Sustainable PHBV/Cellulose Acetate Blends: Effect of a Chain Extender and a Plasticizer

Kjeld W. Meereboer, Akhilesh K. Pal, Manjusri Misra,* and Amar K. Mohanty*

ABSTRACT: Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and cellulose acetate (CA) were blended in the presence of a plasticizer, i.e., triethyl citrate (TEC), and a chain extender, i.e., poly(styrene-acrylic-co-glycidyl methacrylate). To increase the ductility and impact properties of PHBV and to investigate a new biodegradable PHBV-based blend for sustainable packaging, CA was compatibilized with TEC. PHBV and plasticized CA (pCA) blends showed complete immiscibility through separate glass transition and melting peak temperatures in differential scanning calorimetry (DSC), despite the similar Hansen solubility parameters of PHBV, CA, and TEC, indicating partial miscibility. Phase separation between PHBV and pCA was clearly observed by scanning electron microscopy (SEM). PHBV/pCA (70:30) blends had improved impact strength, exceeding that of neat PHBV and pCA, which is attributed to PHBV porosity induced by degradation from the high processing temperature. During processing, the plasticizer migrated from CA to PHBV and partially plasticized it, as evidenced through DSC analysis. The melt temperature of PHBV was reduced, which was confirmed by double melting peaks, representing the formation of secondary crystallites at a lower temperature. Due to processing at high temperatures (210–220 °C), significant porosity was observed in the PHBV/pCA 30:70 blend in SEM analysis. Consequently, the impact strength was improved by 110% as compared to that of virgin PHBV. The addition of CE had no effect on the mechanical properties but did make the PHBV/pCA blends morphologically uniform.

INTRODUCTION

The use of plastic packaging materials, especially single-use plastics produced from petroleum-based sources, is a growing environmental concern. In fact, a large proportion of the materials end up in landfills or in the environment, taking more than a lifetime to degrade. Nearly 36% of plastic was utilized for single-use applications in 2017; of that, approximately 14% was recycled, while the rest was incinerated, landfilled, or remained in the environment.1 Similarly, light-weight and littered plastics migrate into the oceans, take thousands of years to degrade, and significantly increases the removal difficulty, which creates problems for marine life.1 Polyhydroxyalkanoates (PHAs), and more specifically poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), is a potential resource to mitigate further damage to the environment. It is currently sourced from natural renewable fermentation sources and is a 100% biodegradable and compostable polymer,2 making it an attractive sustainable alternative. It is worth mentioning that PHBV is one of the few biopolymers that is marine-biodegradable,3 soil-biodegradable,4 and compostable under appropriate conditions.5

PHAs are bacterial polyesters, synthesized by prokaryotic organisms from several carbon sources, such as agricultural and industrial waste, and other mixed carbon sources.6 With inherent biodegradable properties, PHAs form a closed-loop, sustainable cycle “from cradle-to-cradle” that minimizes their impact on the environment. PHBV, for example, is sourced from natural renewable fermentation sources.2 PHBV can be classified as a very brittle material with a narrow processing window, especially with low hydroxyvalerate contents (2–5%), having a tensile modulus of 3.2 GPa with an elongation at break of 1.4%,7 comparable to that of PLA. However, petro-based polymers such as polypropylene have an elongation at break above 50%.8

Despite this limitation, PHAs are commonly used in biomedical applications. However, they must be free from organic impurities from production, such as carbohydrates or proteins, that can activate the immune system in humans.9

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inertness makes it suitable for active and passive food packaging applications. 

For flexible packaging applications, the thermomechanical properties and the production cost are of far more concern. PHBV, being more ductile than PHB, is still susceptible to thermal degradation due to the high shear, temperature, and residence time during processing, significantly limiting its applications. A common approach to overcome these limitations is to blend PHBV with other biodegradable polymers to increase the processing window and minimize final product costs while optimizing the mechanical and thermal properties.

Cellulose, a common building block of organic life, is a highly crystalline polysaccharide that is insoluble and infusible in all organic solvents. Thus, it is usually derivatized into cellulose esters to improve processability. The most prevalent cellulose acetate esters are cellulose acetate (CA), cellulose acetate butyrate (CAB), and cellulose acetate propionate (CAP). CA esters are commercially produced by substituting hydroxyl groups with acetyl, butyryl, and propionyl groups with a degree of substitution (DS) in the range of 1.7–3.0. Among the CA esters, CA is one of the most used cellulose derivatives.

Miscibility plays an important role in polymer blends, allowing for a homogenous mixture during processing and optimized thermomechanical properties. However, thermodynamically immiscible blends reflect distinct phase separation during melt blending and decimated mechanical properties, which can only be mitigated by compatibilizing agents.

Through solvent casting, PHBV and cellulose triacetate, CA with a DS of 3.0, were reported to be miscible and have improved tensile properties and acid-catalyzed hydrolytic degradation rate. However, the research literature available on CA blends with PHB or PHBV was limited; hence, PHB and PHBV blends with other CA esters were investigated. A number of other studies reported PHB and PHBV to be partially or completely miscible over the entire range with other cellulose esters, including CAB and CAP.

The DS effect in various CA derivatives significantly impacts their utility by changing their properties. Completely substituted CA has a DS of 3. According to Gardner et al., as the DS increases, biodegradability decreases, but CA with a maximum DS of 2.5 degrades to CO2. Other CA esters, such as CAB, are very stable polymers and significantly less susceptible to biodegradation. CA is commonly plasticized due to its poor thermal stability at melt temperature to improve its processability.

Among the available plasticizers (e.g., polyethylene glycol, tributyl citrate, etc.), triethyl citrate (TEC) has been used in both PHBV and CA and is a nontoxic, bio-based plasticizer that is safe for use in food packaging, making it an attractive option to plasticize cellulose acetate. However, the mechanical properties of CA vary significantly depending on the polymer to plasticizer ratio. CA with 20–40% TEC content has better mechanical properties when processed at 180 °C or lower temperatures, with high shear conditions such as extrusion at 100 rpm. Through literature, the optimal ratio of CA to TEC plasticizer was found to be 25% with a melt compounding temperature of 200–210 °C.

The literature survey found that research on PHBV and CA ester blends is limited, mostly containing PHBV and CAB or CAP blends. The processes involved were solvent casting and melt mixing followed by compression molding and injection molding. PHBV/CAP blends indicated improved thermal stability and miscibility due to good phase interaction.

PHBV/CAB blends were evaluated to be thermally miscible with <50% PHBV content; however, El-Shafee et al. reported PHBV to be entirely miscible with CAB. Buchanan et al. reported that improved tear strength positively correlated to PHBV and also reported an elongation of 106% for PHBV/CAB (50:50) compression-molded samples. However, the limits of the literature survey are reflected by the lack of mechanical properties for PHBV and CAB or CAP blends in the sources cited above. PHBV and completely substituted CA (DS = 3) were blended and reported to be miscible to some extent, but only through solvent casting, and only one blend ratio (36:64) was reported. The Young modulus and tensile strength were improved by 12.7 and 36%, respectively, for PHBV/CA (36:64) blends. Melt extrusion or other processing techniques of PHBV/CA blends were not found in any form with other DS for CA.

The expected outcome of blending PHBV and CA together is to incorporate the functional properties of CA into PHBV’s degradation kinetics. Cellulose triacetate was reported to improve the degradation of PHBV in acidic conditions. Cellulose triacetate increases the water uptake and water vapor permeability; therefore, it can potentially increase the water—PHBV interfacial surface area and increase biodegradability in marine water.

Furthermore, it has already been researched that CA plasticized with 25% TEC produced the optimal effect; thus, the processing temperature of PHBV must be considered. PHBV is sensitive to the processing temperature; however, a chain extender such as Joncryl (ADR-4368 S) at 0.25–1% is reported to effectively increase the viscosity and extend the molecular chain length of PHBV, effectively rebuilding the molecular weight. However, no improvement in the mechanical properties was reported.

In this research work, PHBV and CA plasticized by TEC for applications in biodegradable packaging were melt-compounded and extruded to determine the miscibility for the first time. Furthermore, as per our literature review, this is the first study of a sustainable blend using PHBV and CA in extrusion. The objectives of this study were to assess the miscibility of different blend ratios of PHBV/CA by characterizing the thermal and morphological properties. The mechanical, physical, and thermal properties of PHBV/CA blends were thoroughly investigated to optimize the performance. Additionally, the effect of a chain extender on the mechanical, thermal, and morphological properties of PHBV/CA blends was studied and the effect of processing temperature and plasticizer content was discussed based on the mechanical and thermal properties.

### RESULTS AND DISCUSSION

#### Solubility Parameters

The solubility parameters relating to PHBV, CA, and TEC were developed from calculating the cohesive forces between molecules, as outlined in Table 1, and can be a predictor of the solubility parameter (δ) as well as the theoretical degree of miscibility. The cohesive forces are broken down into the polar, dispersive, and hydrogen bonding forces.

| Table 1. Solubility Parameters (δ) of CA, PHBV, and TEC |
| sample | Hoy | Hořejší–van Krevelen | Hansen | average |
|--------|-----|-----------------|-------|--------|
| CA     | 24.8| 25.4            | 25.1  | 25.1   |
| PHBV   | 21.6| 19.9            | 20.6  | 20.7   |
| TEC    | 23.6| 23.1            | 23.8  | 23.5   |

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derived using the Hoftyzer–van Krevelen and Hoy methods. Some variation is seen in the solubility parameter for PHBV relative to that reported by Snowdon et al., which can be the result of the method used to approximate the effect of individual components of each molecule. Both Hoy and Hansen methods produce similar solubility values for each polymer, suggesting that they may be soluble. Forster et al. report that \( \Delta \delta < 2.0 \text{ MPa}^{1/2} \) indicates miscibility and \( \Delta \delta > 10.0 \text{ MPa}^{1/2} \) is immiscible, thus, it can be concluded that CA and TEC are miscible and PHBV, TEC, and CA are all partially miscible with each other. Therefore, a blend of PHBV, TEC, and CA may be miscible and processable in extrusion followed by injection molding but does require experimental evaluation to confirm the degree of miscibility.

**Thermal Properties.** Differential Scanning Calorimetry (DSC). Plasticized CA has completely amorphous characteristics, having no melting peaks in the heating part of the cycle and no crystallization peaks in the cooling part of the cycle. Literature reports that the pCA melt peak thermogram appears like a \( T_g \) and does not conform to a traditional melting peak, making enthalpy measurements unfeasable. However, no melting peak for pCA was observed in this study. Thus, the crystallinity and melting peaks are only attributed to the presence of PHBV. The \( T_g \) of PHBV was also not observed for any blend ratio by DSC, the result of the heating scan rate being too rapid.

The DSC thermograms of PHBV/CA blends (Figure 1A–D) illustrate the effect of cellulose acetate on the PHBV melting and cooling cycles. In all cases, the \( T_g \) values of PHBV and pCA were not observed. The melting peak of PHBV and its enthalpy reduce with the addition of pCA, probably due to the absence of a melting peak structure in pCA. pCA appears to promote double melting peaks in PHBV, although alternative factors can be responsible for the thermogram patterns; PHBV measured with a low DSC heating rate is known to result in double melting peaks.

The formation of double melting peaks is attributed to the formation of a primary and secondary crystal structure that results in the secondary crystal structure melting first. At 30% pCA loading, the melting peak is seen to broaden, indicating a nonuniform crystal morphology. Furthermore, the enthalpy is reduced due to the absence of a melting peak related to CA. As the pCA loading increases, the melting peak broadens and eventually diverges into a complete double melting peak. Furthermore, the PHBV melting peak is decreased with greater pCA and TEC contents. Contrary to literature reports, TEC does not eliminate the double melting peak of PHBV but significantly impacts the melting behavior of PHBV, indicating that it is not entirely associated with cellulose acetate and suggesting that the double melting peak is the result of PHBV being nonuniformly plasticized. TEC migrates to PHBV, which is also supported by the reduction in the crystallization temperature and the enthalpy of crystallization during the cooling cycle, as indicated in Table 2 and Figure 1C. The reduction in crystallinity seen in the PHBV/pCA blends can be attributed to the catastrophic degradation of PHBV by thermal hydrolysis due to high processing temperatures. Molecular weight reduction has been reported to reduce the crystallinity after extensive hydrolysis of PHBV.

The addition of a chain extender to PHBV/pCA blends had no effect on the double melting peak morphology (Figure 1B). The crystallinity of only PHBV is indicated in Table 2 and is slightly reduced in all blend ratios, which indicates reduced chain mobility, reflecting the effect of the CE on PHBV. With increased cross-linking and more complex molecular structures,
the molecular weight increased and the chain mobility reduced, inhibiting crystallization. Furthermore, the enthalpies of 50:50 and 30:70 polymer blends were taken over both melting peaks in DSC, illustrating the fact that the overall enthalpy reduced significantly with the addition of pCA, which does not crystallize. However, the crystallinity for the 30:70 PHBV/pCA blend and the 50:50 blend ratio do not reflect the weight fraction of PHBV, indicating a secondary factor is reducing the ability of PHBV to crystallize. Both blends were produced at the same temperature; however, PHBV was known to be thermally sensitive, indicating that chain scission of PHBV may have occurred. CE is not able to significantly mitigate the issue efficiently (as shown in Figure 1B).

### Thermogravimetric Analysis (TGA)

The TGA illustrates the thermal stability of the virgin polymers (PHBV and pCA) and their blends in Figure 2A. Figure 2A,B indicates a peak degradation at 285 °C and the onset of degradation at 95% mass of 267 °C for pristine PHBV, which is in agreement with the literature. The pCA degradation has two peaks, one associated with the plasticizer and the other corresponding to the polymer, correlating to approximately 303 and 368 °C, respectively. TEC plasticizer has a broad degradation rate that slowly accelerates to a peak of approximately 241 °C (data not shown), in agreement with the literature. Considering the broad range of TEC degradation, the initial two peaks in the PHBV/pCA blend in Figure 2B can be explained by the degradation of unassociated and associated plasticizer and are furthermore within the two ranges reported by Ferfera-Harrar and Dairi. These two ranges correspond to temperatures below 240 °C and between 240 and 300 °C when plasticizing cellulose acetate with TEC. The degradation of the associated TEC is clearly illustrated by the 0:100 blend ratio at approximately 300 °C.

With the addition of pCA, the blend’s thermal stability is seen to improve and is compositionally dependent, indicated by the curve shifting to higher temperatures. The resulting residue at 500 °C is entirely from CA. However, pCA degradation onset is significantly earlier than virgin PHBV, beginning at approximately 100 °C. The initial stages of thermal degradation are entirely the result of TEC and any associated moisture, being the most sensitive component of the polymer blend as illustrated in the TGA curves of CA, TEC, and pCA in Figure S1.

The thermal degradation peaks of PHBV have been observed to shift toward higher temperatures as the PHBV composition is reduced, which as attributed to the overlap of the PHBV

### Table 2. DSC Results of PHBV/PCA Blends with and without 0.3 phr CE

| PHBV/pCA | $T_c$ (°C) | $\Delta H_c$ (J/g) | $T_m1$ (°C) | $\Delta H_m$ (J/g) | $X_c$ (%) |
|----------|------------|------------------|------------|------------------|--------|
| 100:0    | 125.65 ± 0.52 | 94.13 ± 0.87 | 171.85 ± 1 | 64.50 ± 4.49 | 82.16  |
| 70:30    | 111.79 ± 0.30 | 60.38 ± 1.29 | 161.82 ± 1 | 48.00 ± 8.45 | 84.53  |
| 70:30:0.3| 112.10 ± 1.08 | 57.81 ± 2.52 | 161.67 ± 1 | 63.73 ± 8.35 | 83.53  |
| 50:50    | 97.11 ± 0.09  | 40.16 ± 0.40  | 162.84 ± 0.86 | 41.52 ± 6.66 | 76.18  |
| 50:50:0.3| 101.71 ± 1.32 | 37.51 ± 1.55 | 159.70 ± 0.28 | 39.55 ± 7.12 | 72.57  |
| 30:70    | 82.98 ± 0.13  | 17.24 ± 0.17  | 154.80 ± 0.54 | 20.86 ± 6.39 | 63.79  |
| 30:70:0.3| 87.31 ± 0.72  | 19.88 ± 1.15  | 156.66 ± 0.44 | 19.80 ± 6.05 | 60.55  |

The DSC results of PHBV/PCA blends with and without 0.3 phr CE are presented in Table 2. The data shows a decrease in the melting temperature and enthalpy with the addition of pCA, indicating a reduction in crystallinity. The addition of CE also decreases the melting temperature and enthalpy, suggesting a decrease in crystallinity. The thermal stability of the blends is also affected, with the addition of CE increasing the thermal stability, as indicated by the shift in the onset of degradation to higher temperatures.

Figure 2. TGA (A) and derivative thermogravimetric analysis (DTGA) (B) of PHBV/pCA blends and TGA (C) and DTGA (D) of PHBV/pCA/CE blends with 0.3 phr CE.
degradation curve and the degradation curve of the associated plasticizer in CA. However, the 50:50 blend ratio does not follow the compositional trend. It must be noted that the 50:50 PHBV/pCA blend was processed at 210−220 °C, significantly different from the 70:30 blend at 200−210 °C. The degradation of PHBV molecular weight during processing into smaller and more volatile units is exacerbated by the higher processing temperature and can result in the early onset of degradation in TGA, which is visible due to the higher percentage of PHBV relative to pCA but is not found in the PHBV/pCA 30:70 blend. SA-GMA is a chain extender reported to improve the properties of PHBV when processed at higher temperatures by increasing the activation energy and, therefore, improving the thermal stability, as shown in Figure 2C,D.31 The effect is most prominently displayed by the increased CA thermal degradation peaks for all PHBV/pCA blend ratios. An interesting factor is displayed by the TEC degradation peak not overlapping with the PHBV degradation peak in the PHBV/pCA/CE 70:30:0.3 blend, causing the PHBV degradation peak thermogram to follow that of virgin PHBV. This suggests that TEC is almost entirely associated with pCA and degrades separately from PHBV. Furthermore, the limits of a CE’s ability to rebuild the molecular weight of PHBV were observed in the PHBV/pCA/CE 70:30:0.3 blend. The degradation curve of PHBV in the PHBV/pCA/CE 70:30:0.3 blend was decreased back to a temperature similar to PHBV and degrading separately from the associated TEC in pCA.

Dynamic Mechanical Analysis (DMA). Figure 3A,B illustrates the storage moduli of various PHBV/pCA blends and the addition of Joncryl to blends, respectively. Naturally, PHBV is expected to have the highest storage modulus, being a brittle thermoplastic polymer relative to pCA. The addition of a more flexible polymer such as plasticized cellulose acetate, which has one of the lowest storage moduli, significantly reduced the storage modulus of PHBV in all blend ratios assessed. However, in 50:50 blend ratio, produced at a temperature of 210−220 °C, the storage modulus is slightly higher than that of 70:30 and 30:70 blend ratios, which suggests an optimized point where the negative effect of pCA content and partially plasticized PHBV on the blend stiffness is reduced.

The addition of a chain extender was intended to rebuild the molecular weight of PHBV due to the high processing temperature, but no effect was seen for all blend ratios except 50:50, as shown in Figure 3B. The effect of the chain extender on the storage modulus effectively reduced the stiffness of PHBV/CA 50:50 blend to that of other blend ratios. A chain extender is known to decrease crystallinity by inducing cross-linking; therefore, the increased molecular weight can result in a less “glassy” blend with moduli like pCA.41 These results do not coincide with what is expected of the mechanical properties as the overall blend mechanical ductility and flexibility have not been improved relative to the neat constituents.

The tan(δ) was studied to determine the compatibility and potential interactions of a PHBV/CA blend and was evaluated based on the peak position. Figure 3C illustrates the tan(δ) of the virgin PHBV, pCA, and their three blends. Most notable is the fact that individual Tgs are present, indicating that the blends are not perfectly miscible. The addition of 0.3 phr CE did not have a significant effect on the tan(δ), and individual the Tgs remained unaffected (Figure 3D).

The Tg of PHBV measured from the peak in the temperature vs tan(δ) curve, and reported in Table 3, is in agreement with literature reports,45 and the Tg of plasticized cellulose acetate is 116.5 °C. The literature reports the Tg of pCA from DSC...
Table 3. Glass Transition Temperatures of PHBV/pCA Blends with and without CE Measured by DMA Analysis

| PHBV/pCA/CE  | T_\(g\) (°C) | T_\(g\) (°C) |
|---------------|----------|----------|
| 100:0         | 23.98 ± 0.19 |         |
| 70:30         | −0.89 ± 0.19 |         |
| 70:30:0.3     | −0.17 ± 1.94 |         |
| 50:50         | −10.89 ± 0.74 |         |
| 50:50:0.3     | −7.64 ± 3.22 |         |
| 30:70         | −12.01 ± 2.97 | 132.32 ± 0.31 |
| 30:70:0.3     | −14.41 ± 0.42 | 133.72 ± 0.38 |
| 0:100         |         | 0.66     |

The T_\(g\) of PHBV shifts toward lower temperature as the pCA ratio increases, and therefore, the associated TEC in CA increases, as shown in Table 4. This indicates TEC migration from pCA to PHBV, further confirming the findings from DSC. These indications also illustrate that the blends are not partially miscible.

Table 4. Heat Deflection Temperature (HDT) and Density of PHBV/pCA/CE Blends

| PHBV/pCA/CE  | HDT (°C) | density (c/cm³) |
|---------------|----------|----------------|
| 100:0         | 143.03 ± 1.97 | 1.236 ± 0.009 |
| 70:30         | 126.49 ± 1.85 | 1.179 ± 0.010 |
| 70:30:0.3     | 127.16 ± 1.65 | 1.179 ± 0.013 |
| 50:50         | 108.14 ± 6.80 | 1.182 ± 0.009 |
| 50:50:0.3     | 102.08 ± 5.98 | 1.182 ± 0.006 |
| 30:70         | 90.55 ± 0.18  | 1.248 ± 0.006 |
| 30:70:0.3     | 94.19 ± 0.93  | 1.256 ± 0.004 |
| 0:100         | 81.08 ± 2.37  | 1.288 ± 0.001 |

Mechanical Properties. Tensile and Flexural Properties. The tensile properties of virgin PHBV illustrated in Figures 4–6 are in agreement with literature reports; tensile strength of 30–40 MPa, tensile modulus of 2.3–3 GPa, and elongation at break of 3%, with some variation in ductility and impact due to the specific processing conditions. The results do, however, fit within the ranges of the data sheet provided by Eastman.

Park et al. reported a tensile stress at break of 70.0 MPa for cellulose acetate and triethyl citrate blend with a ratio of 75:25, which is in good agreement with the experimentally found parameter. The values of tensile modulus, elongation at yield, flexural strength, and flexural modulus were 2200 MPa, 8.8%, 65.4, and 2370 MPa, respectively, as reported by Park et al., which were slightly lower than those found in this study.

The introduction of pCA into PHBV as a blend resulted in all mechanical properties achieving neither of the individual constituents’ properties. The tensile properties of all blend ratios reduced below those of PHBV and pCA. Buchanan et al. reported similar findings for blends of compression-molded PHBV and CAB, where a 50:50 ratio of PHBV/CAB resulted in lower tensile modulus and strength relative to either constituent. However, the same ratio significantly improved the elongation at break in a narrow ratio percentage range but was not observed in this study.

The addition of 0.3 phr CE did not improve the tensile strength; however, as the CA content increases, the tensile modulus is seen to marginally improve, approaching and exceeding pCA in 50:50 and 30:70 blends. CE was introduced into PHBV prior to processing, indicating that the effect would largely be in PHBV. Thus, as the PHBV molecular weight is rebuilt, the tensile modulus approaches that of virgin PHBV.

Figure 4. Tensile modulus and strength of PHBV/pCA blends: (A) 100:0, (B) 70:30, (C) 50:50, (D) 30:70, (E) 0:100, (F) 70:30 + 0.3 phr CE, (G) 50:50 + 0.3 phr CE, and (H) 30:70 + 0.3 phr CE.

Figure 5. Flexural modulus and strength of PHBV/pCA blends: (A) 100:0, (B) 70:30, (C) 50:50, (D) 30:70, (E) 0:100, (F) 70:30 + 0.3 phr CE, (G) 50:50 + 0.3 phr CE, and (H) 30:70 + 0.3 phr CE.

Notched IZOD Impact and Elongation at Break. Figure 6 illustrates the notched IZOD impact strength and elongation at break of PHBV, pCA, and PHBV/pCA blends, with and without 0.3 phr CE. The PHBV impact strength and elongation at break are considerably lower than literature reports but can be attributed to the difference in the processing temperature profiles, as PHBV is known to be thermally sensitive. The pCA impacted in all blend ratios, although the increased pCA content does correlate with increased flexural strength in the blends. The chain extender is seen to marginally improve the flexural modulus and strength of PHBV/pCA 50:50 and 30:70 blends. The improvement is negligible and may be due to the increased processing temperature relative to that of PHBV/pCA 70:30 blends.

Impact would cause fi...
elongation at break was found to be 16, 100% greater than that reported in the literature, which is attributed to the longer resting period for plasticized CA before processing. Preprocessing, Park et al. rested the plasticized CA for 75 min. The notched IZOD impact strength of pCA is below that reported by Mohanty et al. due to the higher processing temperature used in this study. Furthermore, the elongation at break of amorphous polymers does not always result in a high-notched IZOD impact strength. The elongation at break of PHBV/pCA blends does not show a significant difference compared to that of virgin PHBV, which is a result of the poor chain mobility during tensile testing. Furthermore, the impact strength does improve at higher pCA loadings, particularly with a 110% improvement for PHBV/pCA 30:70 blend, which will be further investigated by SEM to check the interaction between PHBV and pCA. The chain extender did not improve the impact properties of PHBV/pCA blends but mitigated the measured variation seen in tested samples of the 30:70 blend.

Heat Deflection Temperature (HDT) and Density. The heat deflection temperature is the temperature where a polymer deflects 250 μm with 0.455 MPa applied force and is directly correlated with the degree of crystallinity and T_g. High crystallinity of blends correlates to an HDT approaching the melt temperature. Table 4 indicates an HDT of 143 °C for PHBV, which is in agreement with the literature. As the plasticization of CA increases, the HDT is reported to drop, reaching 64 °C at a 30% loading. In this study, the HDT of pCA with a 25% TEC loading was found to be 81.1 ± 2.4 °C, considerably lower than the T_g found through DMA. The TEC exists as a liquid and probably has a crystallinity of around 5%, which is in agreement with the literature.

The HDT appears to be composition-dependent, shifting toward lower temperatures with pCA addition, parallel to the reducing crystallinity, which is found for PHBV blends in the literature. The CE has no effect on the HDT of PHBV/pCA.

The density was observed to reduce in PHBV/pCA blends, which was attributed to PHBV and TEC molecular scission, resulting in increased porosity. Increased porosity can introduce microcellular voids that may impede crack propagation, explaining the mechanical phenomenon discovered before. However, the density addition increases the density, seemingly mitigating the porosity in PHBV/pCA blends. CEs are known to rebuild the molecular weight and appears to have done so for PHBV, warranting further investigation through SEM.

CONCLUSIONS

Biodegradable polymers, i.e., PHBV and cellulose acetate, were blended together in various proportions, with and without the chain extender, using a twin-screw extruder, and specimens were prepared by injection molding. The observed properties such as DSC, DMA, and SEM morphology showed that PHBV and pCA blends are completely immiscible at all blend ratios, despite the calculated solubility parameters and literature review indicating potential miscibility. The mechanical properties of all pCA blends were significantly reduced; however, the impact strength exceeded that of virgin PHBV and pCA in blend ratios containing high pCA contents. This is attributed to PHBV degradation from the high processing temperature, which is reflected by the increased porosity observed by SEM, reduced density, and a reduced measure of crystallinity through DSC. Furthermore, the plasticizer TEC migrated during processing, partially plasticizing PHBV, reducing its melt temperature, and forming secondary crystallite structures. The unique T_g’s for PHBV/pCA blends indicate that PHBV and CA are not miscible. PHBV/pCA 30:70 blend ratio had a 110% improvement in impact strength, resulting from the partial foaming of the sample and, consequently, leading to the deterioration of the other mechanical properties relative to those of virgin PHBV. Hence, PHBV/pCA blends need more research to achieve miscibility and improve the mechanical and thermal properties.
Figure 7. SEM morphology at 1000× of PHBV/pCA/CE blend ratios: (A) 100:0, (B) 70:30, (C) 50:50, (D) 30:70, (E) 0:100, (F) 70:30 + 0.3 phr CE, (G) 50:50 + 0.3 phr CE, and (H) 30:70 + 0.3 phr CE.
MATERIALS AND METHODS

Materials. PHBV pellets, CA powder, and TEC as a plasticizer were the main materials used in this research. The PHBV pellets, with the tradename ENMAT Y1000P, were obtained from Tianan Biological Materials Co. Ltd. and were reported to have 1–5 mol % HV content. The CA powder (CA-398-30; acetyl content, 39.8 wt %; hydroxyl content, 3.5 wt %) was purchased from Chempoint. TEC was purchased from Chempoint. TEC was purchased from TEC (SA-GMA) (Joncryl ADR-4368C, BASF, Germany) was used as was used as a chain extender. All of the polymers and chemicals were used without any further purification. Blends including the chain extender SA-GMA (CE) were prepared by adding CE to PHBV at 0.3 phr of the total blend mass. Following the CE addition, blends were prepared and processed as described below.

Preparation of Plasticized Cellulose Acetate. Prior to processing, both PHBV and CA powder were vacuum dried in an oven at 80 °C overnight. The moisture content of each polymer was measured using a moisture analyzer (Sartorius 14229 ACS) overnight. The moisture content of Each sample (% w/w) was subjected to heating, cooling, and heating cycle under a nitrogen atmosphere with a flow rate of 50 mL/min. In the first heating part of the cycle, the rate was 10 °C/min from ∼50 to 200 °C followed by isothermal conditions for 3 min to erase the thermal history of the polymer blend. The first cooling part was at a rate of 5 °C/min to ∼50 °C and equilibrated for 3 min. The second heating part was at a rate of 10 °C/min to 240 °C. The temperature at the displacement of 250 μm for the two samples was taken as the peak degradation rate temperature for each blend. Two replicates were completed for each sample.

Thermogravimetric Analysis (TGA). Virgin PHBV and CA, in addition to the TEC and fabricated blends, were analyzed using a thermogravimetric analyzer (Q500, TA Instruments, Delaware). Each sample (15–20 mg) was subjected to heating at a rate of 10 °C/min from room temperature (∼21 °C) to 600 °C in a nitrogen-enriched environment with a purge and balance flow rate of 40 and 60 mL/min, respectively. The derivative thermogravimetric analysis (DTGA) peaks were taken as the peak degradation rate temperatures for each blend. Two replicates were completed for each sample.

Heat Deflection Temperature (HDT). The heat deflection temperature (HDT) was analyzed for melt-extruded virgin polymers and their blends using a dynamic mechanical analyzer (Q800 from TA Instruments, Delaware) under three-point bending. In accordance with ASTM D648, 0.455 MPa was applied to impact bars and the strain was measured as the temperature increased. Starting from 30 °C, the heating rate was 2 °C/min until the strain exceeded 0.22%. The average of the strain at the displacement of 250 μm for the two samples was taken as the HDT.

Dynamic Mechanical Analysis (DMA). The storage modulus (E′), loss modulus (E″), and the loss tangent (tan δ = E″/E′) of all fabricated specimens were measured using the dynamic mechanical analyzer (Q800 from TA Instruments, Delaware) under multifrequency strain with a dual cantilever.

Table 5. PHBV/CA Blend Compositions

| Notation | PHBV (%) | CA (%) | TEC (%) | CE (phr) | Processing temp. (°C) |
|----------|----------|--------|---------|----------|----------------------|
| PHBV    | 100      | 0      | 0       | 0        | 180                  |
| PHBV/pCA (70:30) | 70      | 22.5   | 7.5     | 0        | 200–210              |
| PHBV/pCA (50:50) | 50      | 37.5   | 12.5    | 0        | 210–220              |
| PHBV/pCA (30:70) | 30      | 52.5   | 17.5    | 0        | 210–220              |
| pCA     | 70       | 75     | 25      | 0        | 200–210              |
| PHBV/pCA/CE (70:30:0.3) | 70      | 22.5   | 7.5     | 0.3      | 200–210              |
| PHBV/pCA/CE (50:50:0.3) | 50      | 37.5   | 12.5    | 0.3      | 210–220              |
| PHBV/pCA/CE (30:70:0.3) | 30      | 52.5   | 17.5    | 0.3      | 210–220              |
The samples were heated at 3 °C/min from −50 to 140 °C or when the driving force approached 0 N. The applied frequency for all samples was 1 Hz with an amplitude of 15 μm. The loss tangent peak was utilized to determine the glass transition temperature (Tg) of the samples. TA analysis software was utilized to analyze the results. Two replicates were completed for each sample.

**Tensile and Flexural Properties.** Five tensile and flexural samples were conditioned before analysis for 48 h at 21 °C with a relative humidity of 50%. The tensile and flexural strengths were measured using an Instron 3382 universal testing machine (Massachusetts). In accordance with ASTM D638, type IV tensile bars were tested at room temperature and humidity conditions with a rate of 5 mm/min. In accordance with ASTM D790, flexural bars were tested over a 52 mm span in a three-point bend configuration with a rate of 14 mm/min. Bluehill software was utilized to process the test results.

**Notched IZOD Impact Strength.** The impact strength of samples was measured utilizing a Zwick Roell HIT25P impact tester (Ulm, Germany) in accordance with ASTM D256. Each sample was notched immediately after processing. The average of six replicates was taken as the notched IZOD impact strength.

**Density.** The density of samples was measured using an MD 300S electronic densimeter (Florida). Three flexural bars were utilized for each measurement, and the average was taken as the density.

**Scanning Electron Microscopy.** SEM micrographs of the impact fractured sample break surfaces were obtained using a Phenom ProX Desktop from Phenom-World BV (Eindhoven, Netherlands). Charging was minimized by a Cressington 108 F3 sputter (Massachusetts). In accordance with ASTM D638, type IV each sample. The density of samples was measured using an MD 300S electronic densimeter (Florida). Three flexural bars were utilized for each measurement, and the average was taken as the density.

Thermogravimetric analysis (TGA) of cellulose acetate (CA), plasticized cellulose acetate (pCA) and triethyl citrate (TEC). Thermal degradation of pCA over 200–250 °C is only attributed to TEC and associated water which is within the processing conditions of PHBV/pCA blends; TGA and DTGA of TEC, pCA, and CA (Figure S1) (PDF)

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at: https://pubs.acs.org/doi/10.1021/acsomega.9b03369.

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