$$
(1)

where, γ_l is the surface tension of liquid and γ_i is surface tension of polymer *i*. γ_l^p and γ_l^d are polar and dispersive portions of the surface tension of the liquid, γ_l , respectively. γ_i^p and γ_i^d are polar and dispersive portions of the surface tension of the polymer, γ_i , respectively. The average of the CA of the liquids on each polymer film was used in equation 1 to calculate the surface tension of the sample. In this work, deionized water and Formamide (FM) were used to measure the contact angle of the polymers with the liquids. Dispersive and polar portions of the surface tension for water are 22.1 and 50.7 mN/m and for FM are 39.5 and 18.7 mN/m, respectively [2]. The surface tension of Cloisite 15 at room temperature was obtained from literature [3]. The surface tensions of the polymers and Cloisite 15 at melt process temperature (200°C) were extrapolated based on their surface tension at room temperature and its rate of thermal variation, i.e. $d\gamma/dT$, that was considered -0.067 mN/m.K for LDPE, -0.07 mN/m.K for iPB-1 [4] and -0.1 mN/m.K for organo-modified montmorillonite [5]. The interfacial tension between components *i* and *j* were then calculated using the harmonic equation [4]:

$$\gamma_{ij} = \gamma_j + \gamma_i - 4\left(\frac{\gamma_i^d \gamma_j^d}{\gamma_i^d + \gamma_j^d} + \frac{\gamma_i^p \gamma_j^p}{\gamma_i^p + \gamma_j^p}\right) \tag{1}$$

where, γ_i and γ_j are surface energies of components *i* and *j*, γ_i^d and γ_j^d are their dispersive parts and γ_i^p and γ_j^p their polar parts. Table S1 summarizes the contact angles and corresponding surface tension results at room and processing temperatures.

Material	Contact Angle (θ , degree)		Surface tension at 25 °C (mN/m)			Surface tension at 200 °C (mN/m)		
	Water	Formamide	γ^{d}	γ^{p}	γ	γ^{d}	γ^{p}	γ
LDPE	109.1±1	84.6±1	24.5	0.03	24.5	12.8	0.02	12.8
iPB-1	121±1.5	95.7±1	26.4	0.3	26.1	16	0.1	15.9
Cloisite 15	-	-	31.5	11.1	42.5	18.5	6.5	25.0

Table S1. Contact angles and the corresponding surface tension results at room and process temperatures.

Thermodynamic analysis:

The wettability of a solid inclusion by a polymer melt controls the adsorption behavior of a solid particle in a polymer-polymer mixture [6]. The final localization of a solid particle can be predicted by calculating the minimum interfacial energy, ΔG , when the system is at thermodynamic equilibrium. The wettability parameter, ω , is usually used to predict the equilibrium location of solid particles in a mixture of fluids [6]:

$$\omega = \frac{\gamma_{SA} - \gamma_{SB}}{\gamma_{AB}} \tag{2}$$

where γ_{SA} is the interfacial tension between filler and phase A, γ_{SB} is the interfacial tension between filler and phase B, and γ_{AB} is the interfacial tension between A and B. If $\omega < -1$ then solid particles

are located in phase A. For $\omega > 1$, the solid particles are predicted to locate in phase B. The solid particles are at the interface of the phases when $-1 < \omega < 1$. In this work, A, B, and S denote PE, iPB-1, and Cloisite 15, respectively. Table S2 summarizes the interfacial tensions between the components at 200 °C. The wetting parameter based on these results is found to be 0.38 which indicates organoclay thermodynamically prefers to be localized at the interface of LDPE and iPB-1. This is consistent with the morphological results observed in this work.

	Component	Interfacial tension, γ_{ij}
i	j	(IIIIV/III)
LDPE	iPB-1	0.8
LDPE	Organoclay	7.6
iPB-1	Organoclay	7.3

Table S2. Interfacial tensions of the components at process temperature (200 °C).

Morphology development:

The morphology of the iPB-1 phase in the sample containing 10 wt% iPB-1 before and after the heat treatment process is presented in **Figure S2**. These results show that due to the very short time of the process, capillary instabilities do not develop in the systems and the fibrillar shape of the iPB-1 phase is retained after the heat treatment process.



Figure S2. iPB-1 phase morphology before (a) and after (b) the heat treatment process for PEPB10 in MD-ND cross sections.

Crystallization analysis:

Figure S3 shows the different modification of iPB-1 crystals in PEPB10 blends with two different phase morphologies. These results clearly demonstrate that changing the phase morphology of iPB-1 from typical spherical microdomains to nano-scale fibrillar shape confined within the LDPE matrix alters the type of crystals from form II to combination of form I and II. This direct formation of form I is believed to be mainly due to the confinement effect.



Figure S3. (a) WAXD patterns of pure iPB-1, PEPB10 with spherical iPB-1 phase morphology (PEPB10-s), and PEPB10 with fibrillar iPB-1 phase morphology (PEPB10-f), (b) FTIR spectra of PEPB10-s and PEPB10-f.



Figure S4. Magnified WAXD patterns of samples containing a) 5, b) 10, and c) 20 wt% iPB-1 immediately after the heat treatment process.

DSC analysis:

The second heating run of samples right after the heat treatment process is presented in Figure S5. Although the endotherm melting peak of iPB-1 is convoluted with the melting peak of LDPE, a small shoulder can be identified in the samples containing 20wt% iPB-1 indicating the existence of form II crystal. These shoulders correspond well with the melting peak of pure iPB-1 in the second heating cycle.



Figure S5. Second DSC heating run of the samples right after the heat treatment process.



Figure S6. FTIR spectra of samples containing 10 wt% iPB-1 at room temperature compared with those at 100 °C.

References

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