

Green Composites from a Bioplastic Blend of Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) and Carbon Dioxide-Derived Poly(propylene carbonate) and Filled with a Corn Ethanol-Industry Co-product

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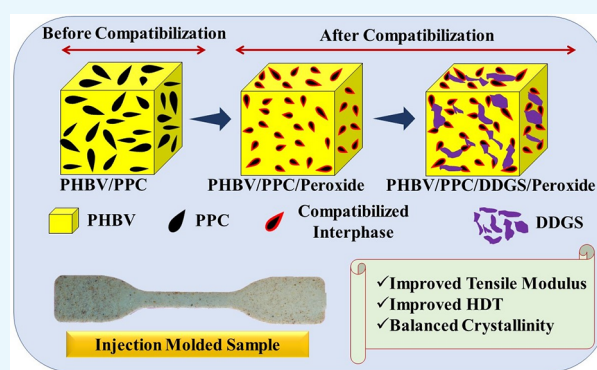
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ABSTRACT: Sustainable green composites were engineered from distillers' dried grains with solubles (DDGS), a co-product from the corn ethanol industry as a sustainable filler in bioplastic matrices made from a carbon dioxide-derived poly(propylene carbonate) (PPC) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) blend. The effect of water-washed DDGS (15 and 25 wt %) on the properties of injection-molded green composites from PHBV/PPC blends (60/40) and (40/60) and DDGS without and with peroxide (0.5 phr) has been investigated. From the results, it was noticed that the glass transition temperature (T_g) of the PHBV/PPC (60/40) bioplastic matrix increased by ~ 9.6 °C by adding a peroxide cross-linking agent, indicating significant interaction (linkage) between PHBV and PPC polymers in this particular composition ratio, which was supported by SEM analysis as no phase separation was observed between PHBV and PPC. The tensile modulus of PHBV/PPC (60/40) and PHBV/PPC (40/60) blends with peroxide was improved by ~ 40.7 and 1.5% after the addition of 25 wt % DDGS, respectively, due to its fibrous flaky structure. The % elongation values at break of the PHBV/PPC (60/40) blend matrices with and without peroxide were drastically improved by 18.5 and 90.7 folds, respectively, as compared to that of brittle pristine PHBV.



INTRODUCTION

In the developing economy, bio-based polymers show their importance in terms of utilization in various applications and are counted as a portion of the new circular economy among various plastics. The shift in financial interest is motivated by the projected cumulative progress of primary polymer wastes produced, which will exceed 12,000 million metric tons by 2050.¹ Every year, plastic wastes (~ 7.7 million tons) leak into aquatic environments from land-living.² This has resulted in a projected growth of 25% in the production of bio-based and biodegradable plastics by 2023.³ For example, bio-polyethylene terephthalate has shown a growth from 7 to 80% of the global bioplastic production capacity between 2010 and 2017.⁴ Major plastic packaging producers have set a goal that 100% recycled, compostable, or reusable plastics will be used in their products by 2025.⁵ However, biodegradable plastics hold significant importance in combating mismanaged plastic wastes, which is expected to double by 2025.⁶

Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) is one of the most well-known biodegradable plastics in the poly(hydroxyalkanoate) (PHA) family, is marine biodegradable, and is suitable to replace single-use plastics. However, despite this potential asset, PHAs are relatively expensive compared to other commercial plastics with comparable

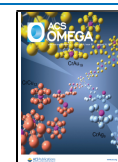
properties,⁷ and the costs increase with greater complexity in the PHA family. Furthermore, PHBV has a narrow processing window and inferior mechanical properties (i.e., highly brittle), making it unsuitable for various applications such as biomedical and flexible packaging.^{8–10}

Overcoming the brittleness properties by incorporating additives such as plasticizers, impact modifiers, chain extenders, and initiators results in reduced biodegradable performance.¹¹ Blending PHBV with other bio-based or biodegradable polymers including poly(butylene succinate) (PBS),¹² poly(lactic acid) (PLA),¹³ and poly(propylene carbonate) (PPC)¹⁴ has shown much potential to balance the various properties such as mechanical, thermal, rheological, and morphological behavior. However, PPC is exceptional among bio-based polymers for being produced by CO₂ fixing, reducing global warming in the process.¹⁵ Furthermore, PPC is

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entirely amorphous, has an elongation at break above 300%, and shows excellent barrier properties.^{16,17}

Several studies on PHBV/PPC blends have been completed showing improved ductility and reduced tensile moduli, resulting in optimized properties of both PHBV and PPC.^{18,19} Enriquez et al. studied the thermal, mechanical, and morphological properties and dimensional stability of PHBV/PPC blends using similar methods to this study and observed improved ductility (elongation at break ranging from 30–300%) at 30–70% PPC content and acceptable thermal stability with at least 30% PHBV.¹⁴ While the polymer blends were not determined to be miscible, incorporation of PPC into PHBV does hold significant potential for flexible packaging applications. The reactive blending of PHBV with PPC (30 wt %) was performed, and a certain extent of hydrogen bonding was observed between PHBV and PPC.¹⁸ It was noted that the crystallization behavior of PHBV was significantly hampered by the addition of PPC and altered the surface morphology of the PHBV/PPC blend, which also changed the mechanical properties of PHBV by 1–2 orders of magnitude. Peng et al. observed low miscibility of PPC into a PHBV matrix and also detected a slow growth rate of PHBV spherulites in the PHBV/PPC blend.¹⁵ However, Li et al. selected the PPC/PHBV (70/30 wt %) blend for their research and concluded that PPC and PHBV were connected together by a transesterification reaction during melt blending, as confirmed via FTIR analysis.²⁰ The crystallization and melting temperatures of the PPC/PHBV blend were reduced by ~8 and ~4 °C, respectively, due to the formation of imperfect crystals of PHBV. The miscibility and mechanical and crystallization properties of a poly(3-hydroxybutyrate) (PHB)/PPC blend were also studied by Yang and Hu.²¹ The solution casting technique was used to prepare various blends. They showed that PHB was completely miscible with PPC for blends, i.e., PHB/PPC (30/70), (20/80), and (10/90). However, the crystallization phenomenon was suppressed in the presence of a higher amount of PPC, as suggested by DSC and POM analysis. The elongation at break was improved significantly for PPC-rich samples. However, Young's modulus was reduced by increasing the PPC amount. The blends of PPC with other biodegradable plastics like PBS were also studied through reactive extrusion in the presence of a compatibilizing agent, i.e., PPC-grafted-maleic anhydride (PPC-g-MA).²² The results suggested that the chemical compatibilization between PBS and PPC was improved significantly by the addition of PPC-g-MA in the blend. The grafting reactions occurred at the interphase of PBS and PPC in the presence of PPC-g-MA, and the development of new grafted copolymers took place as a result. The elongation at break and impact strength of PBS/PPC blends were improved by more than 100%, and up to 50%, respectively, by adding a compatibilizer.

The purpose of this study was to explore the variation in the thermal, mechanical, and morphological properties of PHBV/PPC blends by the addition of a natural filler. Distillers' dried grains with solubles (DDGS) is a low-cost filler derived from the corn ethanol industry and commonly sold as animal feed. DDGS was produced extensively with around 1,016,140 metric tons exported monthly from the US in 2020.²³ DDGS is a combination of cellulose, hemicellulose, and protein and is also referred to as post-fermentation corn biomass.²⁴ The composition of DDGS, i.e., protein and fat percentage, fluctuates drastically due to various factors during ethanol processing and depends on the fusion of soluble and insoluble

constituents.²⁵ This motivates scientists to consume DDGS as a green reinforcement in the production of polymer composites for numerous value-added applications such as packaging.²⁶ The cost benefits of DDGS are countered by the poor mechanical reinforcement and residual oils and sugars, which cause polymer discoloration and odor during processing. Zarrinbakhsh et al. studied the effects of DDGS in PHBV/PBAT blends, reporting improved thermal stability but no improvement in mechanical moduli and a reduction in tensile and flexural strength by 30 and 40%, respectively.²⁷ They also determined that water washing and the use of a compatibilizer such as polymeric methylene diphenyl diisocyanate (PMDI) can improve the interfacial adhesion, resulting in improved performance of the prepared biocomposites.²⁸ Tisserat et al. prepared high-density poly(ethylene) (HDPE)-based DDGS composites and found improved tensile moduli due to solvent treatment of DDGS to remove oils and polar extractables. Furthermore, the addition of maleated poly(ethylene) acted as a compatibilizing agent resulting in optimized tensile strength and modulus in HDPE/DDGS composites.²⁹ DDGS has also been employed in PHAs and 5% poly(lactic acid), respectively, showing improved physical degradation in soil over a period of 24 weeks.^{30,31} As per a literature survey, research on PHBV/PPC/DDGS composites has not been undertaken. However, based on the limitations of DDGS, it is not promising without some form of compatibilization using PMDI, maleated polymer, and peroxide.

Therefore, this study will investigate the effect of peroxide and DDGS on the properties of PHBV/PPC blends. Optimized PHBV/PPC blends are already reported in the literature. However, with the addition of a cross-linking agent, it is expected that the mechanical properties will be further enhanced. DDGS can also be used to reinforce the moduli, resulting in a suitable composite with a lower production cost and useful mechanical properties.

RESULTS AND DISCUSSION

Influence of DDGS on Thermal Transition States. DSC thermograms (Figure 1a,b) indicate the interaction and miscibility between PHBV and PPC polymers. PHBV and PPC are known to be semicrystalline and amorphous polymers, respectively.^{15,32} The physical and thermomechanical properties are strongly dependent on the solid-state morphology and crystalline structure of used polymers.³³ DSC analysis of injection molded PHBV/PPC and its composites after incorporating DDGS in various loadings was performed to examine the thermal behavior with respect to ΔH_c , ΔH_m , and crystallinity (X_C), as illustrated in Table 1. The purpose of the first heating cycle was to remove the attached moisture to the samples.³⁴ Used PPC is entirely amorphous, and the PHBV fraction makes up the entirety of the crystalline fraction; however, the T_g of PHBV was not observed in the second heating cycle. The values of ΔH_c and ΔH_m and their associated temperatures for PHBV are found to be consistent with the reported literature values; PHBV is also reported to not be miscible with PPC but does increase the T_g of PPC from ~24 °C to ~32 °C,¹⁴ attributed to the antiplasticizing effect of PHBV in PPC that inhibits polymer chain mobility and reduces free volume.^{35,36} However, this was not observed in the PHBV/PPC (60/40) and (40/60) blends, and only the T_g of PPC was observed, which may be a characteristic of different processing methods. The T_g value of the PHBV/PPC (60/40) blend was observed to be lower (~29.8) compared to that of

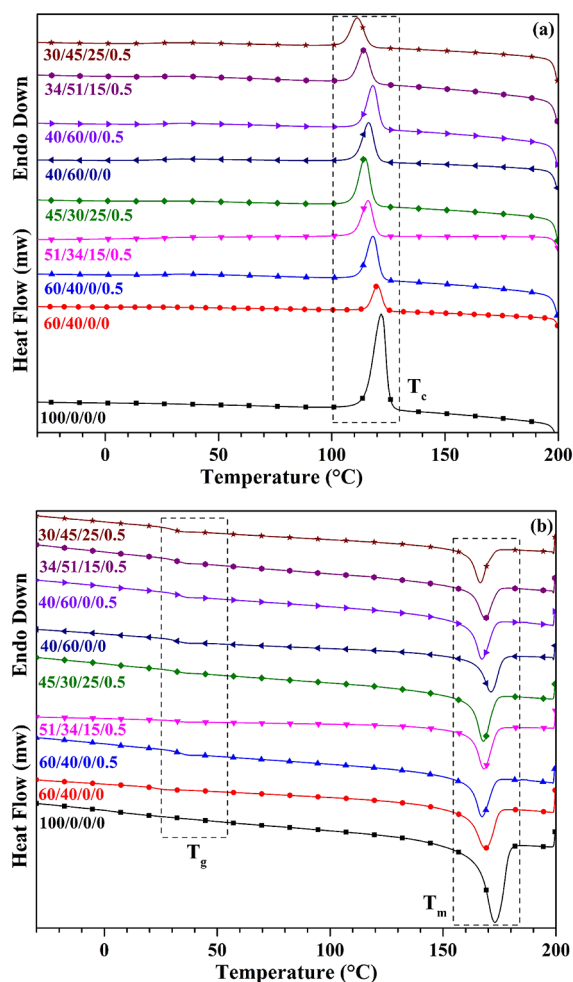


Figure 1. DSC thermograms of PHBV/PPC/DDGS-based composites from the (a) first cooling cycle and (b) second heating cycle.

the PHBV/PPC (40/60) blend, which is due to the higher amount of PPC present in the PHBV/PPC (40/60) blend. It is clearly observed from Figure 1b and Table 1 that the increase (from 23.6 to 33.2 °C) in T_g of the PHBV/PPC (60/40) blend has been observed by adding a very small amount (0.5 phr) of cross-linking agent, indicating significant interaction (linkage) between PHBV and PPC polymers. It is well published that the T_g value of PPC in the PHBV/PPC blend¹⁴ and PLA/PPC blend³⁷ increases due to chemical interaction and partial miscibility behavior. However, the effect of cross-linking was more prominent in PPC in the presence of peroxide.³⁸ Further, the T_g value was decreased from 33.2 to 32.8 and 32.9 °C after adding 15 and 25 wt % DDGS to the PHBV/PPC (60/40)

blend in the presence of the cross-linking agent, which signifies a slight reduction in the interaction between PHBV and PPC. The T_g value of PHBV/PPC (40/60) blend was observed to change from 33.6 to 33.1 and 32.8 and 31.7 °C after adding the cross-linking agent in composites with 15% and 25% DDGS, respectively. The reduction in T_g shows the plasticization effect of PHBV due to the higher amount of amorphous PPC in the blend and composites.

The addition of the cross-linking agent (0.5 phr) reduces the crystallinity of the PHBV/PPC blend by inhibiting chain mobility due to increased cross-linking and increased molecular weight.³⁹ This effect is also observed with PHBV and a chain extender⁴⁰ and PHBV composites with peroxide.⁴¹ The addition of DDGS has no significant impact on the thermal properties of the PHBV/PPC blends. In detail, a sharp crystallization peak was spotted for all types of samples prepared by injection molding, as shown in Figure 1a. This denotes the formation of uniform PHBV crystals. However, the crystallite size may vary based on the intensity and broadness of the observed crystallization peak. The melting temperature of PHBV was observed at 163.3 °C, which is slightly reduced (2.6 °C) after adding PPC that is due to the amorphous nature of PPC. The T_m value of the PHBV/PPC blend was slightly increased after the addition of the cross-linking agent as well as DDGS, as presented in Figure 1b, suggesting some minor influence of the cross-linking agent and DDGS on the melting properties of PHBV/PPC blends. The crystallinity of the PHBV/PPC blend is significantly reduced (~20%) by the addition of the cross-linking agent due to the increased cross-linking phenomena. Li et al. observed similar results for the PHBV/PPC blend after the addition of a glycidyl methacrylate (GMA) monomer and dicumyl peroxide (DCP).¹⁸ However, the crystallinity of the PHBV/PPC/cross-linking agent was further increased by 13.3 and 14.9% after adding 15 and 25% DDGS, respectively. Jiang et al. also observed an increase in crystallinity in poly(propylene carbonate)/poly(3-hydroxybutyrate) (PPC/PHB)-based bionanocomposites after the addition of cellulose nanocrystals.¹⁷

Influence of DDGS on Thermal Degradation. The thermal degradation of PHBV/PPC-based composites were characterized by the differential thermogravimetric analysis (DTGA) and presented in Figure 2a,b. The thermal degradation to obtain the temperature at 10% mass loss and the peak degradation temperature are also summarized in Table 2. The onset of degradation for PHBV/PPC-based samples was found to begin after 200 °C (as shown in Figure 2a), indicating the thermal sensitivity of PHBV and PPC during processing, resulting in a narrow processing window to avoid thermal degradation. PPC addition into PHBV has been

Table 1. Thermal Properties of PHBV/PPC/DDGS-Based Composites from the Second Heating Cycle

PHBV/PPC/DDGS/cross-linking agent	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	X_c (%)	T_g (°C)
100/0/0/0	128.7 ± 1.2	90.2 ± 6.2	163.3 ± 1.8	93.4 ± 0.2	85.7 ± 0.2	
60/40/0/0	121.9 ± 2.7	49.2 ± 1.3	160.7 ± 0.6	59.6 ± 2.9	85.5 ± 3.4	23.6 ± 0.2
60/40/0/0.5	121.8 ± 0.1	45.1 ± 2.5	161.7 ± 0.4	44.7 ± 1.8	68.3 ± 2.8	33.2 ± 1.6
51/34/15/0.5	119.9 ± 0.0	42.4 ± 0.3	162.4 ± 0.0	43.1 ± 0.1	77.4 ± 0.3	32.8 ± 0.2
45/30/25/0.5	118.4 ± 0.3	45.5 ± 13	162.3 ± 0.3	38.5 ± 1.6	78.5 ± 3.3	32.9 ± 0.1
40/60/0/0	120.7 ± 0.2	46.9 ± 0.8	162.2 ± 0.5	35.4 ± 0.6	81. ± 1.4	33.6 ± 1.3
40/60/0/0.5	121.7 ± 0.6	47.0 ± 3.7	161.6 ± 0.4	34.6 ± 2.0	79.3 ± 4.6	33.1 ± 0.9
34/51/15/0.5	118.1 ± 0.1	38.4 ± 1.8	162.4 ± 0.2	28.2 ± 0.4	76.1 ± 1.2	32.8 ± 0.0
30/45/25/0.5	116.9 ± 0.3	38.1 ± 0.2	161.4 ± 0.3	26.1 ± 0.4	79.7 ± 1.5	31.7 ± 1.5

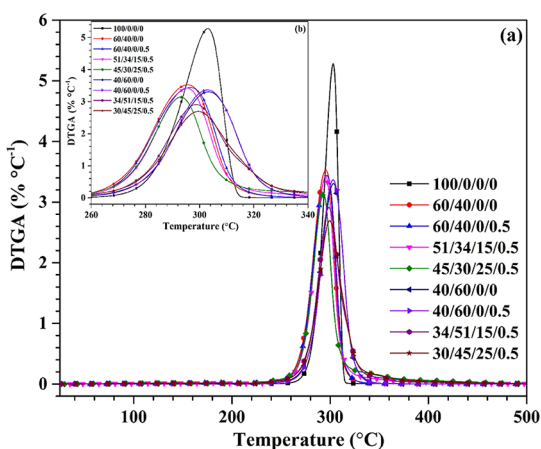


Figure 2. DTG thermograms (a) from 25 to 500 °C and (b) temperature range of 260 to 340 °C of PHBV/PPC/DDGS/crosslinker-based samples.

Table 2. TGA of PHBV/PPC/DDGS-Based Composites

PHBV/PPC/DDGS/crosslinking agent	temp. at 10% weight loss (°C)	peak degradation temperature (T_{max}) (°C)	weight loss (%) at T_{max}
100/0/0/0	287.3	303.0	97.4
60/40/0/0	276.1	295.7	96.9
60/40/0/0.5	276.3	296.6	96.9
51/34/15/0.5	277.0	295.3	95.6
45/30/25/0.5	275.2	293.1	92.7
40/60/0/0	283.8	302.8	96.5
40/60/0/0.5	283.7	302.8	97.1
34/51/15/0.5	280.2	298.8	94
30/45/25/0.5	280.0	299.5	92.8

reported to increase the thermal degradation onset and peak degradation temperature,¹⁴ and is observed in other partially miscible blends due to phase morphology and component interactions.⁴² In this study, higher processing conditions were utilized due to the composites, which would prematurely degrade the PHBV and PPC constituents. Figure 2a reveals a sharp single peak in all PHBV/PPC-based blends and composite samples. The single peak in all samples observed in the range of 260–335 °C has been attributed to the material degradation in one step. Maximum thermal stability is detected in the pristine PHBV film, which is reduced by increasing DDGS loading weight % in PHBV/PPC-based composites. This is ascribed to the increase in the acidic sites created during the thermal degradation of a higher amount of DDGS in PHBV/PPC-based composites, which forces the samples to degrade at reduced temperature. The onset degradation temperature (T_{on}) for PHBV/PPC-based blends and composites is detected to be very close to each other, at ~260 °C, which means the addition of DDGS negligibly impacts the onset thermal degradation properties. This effect may be due to water washing, which removes the water solubles and increases the thermal stability of DDGS by 50 °C, to ~240 °C.²⁴ Further, the offset degradation temperature (T_{off}) for pristine PHBV is detected at ~316 °C, which is dramatically improved up to ~326 °C after adding 40 wt % PPC in PHBV. This significant increment in T_{off} signifies the efficient heat dissipation at higher temperature due to the addition of amorphous PPC. A similar explanation has been provided by Zhao et al.,⁴¹ when PHBV was mixed with natural rubber in

the presence of organic peroxide and a trifunctional acrylic coagent. However, the addition of peroxide and various amounts of DDGS does not change/alter the T_{off} of the PHBV/PPC (60/40) blend. Hence, it can be concluded that the change in thermal degradation properties of PHBV due to DDGS and peroxide is negligible. The temperature at 10% weight loss and weight loss % at T_{max} for all the used formulations are listed in Table 2. It is observed that the temperature at 10% weight loss was lower for PHBV/PPC (60/40)-based samples than for PHBV/PPC (40/60)-based samples. The residual weight percentages are calculated to be 1.32, 1.32, 0.5, 2.48, and 5.42% for 100/0/0/0, 60/40/0/0, 60/40/0/0.5, 51/34/15/0.5 and 45/30/25/0.5, respectively. The calculated residual weight percentages for 40/60/0/0, 40/60/0/0.5, 34/51/15/0.5, and 30/45/25/0.5 are calculated to be 1.66, 0.97, 3.44, and 3.95%, respectively. The formation of carbonaceous char from the addition of DDGS in PHBV/PPC composites may account for the increased residual weight.

Influence of DDGS on Heat Deflection Temperature.

The HDT helps determine the upper thermal limits of the injection molded samples up to which a polymer/polymer composite can be used as a rigid material.²⁷ It measures the temperature at which the polymer undergoes a 0.25 mm deviation under a constant load (0.455 MPa). Figure 3 reveals

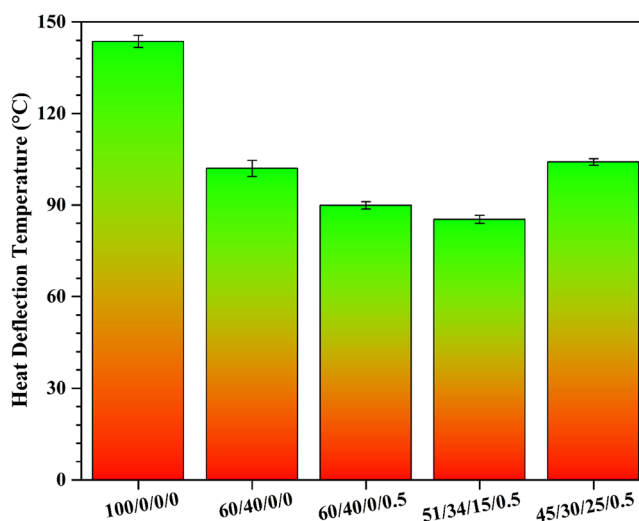


Figure 3. HDT analysis for PHBV/PPC/DDGS-based injection molded samples.

the observed HDT values for the compatibilized PHBV/PPC blend matrix and its composites with DDGS. The HDT values for pristine PHBV and the PHBV/PPC (60/40) blend were 143.62 ± 1.9 and 102.01 ± 2.64 °C, respectively. The reduction in the HDT value after the addition of PPC to PHBV is obvious due to the increment in the amorphous nature. It is worthy mentioning that the amorphous polymer shows an HDT value near its glass transition temperature, whereas the HDT value of a highly crystalline polymer lies at the vicinity of its melting point.⁴³ Thus, the HDT of the blend depends on both the crystallinity and glass transition temperature.⁴⁴ The HDT value of PHBV/PPC has been reduced by 11.87% by adding 0.5 phr peroxide due to the reduced crystallization temperature, as suggested by DSC analysis. The compatibilized PHBV/PPC (60/40) composite with 15 wt % DDGS showed an HDT value of $\sim 85.3 \pm 1.3$ °C. However, the addition of 25 wt % DDGS into compatibilized

PHBV/PPC (60/40) has improved the HDT value significantly up to 104.11 ± 1.1 °C, which is due to the increased degree of crystallinity as shown in Table 1. The increment in the HDT value after the addition of DDGS was also observed by other researchers.²⁷

Influence of DDGS on Mechanical Behavior. The tensile modulus and strength of PHBV/PPC blends and composites are illustrated in Figure 4a. Due to the highly crystalline nature of PHBV, it has a high tensile modulus (3.5 GPa), and with adding amorphous PPC, the tensile and flexural modulus of the PHBV/PPC blend are reduced by 29.8 and 22.8%, respectively, as the elongation at break improves by 1753.1% (Figure 4c). Enriquez et al.¹⁴ reported a similar tensile strength value at break of PHBV with 50–70% PPC. However, the PHBV/PPC (60/40) and (40/60) blends vary slightly by 8 MPa in this study, which can be attributed to distribution of PPC, which does not make up the dominant phase when around 50%, and can have an impact whether the sample shows fracturing or deformation behavior upon break. Both flexural strength and flexural modulus follow a similar pattern (as shown in Figure 4b) to modulus and tensile strength.

The addition of a cross-linking agent (0.5 phr) into PHBV/PPC (60/40) and PHBV/PPC (40/60) blends slightly reduced the tensile strength from 41.1 to 30.5 and 27.8 MPa, respectively, due to the presence of amorphous PPC in the formulations, which reduces the overall crystallinity. In the literature, tensile strength has been reported to improve after mixing in a free-radical initiator, i.e., dicumyl peroxide, with the PHBV/PBS blend due to the in situ compatibilization.¹² The cross-linking agent most importantly increased the % elongation at break of PHBV/PPC (60/40) and PHBV/PPC (40/60) blends by 389.5 and 10.35%, respectively. This clearly signifies that the cross-linking agent works well with PHBV compared to PPC and also suggests that the elongation improvement is already saturated by 60% PPC.

The incorporation of DDGS into PHBV-based blends has not proven to be effective in increasing the tensile modulus and strength,²⁷ which is due to DDGS' poor modulus and tensile strength of 2.41–5.24 and 0.3–0.5 MPa, respectively.⁴⁵ However, the addition of 25 wt % DDGS in PHBV/PPC (60/40) and PHBV/PPC (40/60) blends with peroxide improved the tensile modulus up to 40.7 and 1.5%, respectively (Figure 4a). During processing, peroxides decompose and react with the hydrogen groups commonly found in cellulose and hemicellulose.⁴⁶ The improved interaction of the fiber and matrix benefited the tensile modulus of PHBV/PPC (60/40) blend ratios while minimally impacting that of the 40/60 blends. However, the tensile strength of PHBV/PPC-based blends was reduced significantly after the addition of 25 wt % DDGS, which is due to the formation of a weak interphase between PHBV/PPC and DDGS. The % elongation of all composites reduced with the addition of DDGS; however, this can be related to the poor mechanical properties of DDGS and their non-homogeneous composition/dispersion, which can be seen in SEM pictures. The notched Izod impact strengths of PHBV/PPC (60/40) and PHBV/PPC (40/60) blends were observed to be 12.4 and 14.9 J/m, respectively, which were further improved up to 13.2 and 16.8 J/m, respectively, after incorporation of the cross-linking agent. The addition of 15 and 25 wt % DDGS to the PHBV/PPC (60/40) blend with peroxide improved the impact slightly from 12.5 to 16.1 and 14.3 J/m, respectively. However, this effect is less pronounced

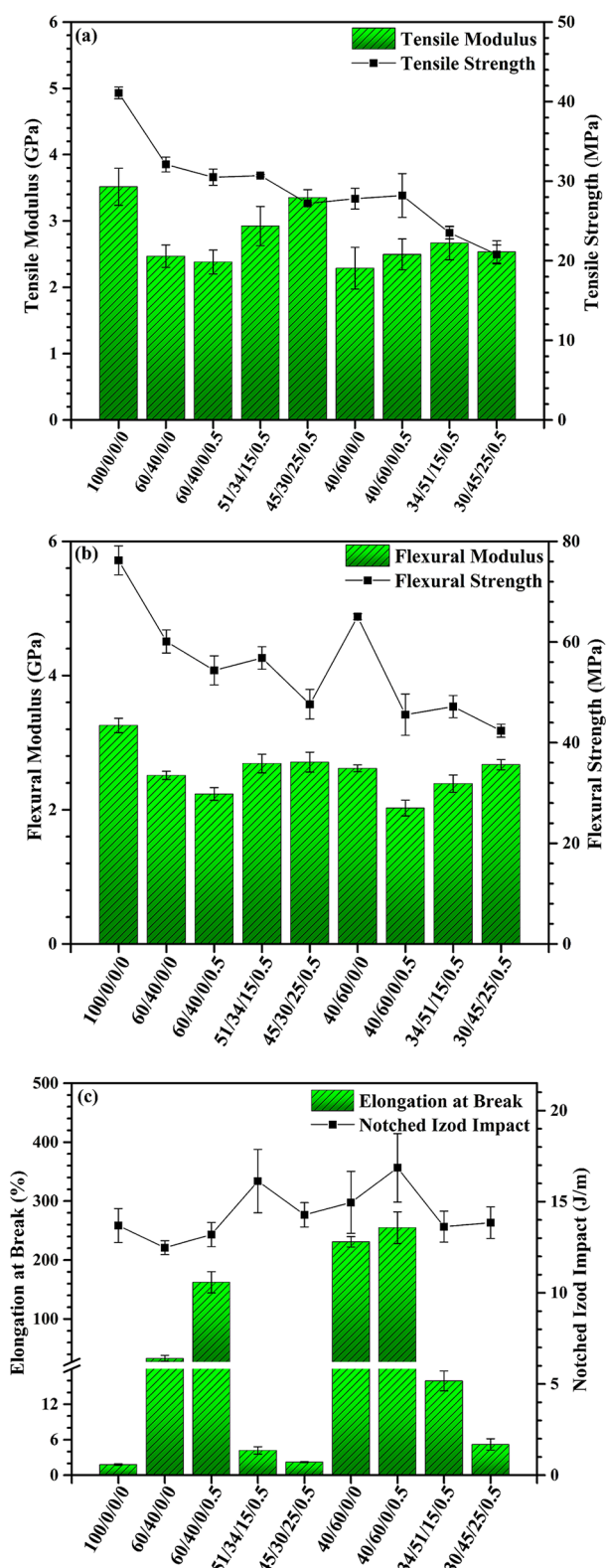


Figure 4. Mechanical analysis of PHBV/PPC/DDGS-based composite samples: (a) tensile modulus and tensile strength, (b) flexural modulus and flexural strength, and (c) % elongation at break and Izod impact strength.

in (40/60) blends with peroxide, and the impacts only increased to 13.6 and 13.8 J/m, respectively. Hence, the PHBV/PPC/DDGS/cross-linking agent (51/34/15/0.5) blend showed the best overall properties in terms of cost

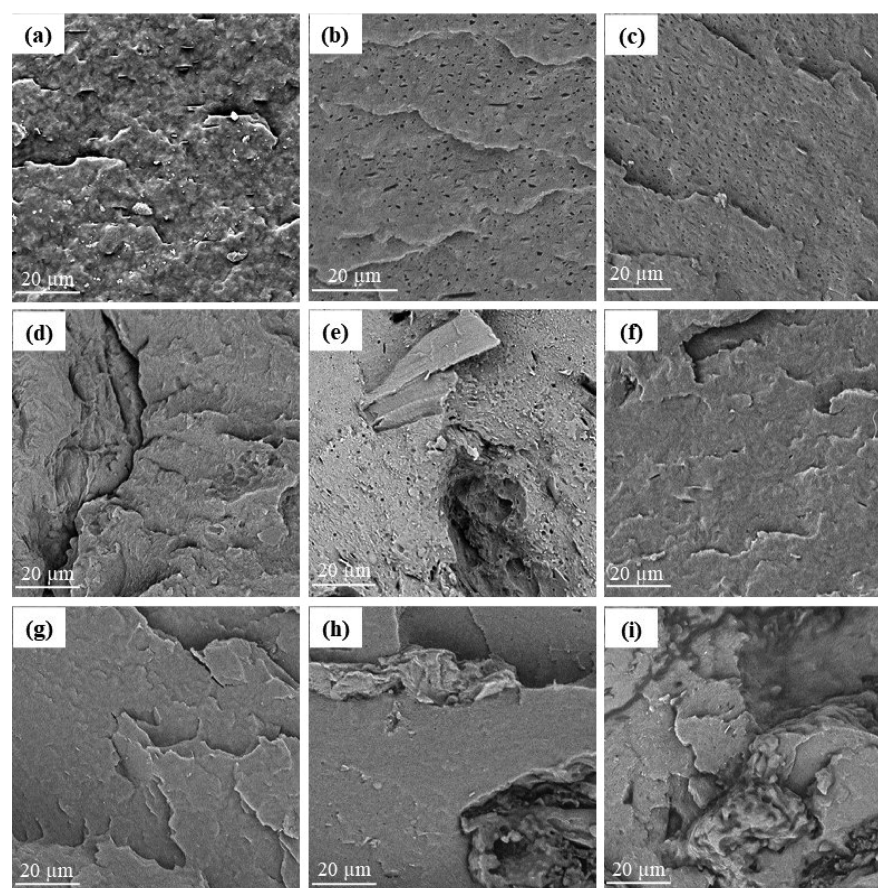


Figure 5. SEM morphology of PHBV/PPC/DDGS/cross-linking agent-based composite samples at surface of impact break: (a) 100/0/0/0, (b) 60/40/0/0, (c) 60/40/0/0.5, (d) 51/34/15/0.5, (e) 45/30/25/0.5, (f) 40/60/0/0, (g) 40/60/0/0.5, (h) 34/51/15/0.5, and (i) 30/45/25/0.5.

performance; however, lower DDGS content composites may have higher flexibility and elongation.

Influence of DDGS on Surface Morphology. SEM morphology of the impact-fractured surface illustrates the interactions between PHBV, PPC, and DDGS in the presence of peroxide, as shown in Figure 5a–i. Pristine PHBV has a homogeneous surface with some imperfections due to impact fracture (Figure 5a). The fractured surface of PHBV becomes porous after the addition of PPC due to the two-phase system. Similar open polymeric networks in other PHA/PPC blends were observed by Yang and Hu.²¹ The surface morphology of pristine PPC was observed as a featureless flat fracture surface by Haneef et al.⁴⁷ PHBV/PPC (60/40) and (40/60) blends with (Figure 5c,g, respectively) and without (Figure 5b,f, respectively) the cross-linking agent showed smoother surfaces compared to PHBV. No distinct phases of PHBV and PPC were observed in Figure 5b,c,f,g, which makes it hard to distinguish between individual components in the blend formulations. Similar results were also observed by other researchers.¹⁴ Li et al.¹⁸ also observed a single phase in the surface morphology of PHBV/PPC (70/30) and (30/70) blends, and it was stated that interfacial adhesion between PHBV and PPC took place. The PHBV/PPC (60/40) blends with and without 0.5 phr peroxide showed small pores where the dispersed PPC phase was pulled out during impact. This droplet-type structure is not observed in PHBV/PPC (40/60) blends with and without peroxide due to the high PPC content, and the samples look entirely homogeneous. With incorporation of 15 wt % DDGS into PHBV/PPC-based

blends, there is clear phase separation observed between DDGS and the PHBV/PPC blend matrix, as shown in Figure 5d,h. However, no pores are visible on the polymer surface that would be expected from PPC pullout. Furthermore, the phase separation between DDGS and the polymer matrix and the fragmentation of DDGS in 25 wt % DDGS composites indicate the poor reinforcement effect of DDGS, as shown in Figure 5e,i. Hence, the inclusion of DDGS results in reduced mechanical properties of PHBV/PPC-based composites.

CONCLUSIONS

Research work has been conducted utilizing a natural filler, i.e., DDGS, in a PHBV/PPC blend matrix to analyze the effect on various properties such as thermal, mechanical, and surface morphology. With this aim, PHBV and PPC have been injection-molded in various proportions in the presence/absence of peroxide and DDGS to prepare specimens and further all formulations have been characterized, to observe an interfacial adhesion among the matrix and matrix and the matrix and filler. The surface morphology clearly showed homogeneity between PHBV and PPC phases before and after the addition of peroxide. As a result of no phase separation, the % elongation at break of the PHBV/PPC (60/40) blend matrix was improved by ~1753% compared to that of pristine PHBV and was further increased by 8970.4% after adding peroxide. The % elongation at break of the PHBV/PPC (40/60) blend matrix was found to be higher (~569.4%) compared to that of the PHBV/PPC (60/40) blend matrix. Similarly, the PHBV/PPC (40/60) blend matrix with peroxide showed improved %

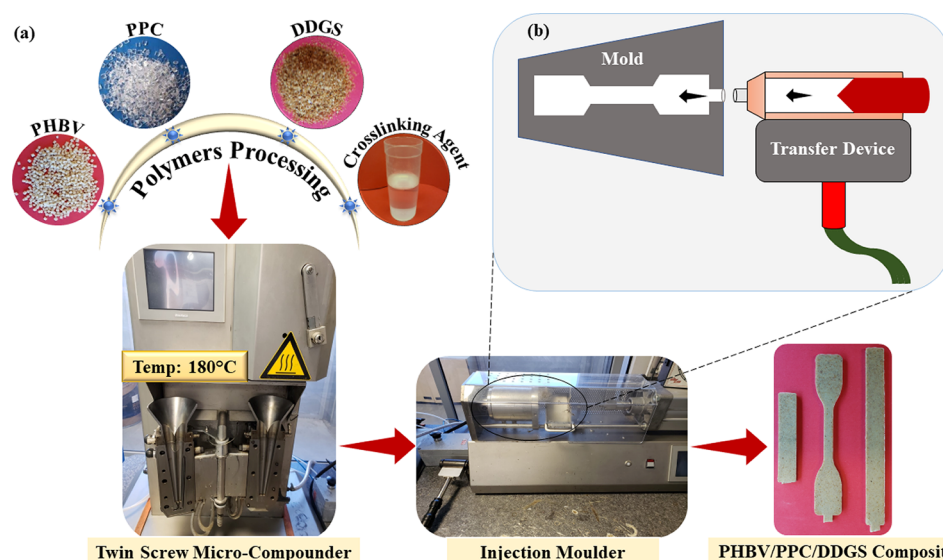


Figure 6. Schematic representation of (a) PHBV/PPC/DDGS-based composites fabrication and (b) injection molding process.

elongation by $\sim 57\%$ compared to the PHBV/PPC (60/40) blend matrix with peroxide. The crystallinity of PHBV/PPC-based blends was slightly reduced after the incorporation of DDGS compared to that of pristine PHBV, which was due to the increased amorphous phase and relative movement of polymer chains. The significantly increased glass transition temperature of PHBV/PPC-based blends indicated the homogeneous distribution of PPC into PHBV, which was slightly reduced after the addition of DDGS. Hence, the overall compositions of the polymer composites deliver a sustainable option with possible applications in the commercial market.

MATERIALS AND METHODS

Materials. PHBV pellets (ENMAT Y1000P; 1–5% hydroxyvalerate content) and PPC (QPAC 40), with a molecular weight of 186,000 were procured from Tianan Biological Materials Co. Ltd. China, and Empower Materials, United States, respectively, and were used as the blend matrix. DDGS was purchased from IGPC Ethanol Inc. DDGS was water washed with a ratio of 1:15 for DDGS to water, for a duration of 15 min.²⁴ Luperox 101 (2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane) was procured from Sigma-Aldrich (technical grade, 90%; half-life ($t_{1/2}$) = 0.6 h at 145 °C) was utilized as a cross-linking agent.

Blend/Composite Processing. Prior to processing, the cross-linking agent (0.5 phr) was dispersed in acetone, and the solution was distributed over PHBV and was left to adhere for 5 min, after which PPC and the filler were mixed at the required ratios. For all blends and composites, a ratio of PHBV to PPC of 60:40 and 40:60 was utilized, with 0, 15, and 25 wt % DDGS loadings. Composites were processed using a twin-screw compounding machine (DSM Xplore, microcompounder, Netherlands with L/D ratio of 150:18) at 180 °C for a 2 min retention time. The fill, pack, and hold pressures were fixed at 14, 16, and 16 MPa with a 6 s hold time in the injection molder. The schematic representation of the preparation of PHBV/PPC/DDGS-based composites is shown in Figure 6, and the blend compositions are outlined in Table 3.

Influence of DDGS on Thermal Transition States. The enthalpy measurements of PHBV/PPC/DDGS-based compo-

Table 3. PHBV/PPC/DDGS/Cross-linking Agent-Based Formulation Nomenclature

formulation	PHBV (wt %)	PPC (wt %)	DDGS (wt %)	crosslinking agent (phr)
100/0/0/0	100	0	0	0
60/40/0/0	60	40	0	0
60/40/0/0.5	60	40	0	0.5
51/34/15/0.5	51	34	15	0.5
45/30/25/0.5	45	30	25	0.5
40/60/0/0	60	40	0	0
40/60/0/0.5	60	40	0	0.5
34/51/15/0.5	34	51	15	0.5
30/45/25/0.5	30	45	25	0.5

sites were examined using a differential scanning calorimeter (DSC) (Q200, TA instruments, Delaware). Approximately 10 mg of samples was used in DSC analysis, with a heating cycle from -40 to 200 °C at a rate of 10 °C/min followed by cooling down to -40 °C at 10 °C/min under isothermal conditions for 3 min. The melting temperature (T_m) and enthalpy of melting (ΔH_m) were acquired during second heating. The peak crystallization temperature (T_c) and enthalpy of crystallization (ΔH_c) were collected from the first cooling cycle. The crystallinity (X_C) of the PHBV/PPC/DDGS-based composites was calculated using eq 1.⁴⁸

$$X_C = \left(\frac{\Delta H_m}{\Delta H_m^0 \times w_f} \right) \times 100\% \quad (1)$$

where ΔH_m^0 is the enthalpy of fully crystalline (100%) PHBV (109 J/g)⁴⁹ and w_f signifies the weight fraction of PHBV.⁴⁸

Influence of DDGS on Thermal Degradation. TGA (Q500, TA instruments) of PHBV/PPC/DDGS-based composites were completed with 15–20 mg of samples at a scanning rate of 10 °C/min under a nitrogen-enriched atmosphere until 700 °C.

Influence of DDGS on Heat Deflection Temperature. Heat deflection temperature (HDT) of injection molded samples was examined using a dynamic mechanical analyzer (TA Q800, USA) with a three-point bending attachment and worked from 30 to 250 °C at 2 °C/min under 0.455 MPa load.

The deflection of 250 μm as mentioned in the ASTM D 648 standard was monitored. Each sample was repeated three times, and the values are presented in terms of average \pm standard deviation.

Influence of DDGS on Mechanical Behavior. As per ASTM D618, tensile, flexural, and notched Izod impact specimens were kept at 50% relative humidity and room temperature for 48 h. Tensile and flexural properties were characterized with an Instron 3382 (Massachusetts, USA). The tensile test was conducted at 5 mm/min, as per ASTM D638. Flexural analysis was done as per ASTM D790. Notched Izod impact analysis was done using a Zwick Roell HIT25P (Ulm, Germany) following ASTM D256.

Influence of DDGS on Surface Morphology. SEM of fractured impact samples was completed with a Phenom ProX desktop (Eindhoven, Netherlands). A thin gold coating using a Cressington sputter coater (Watford, England) was placed over samples, and the sample was analyzed at 10 kV accelerating voltage.

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Notes

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