# Microstructure Effects on the Rheology of Nanoclay-Filled PHB/LDPE Blends

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The rheological and morphological properties of the nanoclay-filled LDPE/PHB blends using LDPE-g-MAH as compatibilizer were determined. SEM data showed that the morphology was more sensitive to organoclay incorporation, compared to inclusion of the compatibilizer. Moreover, the results of image analysis and rheological studies indicated that nanoclay was located in the PHB phase after migrating from the LDPE phase, due to the thermodynamic and viscosity effects. The data obtained also showed that the stabilization mechanisms of PHB and LDPE matrix nanocomposites is due to coalescence prevention (due to the physical barrier) and alteration in the viscosity ratio of the phases, respectively. The obvious, pseudo-solid-like behavior over a wide range of frequencies in the PHB/LDPE/nanoclay systems demonstrated that the strong interaction between PHB/LDPE and nanoclay restricted the relaxation process of polymer chains. Therefore, PHB/LDPE/nanoclay was associated with a greater melt strength, which is essential for its favorable processability and applications. POLYM. COM-POS., 40:4125–4134, 2019. © 2019 Society of Plastics Engineers

## INTRODUCTION

Most immiscible polymer blends are incompatible and hence result in weak materials with low interfacial adhesion. One method to enhance the adhesion between phases is to utilize a compatibilizer as the third component. Compatibilizers are often a graft or block copolymer, designed to lower the interfacial tension, leading to reduction of the droplet size of the dispersed phase making it more stable against coalescence

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Published online in Wiley Online Library (wileyonlinelibrary.com). © 2019 Society of Plastics Engineers during melt mixing via strong interfacial adhesion between the phases [1]. Ramsden and Pickering [2] introduced a new compatibilizing method based on incorporating inorganic particles, in which emulsions are stabilized using dispersed colloidal particles. Since immiscible polymer blends can be considered as viscous fluid emulsions, utilization of nanoparticles may also be beneficial in compatibilization [3]. Among different nanofillers, organomodified nanoclays have attracted a great deal of attention due to their initial interlayer spacing and their ability to reduce the interfacial tension and average particle size [3]. However, the efficiency of nanoclays in reducing the interfacial tension and stabilization of a dispersed phase depends on localization and intercalation level [1, 3, 4] The morphological and microstructural features determine the rheological behavior and the resulting physical and mechanical properties [5]. Final localization of nanoparticles is dictated by the winner of the competition between hydrodynamic forces and thermodynamic preference [3, 6].

Polyhydroxybutyrate (PHB) is among biodegradable polyesters with mechanical properties comparable to those of conventional polymers [7]. Due to the increasing concerns about plastic wastes, researchers have focused on replacing nonbiodegradable polymers with biodegradable ones, such as PHB [8]. Like other biodegradable polymers, PHB suffers from some drawbacks (such as low thermal stability [9], low melt viscosity [10], and brittleness [11]), which limit its industrial applications. Blending is a successful and cheap method to overcome such processing difficulties [12]. To improve its thermal stability, the effects of organoclays and other additives on PHB thermal degradation kinetics have been extensively reported, and some interesting results have been obtained [9, 13, 14]. Aiming at controlling brittleness, PHB crystallization kinetics have been studied, and the effects of blending with other

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polymers and organoclay incorporation have been well documented [15, 16]. In order to overcome the low melt viscosity of PHB, rheological investigation can be used as a powerful tool to find the structure–property relationships and processability of the melt [4].

The rheology of PHB combined with other biodegradable polymers, such as polylactic acid (PLA) or PHB copolymers or other biodegradable polymers, has been investigated in a number of previous studies. For instance, Nerkar et al. [17] investigated the rheological aspects of PHB and polyhydroxyoctanoate (PHO) and reported a significant viscosity mismatch between the two polymers. They also studied the effect of chain extenders on the viscosity ratio of the phases. Zembouai et al. [18] studied the thermal and rheological properties of polyhydroxybutyratevalerate (PHBV)/PLA blends prepared through melt mixing. Additional studies by Mousavioun et al. [19] in 2013, assessed the thermophysical and rheological properties of PHB/lignin blends. Furthermore, Choi et al. [20] studied the rheological properties of miscible PHB blends with polyethylene oxide (PEO) prepared by solvent casting. Based on their results, the shear viscosity of PHB80/PEO20 was much higher than that of pure PHB. Zhao et al. [21] studied the effect of nanoclay incorporation on the rheological properties of PLA/PHBV blends and found that nanoclay addition enhances the modulus and melt strength of such blends.

In several studies, the rheology of PHB blended with other nonbiodegradable polymers, like low-density polyethylene (LDPE) or poly(ethylene terephthalate) (PET), has been investigated [22, 23]. These unique pairs currently are found in the film packaging industry.

We have previously demonstrated the effects of organoclay Cloisite 10A on PHB thermal degradation kinetics [14] and also PHB crystallization kinetics in PHB/LDPE/clay nanocomposites [24]. In the present work, rheological measurements were utilized as the powerful tools for studying nanoclay dispersion level and localization within a multicomponent PHB/LDPE/compatibilizer/clay system. Other techniques such as SEM, TEM, and XRD were also used to validate the rheological results.

# EXPERIMENTAL

## Materials

A commercial grade PHB (Biomer P209) with a melt flow index (MFI) of 10 g.(10 min)<sup>-1</sup> at 180°C and given weight of 2.16 kg was purchased as granules from Biomer Company (Krailling, Germany). LDPE (Petrothene NA 214000) with a MFI of 10 g.(10 min)<sup>-1</sup> at 190°C and given weight of 2.16 kg was supplied by Lyondellbasell (Houston, TX). The organically modified montmorillonite Cloisite 10A was kindly provided by BYK additives (Louisville, KY). LDPEg-MAH (Fusabond E265) with a melt flow index (MFI) of 12.3 g.(10 min)<sup>-1</sup> was purchased from DuPont.

# Sample Preparation

Samples with compositions shown in Table 1 were prepared in a vertical co-rotating twin screw micro-compounder (DACA instruments, Santa Barbara, CA) at 180°C with a screw speed of 100 rpm for 7 min, under nitrogen flow to prevent PHB oxidative degradation. PHB, Cloisite 10A, and LDPE-g-MAH were dried in an oven at 60°C for at least one day prior to melt mixing. Compositions of PHB/LDPE are reported in weight percentages. The amount of additives (nanoclay [N] and compatibilizer [C]) is expressed in parts per hundred PHB or parts per hundred PHB/LDPE blends.

## Characterization

X-Ray Diffraction (XRD). XRD analysis was performed on compression-molded specimens using a MiniFlex 600 instrument (Rigaku, Japan), with CuK $\alpha$  radiation (40 kV, 15 mA and  $\lambda = 0.154$  nm). Measurements were

TABLE 1.	Codes and compositi	ons of different	samples prepare	ed in DACA	micro-compounder.
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Group	Composition	Code	Group	)	Composition	Code
PHB/LDPE binary blends	0/100	LDPE-P	LDPE- matrix samples	PHB/LDPE/C	25/75/2.5	PHB25/LDPE/C2.5
-	10/90	PHB10/LDPE	*		25/75/5	PHB25/LDPE/C5
	25/75	PHB25/LDPE			25/75/7.5	PHB25/LDPE/C7.5
	50/50	PHB50/LDPE		PHB/LDPE/N	25/75/1	PHB25/LDPE/N1
	75/25	PHB75/LDPE			25/75/3	PHB25/LDPE/N3
	90/10	PHB90/LDPE			25/75/5	PHB25/LDPE/N5
	100/0	PHB-P		PHB/LDPE/C/N	25/75/5/1	PHB25/LDPE/C5/N1
					25/75/5/5	PHB25/LDPE/C5/N5
LDPE nanocomposite	100/3	LDPE/N3	PHB matrix samples	PHB/LDPE/C	75/25/2.5	PHB75/LDPE/C2.5
-			•		75/25/5	PHB75/LDPE/C5
					75/25/7.5	PHB75/LDPE/C7.5
PHB nanocomposites	100/1	PHB/N1		PHB/LDPE/N	75/25/1	PHB75/LDPE/N1
-	100/3	PHB/N3			75/25/3	PHB75/LDPE/N3
	100/5	PHB/N5			75/25/5	PHB75/LDPE/N5
				PHB/LDPE/C/N	75/25/5/1	PHB75/LDPE/C5/N1
					75/25/5/5	PHB75/LDPE/C5/N5

made over the scattering angle range of  $2\Theta = 1-10^{\circ}$  at a scan speed of 1 °/min.

Rheometry. The melt linear viscoelastic behavior of samples was investigated using a high-resolution discovery-HR3 instrument (TA instruments, Newcastle, DE). Oscillatory shear measurements were carried out at 180°C over a frequency range of 1-100 rad/s in the linear viscoelastic region using parallel plate geometry with a plate diameter of 20 mm and a gap of 500  $\mu$ m. Prior to frequency sweep experiments, the linear viscoelastic domain was determined through monitoring the elastic modulus. Time sweep tests were conducted at a strain of 0.1%, an angular frequency of 5 rad.s<sup>-1</sup>, and temperature of 180°C to study the stability of PHB blends and nanocomposites.

Scanning Electron Microscopy (SEM). The morphology of blends and nanocomposites was studied through scanning electron microscopy (TEScan, Vega II) with an accelerating voltage of 20 kV. Samples were cryo-fractured in liquid nitrogen so as to prevent any changes in morphology.

Transmission Electron Microscopy (TEM). Themicrostructures of PHB/LDPE/Cloisite 10A nanocomposites were studied using a transmission electron microscope

(Zeiss-EM10C-100KV, Germany). Ultra-thin sections were prepared for TEM imaging through cryo-microtoming at -60°C using a LEICA EM UC instrument and a diamond knife.

# RESULTS AND DISCUSSION

X-ray Diffraction (XRD)

Figure 1 shows the XRD patterns of the following

# samples: PHB25/LDPE/C5/N1, LDPE/N3, PHB/N3, and

Nanoclay Cloisite 10A. As can be observed, the peak corresponding to the interlayer spacing d (001) of nanoclay in the nanofilled LDPE (LDPE/N3) appeared at the higher  $2\Theta$  angle than that of Cloisite 10A. This phenomenon has been previously reported and attributed to the partial degradation of modifiers in organomodified nanoclay [3, 4]. However, this characteristic peak almost disappeared for the PHB/N3 sample. These results may indicate that in contrast to LDPE, PHB is capable of fully intercalating nanoclay platelets, leading to an exfoliated microstructure.

Figure 1 also shows that the XRD pattern of nanoclayfilled blend (PHB25/LDPE/C5/N1) was similar to that of PHB/N3, suggesting that nanoclay particles were preferentially localized in the PHB phase where they could be fully exfoliated.

#### Thermodynamics of Nanoclay Localization

It is well known that nanoparticle localization in immisci-DOI 10.1002/pc



FIG. 1. Intensity as a function of  $2\Theta$  for Cloisite 10A organoclay, LDPE nanocomposite, PHB nanocomposite, and compatibilized PHB25/LDPE/C5/N1. [Color figure can be viewed at wileyonlinelibrary.com]

wetting coefficient,  $\omega_a$ , in the thermodynamic equilibrium state. It can be calculated using Young's equation, which is defined below [3, 25]:

$$\omega_{12} = \frac{\gamma_{f-2} - \gamma_{f-1}}{\gamma_{12}} \qquad \qquad \delta_1 \models$$

where  $\gamma_{f-1}$  and  $\gamma_{f-2}$  are the interfacial tensions between organoclay and polymer 1 or 2, respectively.  $\gamma_{1,2}$  represents the interfacial tension between polymer 1 and 2. If  $\omega_{12} > 1$ , the organoclay is located within phase 1, if  $-1 < \omega_{12} < 1$ , the organoclay is concentrated at the interface, and if  $\omega_{12} < -1$ , the organoclay is selectively distributed in phase-2 [3, 25]. The interfacial energy between two com- ponents can be calculated based on the surface tension of components using the geometric mean, which is valid for high energy materials [5].

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2 \frac{q}{\gamma^d \gamma^d - 2} \frac{q}{\gamma^p} \frac{\delta 2 b}{\gamma}$$

ble polymer blends can be predicted through determining the

1 2 1 2

Here,  $\gamma_i$  is the surface tension of component *i*, while  $\gamma_d$  and  $\gamma_p$  denote the dispersive and polar parts of surface tension, respectively [5]. The surface tension values of LDPE, Cloisite

10 A, and PHB were found from the previous reports [26–28]. The surface tension value of PHB, LDPE, and Cloisite 10A have been summarized in Table 2. The surface tension levels reported in the literature have been measured at room temperature and need to be corrected for the processing temperature (here, 180°C). The Guggenheim equa- tion developed for small molecule liquids can be applied to

 TABLE 2. Surface tension and temperature coefficient for

 LDPE, PHB, and Cloisite 10A at room temperature.

γ(<u><sup>mN</sup></u>)

γ ( <u><sup>mN</sup></u> )	γ ( <u><sup>mN</sup></u> )	$- d\gamma(m^N)$	Sample	m	d m	p m	$\overline{dT}  \overline{m^{\circ}  \mathrm{C}}$
			LDPE [26]	33.1	32.0	1.1	0.05
			PHB [27]	46.89	38.08	8.81	0.06

45.3

33.4

11.8

0.1

Cloisite 10A [28]

TABLE 3. The calculated values of interfacial tension and wetting coefficient of the blend and nanocomposites.

Pair	LDPE/PHB	LDPE/C10A	PHB/C10A
$\begin{matrix} \gamma_{12} \\ \omega_{12} \end{matrix}$	1.24 -4.52	18.93	21.54

polymers to calculate surface tension levels at the desired temperatures [3].

$$-\frac{d\mathbf{Y}}{dT} = \frac{11}{9} \frac{\mathbf{Y}_0}{T_c} \quad 1 - \frac{T}{T_c} \quad \mathbf{\delta} \mathbf{3} \mathbf{P}$$

where  $\gamma_0$  is the surface tension at T = 0 and  $T_c$  represents the critical temperature. The value of  $-\frac{dy}{dT}$  was taken from the literature [3].

Based on the values of surface tension, the interfacial tension between pairs of components was calculated according to Eq. 2, and the data are shown in Table 3. According to this table, since the wetting coefficient ( $\omega_{12}$ ) was smaller than -1, the organoclay is located in the PHB phase, based on thermodynamic preference.

#### Melt State Viscoelastic Properties

To assure that samples would not undergo thermal degradation during the melt viscoelastic measurement, time sweep tests were performed on each sample. The storage moduli of PHB/LDPE binary blends and PHB nanocomposites were approximately constant during the 8-min measurement time, indicating that no significant detectable thermal degradation had occurred.

Figure 2 shows the transition from linear to nonlinear viscoelastic behavior for all samples. To compare the onset of shear thinning behavior, the raw data of the storage modulus,  $G^{0}$ , over the full frequency range was normalized to the initial



FIG. 2. Normalized strain amplitude dependence of the storage modulus for PHB/LDPE blends and nanocomposites. [Color figure can be viewed at wileyonlinelibrary.com]



FIG. 3. Complex viscosity as a function of PHB weight fraction (phr) in PHB/LDPE binary blends at 1 Hz. [Color figure can be viewed at wileyonlinelibrary.com]

shear modulus,  $G_0$ . The normalized storage moduli,  $G^0/G_0$ , revealed that the linear viscoelastic region (LVR) was relatively sensitive to the presence of nanoclay. The critical strain amplitude for transition from linear to nonlinearviscoelastic behavior decreased with nanoclay addition. According to Fig. 2, a strain amplitude of 0.1% was chosen for both time sweep and frequency sweep modes. This finding has been also reported for the PLA/PHBV/C30B nanocomposite in which the linear viscoelastic region is sensitive to the presence of nanoclay [7, 21].

It will be shown later that the nanoclay Cloisite 10A is predominantly located in the PHB phase. Hence in comparison with the PHB-dominant samples, the samples with lower PHB contents (PHB50/LDPE/N5) were associated with higher concentrations of Cloisite 10A in the PHB. Consequently, these samples began to deviate from the linear trend at smaller amplitudes.

Changes in  $\eta^*$  with PHB composition have been plotted in Fig. 3. The experimental data were compared with the results of calculation based on the proposed mixing law (Eq. 4) [18].

As it can be seen, PHB/LDPE binary blends did not obey the mixing law, since the experimental and theoretical plots did not overlap.

It can be seen in Fig. 4 that the viscosity of PHB was lower than that of LDPE at all angular frequencies, which negatively affected the dispersion of dispersed phase when PHB formed the matrix. This finding elucidated SEM results on the larger size of droplets when PHB formed the matrix and the smaller size of droplets when LDPE formed the matrix. It was interesting that the complex viscosities of the LDPE samples with less than 50 wt% PHB content were greater than that of the neat LDPE. This observation



FIG. 4. Complex viscosity versus angular frequency for PHB/LDPE blends over the full composition range. [Color figure can be viewed at wileyonlinelibrary.com]

might be due to the fact that a LDPE sample with less than 50 wt% PHB content has a higher mobility when being subjected to shear deformation [29]. Utracki [30] and Steinman [31] proposed two different models (Eqs. 5 and 6, respectively) to predict phase inversion ratios from rheological data in binary blends.

$$\phi_2 = \frac{()_{1 - \log \eta_{\beta_1}}}{2}, \eta = 1.9$$
 (55)

$$\phi_2 = -0:12 \log \eta_2 + 0:48$$
 (6)

In these relations,  $\varphi_1$  and  $\varphi_2$  represent volume fractions of the two components with viscosities of  $\eta_1$  and  $\eta_2$ , respectively [30, 31]. Here, considering the viscosity ratio at a frequency of 1 rad/s from  $\eta^*$  versus  $\omega$  plot, the phase inversion composition of PHB was found to be 0.50 from Utracki and 0.41 from Steinman equations. These compositions are close to the experimental composition observed in the SEM analysis.

Rheology is a powerful tool for studying the intercalation/exfoliation level of nanoparticles in a matrix [32]. In this regard,  $G^{\circ}$  values of PHB/organoclay and LDPE/ organoclay samples are shown in Fig. 5.

It is well known that organoclay increases the elastic modulus of the system. It is evident in Fig. 5 that the effect of organoclav Cloisite 10A on the elastic modulus of PHB was much more than its effect on LDPE. In other words, the affinity of PHB molecules toward organoclay Cloisite 10A was much greater than that of LDPE molecules. Therefore, in the case of PHB/LDPE binary blends, the main part of Cloisite 10A would be expected to be found in the PHB phase. This hypothesis has been proven by the data presented in Figs. 6 and 7. Moreover at low frequen- cies, the storage moduli of the PHB/clay nanocomposites exhibited a pseudosolid-like behavior due to the particle- particle interconnectivity of organoclay platelets or polymer chain confinement by the surrounding organoclay [25].

Figure 5 depicts the storage modulus versus frequency data

for uncompatibilized and compatibilized PE nanocomposites, LDPE/N3, and LDPE/C2.5/N3, respectively. The results indicate, that the uncompatibilized PE nanocomposite exhibits a melt viscoelastic behavior similar to that of the compatibilized

LDPE nanocomposite, demonstrating that LDPE does not play any role in exfoliating or migrating nanoclay platelets.



FIG. 5. Storage modulus as a function of angular frequency for (a) PHB and its nanocomposites; (b) LDPE and its nanocomposites. [Color figure can be viewed at wileyonlinelibrary.com]



FIG. 6. Complex viscosity as a function of angular frequency for PHB and LDPE nanocomposites. [Color figure can be viewed at wileyonlinelibrary.com]

It is well known that particle-filled molten polymers exhibit a liquid-solid transition due to the formation of a gellike structure by solid particles. Such gel behavior is characterized by a constant elastic modulus at low frequencies corresponding to yield stress behavior of the viscosity [3]. In the PHB/N5 nanocomposite, a plateau was observed at low angular frequencies due to strong interaction between PHB and nanoclay particles and may be an indica- tion of exfoliated structure of the organoclay. The exfoli- ated structure is formed by PHB chains and nanoclay particles or the filler network structure within the PHB matrix. The exfoliated structure is also observed in TEM micrographs.

The complex viscosities of the neat PHB and LDPE along with their corresponding nanocomposites are shown in Fig. 6. The neat PHB showed a very low viscosity and dis- played a Newtonian plateau with minimal shear thinning, as reported by Kolahchi and Kontopoulou [13]. As can be seen,



FIG. 7. Storage modulus versus angular frequency of PHB-rich blends. [Color figure can be viewed at wileyonlinelibrary.com]

the PHB nanocomposite exhibited a shear thinning behavior, which was intensified with the addition of more organoclay Cloisite 10A to the PHB matrix. The more considerable shear thinning behavior of the PHB nanocomposite was indicative of the greater affinity of PHB molecules to Cloisite 10A organoclay [4]. Moreover, Fig. 5(a) indicates that incorporation of nanoclay Cloisite 10A resulted in nonterminal behavior at low frequencies, implying the formation of a pseudo-network structure in the samples[33].

Incorporation of a well-located and proper compatibilizer enhances the storage modulus, due to the increased effect of interface on elasticity as a consequence of the enhanced interfacial area and reduced coalescence due to the stabilizing interface between the two phases [25]. However, in Fig. 7, the compatibilizer had no significant effect on the elastic modulus of the PHB75/LDPE sample. Moreover, a reduction in the elastic modulus of PHB-rich samples was observed due to LDPE-g-MAH incorporation. As was evident from the SEM micrographs, in the case of PHB as the matrix, the droplet sizes are enlarged due to incorporation of LDPE-g-MAH. This observation might be due to the formation of hydrogen bonds between MAH groups in the LDPEg-MAH and the carboxyl groups in PHB, which segregate the remaining compatibilizer in the PHB phase [34]. Hence, LDPE-g-MAH is diluted in the PHB and cannot reach the interface of the two phases. The energy of hydrogen bond formation ranges from 1 to 20 kJ.mol<sup>-1</sup>, which is easy to achieve. Moreover, the melt flow index of PE-g-MAH is a bit higher than that of PHB. Therefore, in the presence of LDPE-g-MAH in the PHB phase, the viscosity of PHB is reduced and negatively affects the stress transfer, which is necessary for droplet break-up. Therefore, the SEM data are in agreement with rheological results.

Furthermore, as illustrated in Fig. 7, the elasticities of the compatibilized PHB-rich systems are lower than that of the uncompatibilized PHB75/LDPE25 sample. Hence, the compatibilizer (LDPE-g-MAH) could not enhance the interfacial area between the PHB and the LDPE phases. This finding is consistent with SEM data where we observed larger droplet sizes in the case of PHB forming the matrix.

Since the storage modulus of PHB75/LDPE/C5/N1 is not lower than that of PHB75/LDPE/N1, we concluded that the compatibilizer did not transfer a portion of organoclay into LDPE droplets, resulting in a weaker 3-D network structure in the PHB matrix [25].

As it can be seen in Fig. 8 (in contrast to Fig. 7), no significant increase in the storage modulus of PHB25/LDPE samples is observed, even after compatibilizer or nanoclay incorporation. The reason behind this was most likely the nanoclay localization. This result is additional evidence confirming that nanoclay was located in the PHB droplets, and the droplets had very negligible effects on the overall storage modulus of the blend. Again, a slight increase in the storage modulus was observed when using com- patibilizer, as a result of compatibilizer localization in the PHB phase, and the presence of a part of compatibilizer at the interface of phases.



FIG. 8. Storage modulus as a function of angular frequency for LDPErich samples. [Color figure can be viewed at wileyonlinelibrary.com]

## Morphology

SEM. Figure 9 shows SEM micrographs of PHB/LDPE binary blends with different PHB contents. PHB/LDPE blends exhibited a matrix-droplet morphology (Fig. 9a and b), which is a indicative of immiscibility between the phases. This observation can be explained in terms of the higher viscosity of LDPE compared to the PHB phase. According to Fig. 6, the complex viscosity of the neat PHB is much lower than that of the neat LDPE at all angular fre- quencies. Hence, stress transfer had been much stronger when LDPE formed the matrix, resulting in smaller droplet sizes. From a rheological perspective, in PHB25/LDPE, the higher viscosity of the LDPE matrix induces greater shear stress to the blend during melt mixing. This acts in favor of breaking up of the PHB droplets, leading to smaller droplet size. Whereas an opposite condition exists for the PHB75/ LDPE blend in which, not only is lower stress applied on the blend, but also the higher viscosity of LDPE droplets causes the droplet-breakup process to be more difficult. Another look to this phenomenon is by Maxwell fluid

theory. It is generally accepted that in an immiscible polymer blend system the stress imposed on two phases are equal (iso-stress system). Therefore, in PHB75/LDPE, the shear rate applied on the PHB phase is much higher com- pared to that of LDPE droplet [35]. The blend with 50/50 composition exhibited co-continuous type morphology with some dispersed particles (Fig. 9c). Considering the lower viscosity of PHB during melt blending (Fig. 6), one can distinguish between PHB and LDPE constituents in Fig. 9c.

Nanoclays may reduce the droplet sizes and the polydispersity index of droplets in five possible ways: (1) alteration in the viscosity ratio of the phases due to an uneven distribution of the filler; (2) the compatibilizing effect of organoclay by lowering the interfacial tension; (3) coalescence prevention by acting as a physical barrier; (4) immobilization of the dispersed drops (or the matrix) by creating a physical network of particles when the solid concentration is above the percolation threshold; or (5) a strong interaction between polymer chains and the solid particles inducing steric hindrance [1].

As it can be seen in Figs. 10(b-d) and 11(b-d), nanoclay sharply reduced the droplet sizes. When LDPE formed the matrix (Fig. 10a), the initial particle size dispersion was smaller than its opposite counterpart (Fig. 11a).

At equilibrium, the nanoclay is confined to the PHB phase, such that the concentration of nanoclay in this phase is high since no nanoclay is present in the LDPE phase (as can be seen in TEM images). Such a high concentration of nanoclay in the PHB droplets does not indicate that the liquid–solid transition has occurred, and that the PHB droplets are highly viscous because of the strong shear thinning behavior of PHB during processing [3]. Therefore, the particle size reduction due to nanoclay incorporation is mainly due to the first possible reason, that is, C10A increased the viscosity of PHB phase and altered the viscosity ratio toward 1, reducing the coalescence between nodules of the same phase.

The effect of compatibilizer (LDPE-g-MAH) on the binary blend morphology was studied, and the obtained data



FIG. 9. Matrix-disperse and co-continuous morphologies for different PHB/LDPE binary blends: (a) PHB25/LDPE; (b) PHB75/LDPE; and (c) PHB50/LDPE. The scale bar for figures a and b is 10  $\mu$ m and for figure c is 100  $\mu$ m.



FIG. 10. SEM micrographs of (a) PHB25/LDPE; (b) PHB25/LDPE/N1; (c) PHB25/LDPE/N3; (d) PHB25/LDPE/N5; (e) PHB25/LDPE/C2.5; (f) PHB25/LDPE/C5; and (g) PHB25/LDPE/C7.5. The scale bar is 10 µm.

are illustrated in Figs. 10e-g and 11e-g. Two different behaviors are observed during LDPE-g-MAH incorporation. When PHB forms the matrix, LDPE-g-MAH remains in the PHB phase due to the formation of hydrogen bonds between hydroxyl groups in PHB and maleic anhydride groups in LDPE-g-MAH [34].

Incorporation of the compatibilizer into nanocomposites did not induce a significant effect on droplet size reduction (see Table 4), while its impact on the PHB75/LDPE25 binary blend was considerable. Wang demonstrated that the reduced efficiency of compatibilizer in decreasing the droplet size is due to the interaction of dissolved excess



FIG. 11. SEM micrographs of (a) PHB75/LDPE; (b) PHB75/LDPE/N1; (c) PHB75/LDPE/N3; (d) PHB75/ LDPE/N5; (e) PHB75/LDPE/C2.5; (f) PHB75/LDPE/C5; and (g) PHB5/LDPE/C7.5. The scale bar is 10 µm.

TABLE 4. Morr	phological	parameters of P	HB/LDPE binar	v blends and	their corresi	ponding cor	npatibilized a	and/or nanocom	oosite syste	ems.
	JHOIO GIOGI	parameters or r	TID, DDT D OIIIM	, oreners and	anen eoneo	ponening eor	inparto incoar e	and of manoworn		
	<u> </u>									

Sample	$R_v (\mu m)$	PDI	Sample	$R_v (\mu m)$	PDI
PHB75/LDPE	8.72	1.49	PHB25/LDPE	3.06	1.75
PHB75/LDPE/N1	3.51	1.69	PHB25/LDPE/N1	1.19	1.20
PHB75/LDPE/N3	1.73	1.66	PHB25/LDPE/N3	1.18	1.61
PHB75/LDPE/N5	1.08	2.43	PHB25/LDPE/N5	0.82	1.63
PHB75/LDPE/C2.5	13.10	1.38	PHB25/LDPE/C2.5	1.65	1.49
PHB75/LDPE/C5	12.64	1.44	PHB25/LDPE/C5	1.50	1.42
PHB75/LDPE/C7.5	12.72	1.49	PHB25/LDPE/C7.5	1.33	1.36
PHB75/LDPE/C5/N1	9.60	1.53	PHB25/LDPE/C5/N1	1.04	1.56
PHB75/LDPE/C5/N5	3.90	1.66	PHB25/LDPE/C5/N5	0.51	1.56



FIG. 12. TEM micrograph of PHB25/LDPE/N5 sample. [Color figure can be viewed at wileyonlinelibrary.com]

surfactant of the organoclay with functional groups in MAH during processing [36]. In Table 4, PDI stands for polydispersity index, and  $R_v$  is radius of dispersed phase.

# TEM

PHB25/LDPE/N5 exhibited a matrix-droplet morphology. The exfoliated morphology of nanoclay platelets whithin PHB droplets is shown in Fig. 12b. Figure 12c illustrates how some nanoclay platelets are located at the interface of phases.

## CONCLUSIONS

Based on the results, the following conclusions could be drawn:

- XRD and TEM data demonstrate that organoclay Cloisite 10A is fully exfoliated in the PHB phase.
- (2) The dynamic elastic modulus measurements showed a pseudo-solid-like behavior in PHB75/LDPE/N5 or PHB/N5,

suggesting the enhanced elasticity and melt viscosity is due to the presence of nanoclay as a solid network former and is beneficial in improving PHB processability.

(3) All nanocomposites at low shearing frequencies show a viscosity upturn and nonterminal behaviors that are observed in the complex viscosity and storage modulus curves, respectively. Such a trend increased with the addition of more nanoclay, indicating rheological percolation and the formation of networks in polymer matrices.

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