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# Influence of Calcium Carbonate Nanoparticles on Mechanical Behavior of Poly(lactic acid)/Poly(butylene succinate) Blend

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## Abstract

PLA/PBS blends in various blend ratio (70:30, 50:50, and 30:70 wt%) containing calcium carbonate nanoparticles (nano-$CaCO_3$) of 1 and 5 phr were prepared. Tensile tests with 3 strain rates and Izod impact test were carried out in order to investigate the influence of $CaCO_3$ nanoparticles on mechanical behavior of nanocomposites under different deformation rates. Morphology and compatibility of nanocomposites were studied using SEM and DSC. It is found that PBS/PLA 50/50 wt% blends exhibited the highest percentage of elongation at break due to co-continuous phases as seen in SEM. $CaCO_3$ nanoparticles were dispersed uniformly in polymer matrix although they showed agglomeration sizes in micro-scale. $CaCO_3$ nanoparticles of 1 phr increased toughness of polymer matrix as evident in higher elongation at break in all straining rates and higher impact strength. This indicates lubricating effect of $CaCO_3$ nanoparticles during the deformation of polymer samples. Nevertheless, adding $CaCO_3$ nanoparticles of 5 phr showed positive effect to improve mechanical properties for brittle polymer matrix since they offered better molecular mobility to withstand applied stresses. However, NPCC of 5 phr gave negative effect on ductile matrix or low strain rates. This would be attributed to loss of molecular mobility during the deformation from nano-$CaCO_3$ agglomeration.

**Key words:** PBS, PLA, Calcium carbonate nanoparticle, SEM

## Introduction

Environmental pollution has become a great concern due to high volume of plastic waste in modern life style. One of the possible solutions to solve the pollution and fulfill the public need is to replace commodity synthetic polymers with biodegradable polymers which are readily susceptible to microbial action. Poly(lactic acid (PLA) and poly(butylene succinate) (PBS) are two main biodegradable polymers which have been interested to replace the commodity synthetic polymers. High brittleness and cost of PLA is the major issue for its commercialization and many applications. Blending PLA with flexible biodegradable polymer such as PBS would provide the blend with desired properties. Bratia et al.(1) suggested that blends of up to 20 wt% PBS content in PLA was expected to overcome the deficiencies of PLA such as brittleness. Tensile strength and modulus of the blends decreased with PBS content but followed approximately the mixing rule for 90/10 and 80/20 (PLA/PBS) blends. Eslami and Kamal(2) also observed a strong strain hardening behavior in PLA/PBSA blends, in which PBSA forms the continuous phase (PBSA wt% ≥ 50).

Calcium carbonate nanoparticles (NPCC) have currently taken center stage for their manifold applications such as their usage as fillers in the polymeric materials with the aim of reducing costs as well as enhancing the impact resistance in association with higher elastic modulus when calcium carbonate nanoparticles are incorporated within the structure. Chan et al.(3) prepared nano-composites of PP/NPCC and found that the notched fracture toughness of the nano-composites was substantially higher than that of the neat PP. They explained that the NPCC introduced massive number of stress concentration sites in the matrix and promoted cavitations at the particle-matrix boundary when loaded, which these cavities released the plastic constraint and triggered large-scale plastic deformation of the matrix and thus tremendous fracture energy was consumed. Xie et al.(4) synthesized PVC/NPCC nano-composites via in-situ polymerization of vinyl chloride (VC) in the presence of NPCC. They found that NPCC could stiffen and toughen PVC simultaneously. They discussed that NPCC acted as stress raisers leading to debonding/voiding and deformation of the matrix around the nanoparticles. These mechanisms lead to impact toughening of the nanocomposites.

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Jiang et al.⁽⁵⁾ added NPCC into PLA and reported that the strain-at-break of PLA increased with NPCC concentration ranging from 0 to 7.5 wt%. Their evidences of micromechanical deformation from SEM and TEM micrographs suggested that NPCC increased the strain-at-break by massive crazing across the whole gauge length and the matrix eventually failed due to the coalescence of the microvoids. From these reports, the toughening mechanism of NPCC on polymeric materials involves the massive crazing initiated by NPCC, followed by debonding between NPCC and matrix that requires high energy to do as such. However, the role of NPCC in the blend based on PLA has not been reported. Thus, in this study, NPCC of 1 and 5 phr was added into the blend between PLA and PBS in various ratios, and the influence of NPCC content on mechanical behavior of PLA/PBS blend, especially toughening and strain-at-break, was investigated.

## Materials and Experimental Procedures

### *Materials*

Poly(butylenes succinate) (PBS) (GS Pla®, Grade AZ71TN,) with MFI of 220 g/10 min (155 °C, 2.16 kg) was purchased from Mitsubishi Chemicals, Japan. Poly(lactic acid) (PLA), (Ingeo® Grade 3051D,) with MFI of 1.12 g/10 min (155°C, 2.16 kg) was purchased from Nature Work LLC, USA. The nano-sized precipitated calcium carbonate (NPCC201) was supplied by Behn Meyer Chemical (Thailand). It was coated with stearic acid for better dispersion. Prior to compounding, PBS and PLA pellets were dried in an air-circulating oven at 60°C for 12 hours to remove moisture.

### *Melt Compounding*

Neat PLA, neat PBS, PLA/PBS blends, and their nanocomposites adding NPCC of 1 and 5 phr were melt compounded in a twin-screw extruder (SHJ-25, Yongteng, China). The formula of all specimens is presented in Table 1. The temperatures along the extruder were controlled to achieve a temperature profile ranging from 160°C to 165°C with a screw speed of 80 rpm. The extrudate was pelletized and dried in an oven at 60°C for 12 hours. Type IV dogbone and impact specimens were fabricated by injection molding (Battenfeld PLUS 350/75) using melting temperature of 180°C and mold temperature of 40°C.

**Table 1.** Formula of PBS/PLA blend and nanocomposite blends

| Sample | PLA (wt%) | PBS (wt%) | NPCC (phr) |
|---|---|---|---|
| 1 | 100 | 0 | 0 |
| 2 | 70 | 30 | 0 |
| 3 | 50 | 50 | 0 |
| 4 | 30 | 70 | 0 |
| 5 | 0 | 100 | 0 |
| 6 | 100 | 0 | 1 |
| 7 | 70 | 30 | 1 |
| 8 | 50 | 50 | 1 |
| 9 | 30 | 70 | 1 |
| 10 | 0 | 100 | 1 |
| 11 | 100 | 0 | 1 |
| 12 | 70 | 30 | 5 |
| 13 | 50 | 50 | 5 |
| 14 | 30 | 70 | 5 |
| 15 | 0 | 100 | 5 |

### *Mechanical Testing*

Tensile test was performed accordance to ASTM-D638 using a Universal Testing Machine (Instron, Model 5969, Instron Engineering Corporation, USA). The test specimens of neat PLA, neat PBS, PLA/PBS blends and their NPCC nanocomposites were conditioned at 25°C for 48 hours prior to testing. The test was performed with crosshead speed of 5, 50, and 200 mm/min, which corresponds to the strain rates of 0.0025, 0.025, and 0.100 $s^{-1}$, respectively, for the IV type specimens. The average and standard deviations of five measurements was calculated and reported.

Notched Izod impact test was performed accordance to ASTM-D256 using an impact tester (Zwick, B5102.202, Germany) with a pendulum hammer of 4.0 J. The test specimens of neat PLA, neat PBS, PLA/PBS blends and NPCC nanocomposites were conditioned at 25°C for 48 hours prior to testing. The test was performed at room temperature. The average and standard deviations of ten measurements was calculated and reported.

### *Thermal Properties Study*

Thermal properties of neat PLA, neat PBS, PLA/PBS blends and NPCC nanocomposite samples were determined under nitrogen atmosphere using a differential scanning calorimeter (DSC, Mettler DSC 1). The sample weight used was approximately 5-10 mg weight. The samples were tested in a heat-cool-heat mode, with the heating rate and the cooling rate of 5°C/min. Temperature scan was performed from 30°C to 180°C.

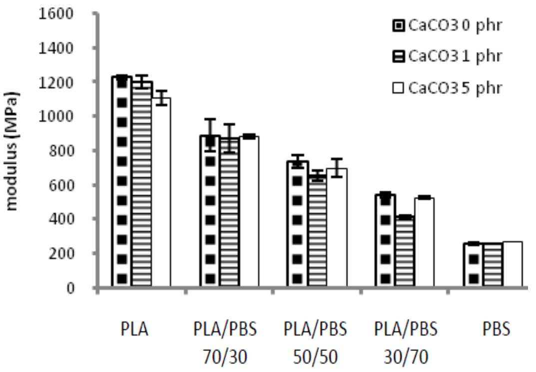
### *Morphology Study*

Morphology of neat PLA, neat PBS, PLA/PBS blends and NPCC nanocomposite specimens were examined by a scanning electron microscope (SEM) (Jeol, JSM 5410LV). Specimens were cryo-fractured in liquid nitrogen. The fractured surface was gold coated prior to inspection to avoid electrostatic charging.

## Results and Discussion

### *Effect of Calcium Carbonate Nanoparticles on Tensile Properties under Conventional Strain Rate*

Figure 1 presents modulus, tensile strength and elongation at break of neat PLA, neat PBS, PLA/PBS blends and NPCC nanocomposite which they were tested using the conventional strain rate of 0.025 $s^{-1}$ (crosshead speed of 50 mm/min). It is seen that adding NPCC into PLA reduced modulus and tensile strength of the composites while their elongation at break was slightly increased. Hoffman et al.$^{(6)}$ proposed that such rigid inorganic particles could promote localized yielding of the polymer matrix leading to void coalescence and fracture. We believe the reason behind such a phenomenon in this study involves organic substance on NPCC. The commercial NPCC is usually surface modified with an organic material such as steric acid$^{(3,5)}$ to prevent them for agglomeration. The steric acids coating on NPCC behave as lubricating barrier between PLA and NPCC prompting better molecular mobility of PLA phases when stress was applied.



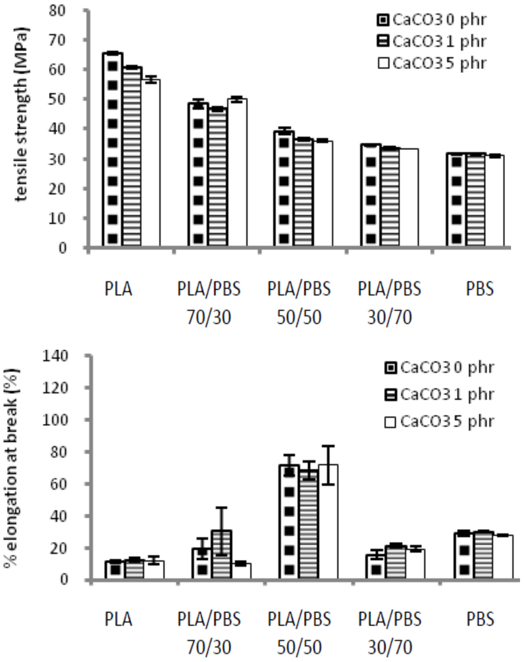


**Figure 1**. Modulus, tensile strength, and elongation at break of neat PLA, neat PBS, PLA/PBS blends, and NPCC nanocomposites under strain rate of 0.025 $s^{-1}$.

Similarly to Jiang et al. report$^{(5)}$, all NPCC/PLA nanocomposites in this study showed yielding with noted stress whitening across the whole gauge length but without necking and their tensile strength at yield decreased with the amount of NPCC loading.

In the other hand, adding NPCC into PBS increased modulus slightly but reduced its tensile strength. The elongation at break of PBS was increased with adding NPCC of 1 phr and did not change when adding NPCC of 5 phr. This indicates that the localized yielding by NPCC did not have significant effect on ductile PBS compared to brittle PLA. Despite of mobility enhancement, the relatively flexible PBS molecules could be constrained by the surrounding NPCC causing them to respond in elastic behavior and massive crazing creating by NPCC in the PBS matrix caused them to be broken at lower strain.

Similarly to other reports$^{(1,2)}$, the phase separation is evident in PLA/PBS blends as seen in SEM results later. Under the same blending condition, the dispersed phases of PBS in PLA/PBS 70/30 wt% were smaller than PLA dispersed phases in PLA/PBS 30/70 wt%. The modulus and tensile strength of the blends were in the trend of the mixing rule, however, the elongation at break of

PLA/PBS 50/50 wt% was exception. As presented in DSC and SEM studies, PLA/PBS blend is partial-compatible blend and form co-continuous phases when blending them in 50/50 wt%. The partial-compatible co-continuous phases of PLA/PBS blend showed outstanding elongation at break at which necking was observed followed by stress whitening during the extension. It is worth to note that the necking of the tensile specimens occurred only in specimens of PLA/PBS 50/50 wt% and 70/30 wt%, but the necking in the latter occurred randomly. The mechanism of this phenomenon could not yet be explained since further investigation is required.

Adding NPCC of 1 phr increased the elongation at break of the blends except the 50/50 wt% blends; however, the values were less than those of sole PBS. The localized yielding by NPCC among polymer matrix allowed the yielding to occur at less stress in polymer blends, thus modulus and tensile strength of nanocomposites were lowered. When NPCC loading was increased to be 5 phr, higher modulus of the blends were observed. This implies that NPCCs were dispersed better in PBS than PLA. This also correlates nicely with the decreasing of the percentage of PBS crystallinity when adding NPCC of 5 phr.

### *Effect of Calcium Carbonate Nanoparticles on Mechanical Behavior under Different Strain Rates*

In order to understand further the role of NPCC on mechanical behavior of nano-composites, the tensile tests using different strain rates were carried out. The strain rates used were 0.0025, 0.025, and 0.100 $s^{-1}$. Also, the Izod impact test was performed to study how NPCC toughen the nanocomposites based on PLA/PBS blend. Since the elongation at break could be correlated with toughening by NPCC, the following discussion is thus based on these results. Figure 2 shows elongation at break of neat PLA, neat PBS, PLA/PBS blends, and NPCC nanocomposites adding NPCC of 1 and 5 phr. In general, it is seen that increasing the strain rate reduces the elongation at break significantly in the blends, since dispersed phases acted as stress concentrators and retarded load transfer under higher strain rates.

It is found that the localized yielding by NPCC on PLA and PBS was more pronounced in the slowest strain rate when adding NPCC of 1 phr. This is due the toughening mechanism that involves massive crazing and the matrix eventually failed due to the coalescence of the microvoids. PLA benefitted from localized yielding by these well-dispersed NPCC even at the highest strain rate. The higher elongation at break was observed in PLA nanocomposites even the loading was up to 5 phr. In the other hand, NPCC of 5 phr became the stress concentrators in PBS matrix causing them to be broken at lower elongation at break in faster strain rates. In PLA/PBS blend, adding NPCC of 1 phr helped to promote toughening mechanism in the blends especially the blends with high content of PLA (i.e. PLA:PBS 70:30 wt%).

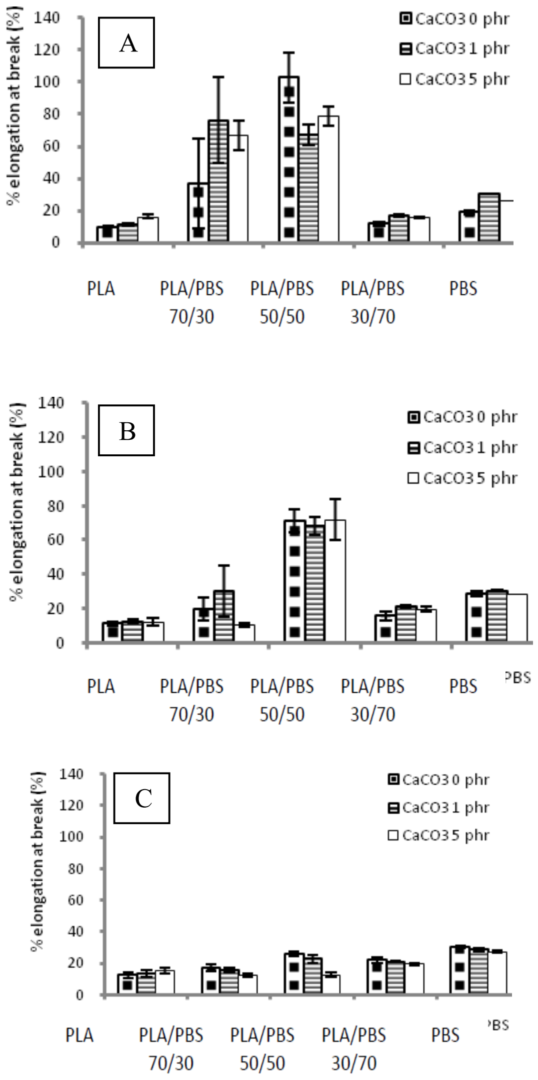


**Figure 2**. Elongation at break of neat PLA, neat PBS, PLA/PBS blends and NPCC nano-composites under strain rate of a) 0.0025, b) 0.025, and c) 0.100 $s^{-1}$.

Figure 3 show impact strength of neat PLA, neat PBS, PLA/PBS blends and NPCC nanocomposites. It is found that NPCC of 1 phr increased the impact strength of all formula. Massive crazing and shear yielding are two toughening mechanisms of polymers. For polymer toughening by rigid (non-deformable) particles, debonding at the particle surface can induce massive crazing, and/or shear yielding if the plastic resistance of the matrix is decreased to below the applied stress due to the release of strain constraints(5).

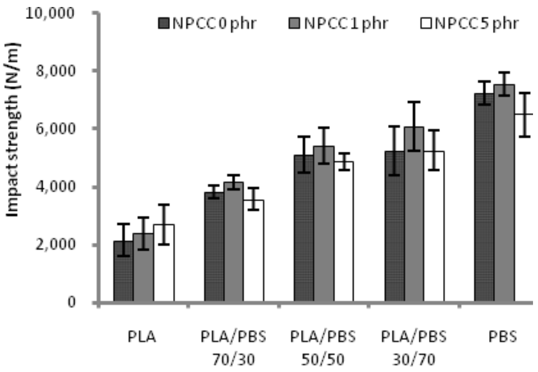


**Figure 3**. Impact strength of neat PLA, neat PBS, PLA/PBS blends and NPCC nanocomposites.

In these nanocomposites, the relatively easy debonding of NPCC was probably attributed to two factors. First, the stearic acid coating on the particles did not have interactions between NPCC and polymer matrix as revealed by DSC. Second, the cubic shaped NPCC particles caused a high stress concentration around the NPCC particles and promoted the debonding. However, the NPCC of 5 phr reduced the impact strength of the samples except in the neat PLA. This could be attributed to faster cracks generated by massive crazing in the area that would prevail the localized yielding in the polymer matrix

### *Thermal properties of neat PLA, neat PBS, PLA/PBS blends and NPCC nanocomposites*

Table 2 shows thermal properties of neat PLA, neat PBS, PLA/PBS blends, and NPCC nanocomposites studied by DSC technique. It is seen that adding NPCC into PLA did not affect glass transition ($T_g$) of PLA. This indicates that the PLA molecules were not plasticized by steric acids on the NPCC. PLA and NPCC/PLA nanocomposite samples showed only one peak of crystalline melting peak, which the percentage of crystallinity was reduced with the presence of NPCC. For pure PBS, the $T_g$ was not reported in this study. In contrast, the percentage of crystallinity ($\chi$) of PBS was increased when adding NPCC of 1 phr indicating the nucleating effect of NPCC in the PBS matrix. However, the percentage of crystallinity of PBS was reduced when NPCC loading was 5 phr. This implies that NPCC of 1 phr was well dispersed in the PBS matrix.

For PLA/PBS blend, the $T_g$ of PLA was decreased for about 2.5-3.0 oC compared to neat PLA, indicating that PBS is partially miscible with PLA molecules which is matched to Bhatia(1) report. It is interesting to observe that there were two crystalline melting peaks of PLA when blending

**Table 2**. Thermal properties of neat PLA, neat PBS, PLA/PBS blends, and NPCC nanocomposites

| PLA :PBS | $CaCO_3$ (phr) | PLA | | | | | PBS | |
|---|---|---|---|---|---|---|---|---|
| | | $T_g$ (°C) | $T_m$(°C) | | $\chi$ (%) | | $T_m$ (°C) | $\chi$ (%) |
| | | | Peak 1 | Peak 2 | Peak 1 | Peak 2 | | |
| 100:0 | 0 | 60.01 | 148.60 | - | 19.33 | - | - | - |
| 70:30 | 0 | 57.52 | 146.37 | 152.25 | 5.63 | 2.26 | 110.68 | 1.42 |
| 50:50 | 0 | 57.57 | 146.30 | 152.52 | 5.15 | 2.42 | 111.10 | 25.06 |
| 30:70 | 0 | 58.65 | 145.62 | 151.99 | 2.75 | 1.73 | 111.08 | 42.30 |
| 0:100 | 0 | - | - | - | - | - | 110.85 | 58.78 |
| 100:0 | 1 | 60.11 | 151.10 | - | 0.91 | - | - | - |
| 70:30 | 1 | 57.70 | 146.46 | 152.26 | 4.39 | 2.89 | 111.02 | 5.23 |
| 50:50 | 1 | 57.06 | 146.45 | 152.08 | 4.17 | 1.68 | 111.25 | 30.39 |
| 30:70 | 1 | 56.09 | 146.62 | 152.68 | 2.80 | 1.31 | 111.68 | 38.40 |
| 0:100 | 1 | - | - | - | - | - | 111.27 | 62.57 |
| 100:0 | 5 | 60.10 | 150.92 | - | 7.30 | - | - | - |
| 70:30 | 5 | 57.50 | 144.73 | 152.18 | 2.97 | 7.34 | 110.44 | 4.15 |
| 50:50 | 5 | 57.06 | 145.81 | 152.43 | 4.75 | 2.72 | 111.11 | 23.28 |
| 30:70 | 5 | 56.70 | 145.82 | 151.95 | 2.35 | 1.74 | 111.03 | 31.93 |
| 0:100 | 5 | - | - | - | - | - | 111.10 | 54.42 |

PLA with PBS indicating that there were two components crystallized individually. These peaks are attributed to re-melting of newly formed crystallite during heating. Lee(7) explained that the appearances of double endothermic peaks are due to quenching after the first heating cycle. It does not give sufficient time for high melting crystallite to form. Therefore, more low crystallites are produced.

### *Morphology of neat PLA, neat PBS, PLA/PBS blend, and NPCC nanocomposites*

Figure 4 presents SEM of cryo-fractured surfaces of neat PLA, neat PBS, and their blends. Under 1,000X magnification, neat PBS was fractured showing rougher surface than neat PLA revealing ductile behavior. Meanwhile, smoother fracture surface of neat PLA indicates brittleness of polymer matrix. In the blend, it is clearly seen that phase separation was observed. The fracture surfaces were rough in the PLA/PBS 30/70 wt% and dispersed phases of PLA were clearly observed, indicating the ductile failure of PBS matrix was dominant. Also, debonding of PLA dispersed phases was evident implying poor interfacial adhesion between PLA dispersed phases and PBS matrix.

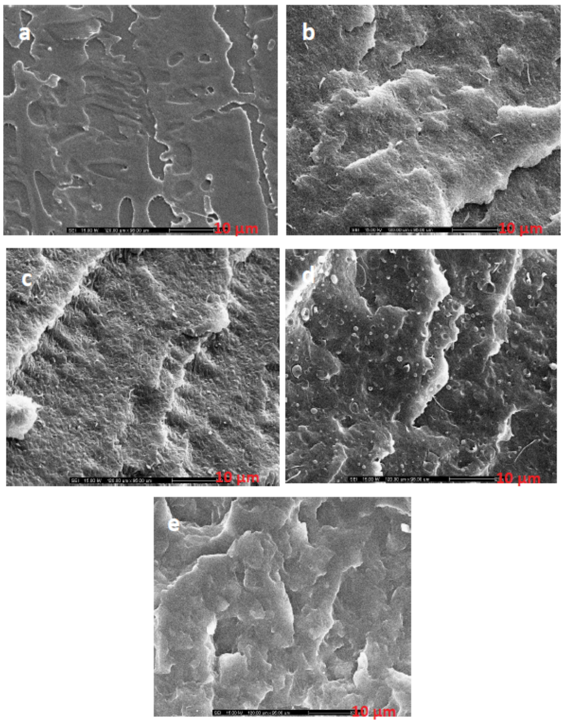


**Figure 4.** SEM micrographs of cryo-fractured surface of a) neat PLA, b) PLA/PBS 70/30 wt%, c) PLA/PBS 50/50 wt%, d) PLA/PBS 30/70 wt%, and e). neat PBS.

In the other hand, the fracture surfaces of PLA/PBS 70/30 wt% blend presents localized yielding indicating the brittle failure of PLA matrix inhibited by the yielding of PBS dispersed phases. Interestingly, the fracture surface of PLA/PBS 50/50 wt% blend shows oriented strips of ductile failure alternating with smooth areas. These strips could be attributed to the failure of PBS phases while the smoother areas would belong to the PLA phases.

Figure 5 shows SEM of cryo-fractured surfaces of PLA, PBS, and PLA/PBS blends adding NPCC of 1 phr. Compared to non-added NPCC, the fracture failure of all specimens showed more evidences of crack propagation induced by the NPCC adding into the polymer matrix. In PLA/NPCC nanocomposites, there was localized ductility present in the fracture surfaces which are not observed in the neat PLA.

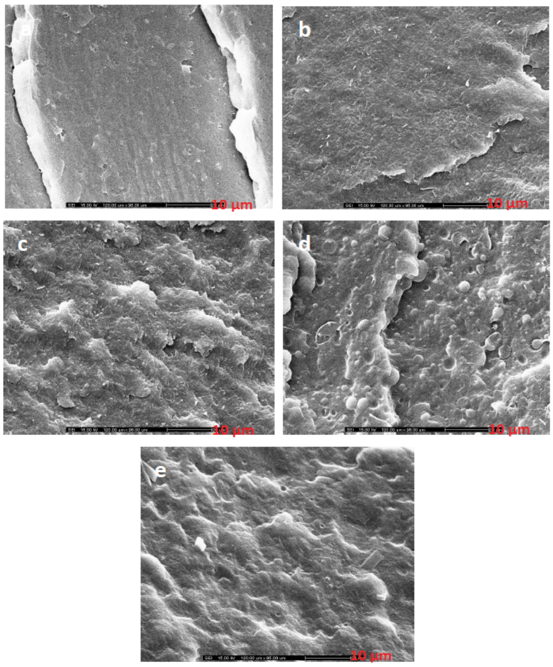


**Figure 5**. SEM micrographs of cryo-fractured surface of a) PLA, b) PLA/PBS 70/30 wt%, c) PLA/PBS 50/50 wt%, d) PLA/PBS 30/70 wt%, and e) PBS adding NPCC of 1 phr.

This confirms that NPCC initiated localized yielding in the matrix; therefore, higher impact energy is required to break the specimens as shown in the impact test. In PBS/NPCC specimen, the surface shows grooves of small cracking initiated by NPCC, where yielding of matrix is limited in a certain distance.

In Figure 6, the SEM micrographs of cryo-fractured surface of PLA, PBS and PLA/PBS blends adding NPCC of 5 phr, show that the fracture failure of all specimens occurred in brittle mode. Localized yielding of specimens disappeared even in the PBS nanocomposites.

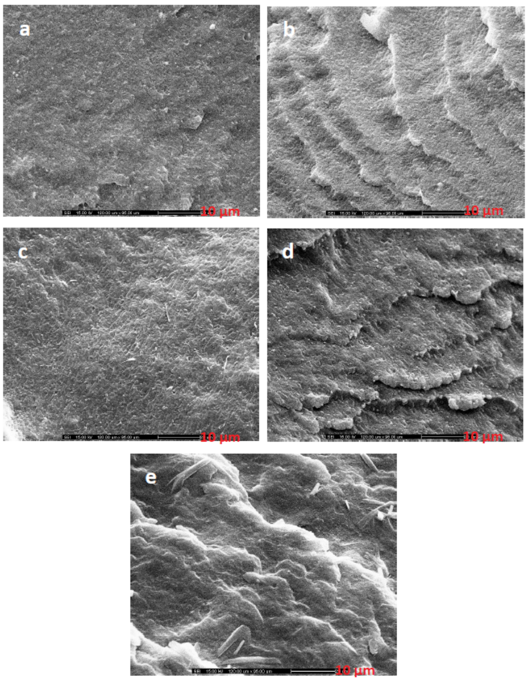


**Figure 6.** SEM micrographs of cryo-fractured surfaces of a) PLA, b) PLA/PBS 70/30 wt%, c) PLA/PBS 50/50 wt%, d) PLA/PBS 30/70 wt%, and e) PBS adding NPCC of 5 phr.

## Conclusions

It is found that PLA/PBS 50/50 wt% blends exhibited the highest percentage of elongation at break due to co-continuous phases as seen in SEM. NPCC were dispersed uniformly in polymer matrix although they showed agglomeration sizes in micro-scale. NPCC of 1 phr increased toughness of polymer matrix as evident in higher elongation at break in all straining rates and higher impact strength. This indicates lubricating effect (locailized yielding) of NPCC during the deformation of polymer samples. Nevertheless, adding NPCC of 5 phr showed positive effect to improve mechanical properties for brittle polymer matrix since they offered better molecular mobility to withstand applied stresses. However, NPCC of 5 phr gave negative effect on ductile matrix or low strain rates. This would be attributed to loss of molecular mobility during the deformation from NPCC agglomeration.

## Acknowledgement

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