High Strength, High Toughness Polyhydroxybutyrate-Co-Valerate Based Biocomposites

S. Z. A. Zaidi, A. Crosky

Abstract—Biocomposites is a field that has gained much scientific attention due to the current substantial consumption of non-renewable resources and the environmentally harmful disposal methods required for traditional polymer composites. Research on natural fiber reinforced polyhydroxyalkanoates (PHAs) has gained considerable momentum over the past decade. There is little work on PHAs reinforced with unidirectional (UD) natural fibers and little work on using epoxidized natural rubber (ENR) as a toughening agent for PHA-based biocomposites. In this work, we prepared polyhydroxybutyrate-co-valerate (PHBV) biocomposites reinforced with UD 30 wt.% flax fibers and evaluated the use of ENR with 50% epoxidation (ENR50) as a toughening agent for PHBV biocomposites. Quasi-unidirectional flax/PHBV composites were prepared by hand layup, powder impregnation followed by compression molding. Toughening agents – polybutylene adiphate-co-terephthalate (PBAT) and ENR50 – were cryogenically ground into powder and mechanically mixed with main matrix PHBV to maintain the powder impregnation process. The tensile, flexural and impact properties of the biocomposites were measured and morphology of the composites examined using optical microscopy (OM) and scanning electron microscopy (SEM). The UD biocomposites showed exceptionally high mechanical properties as compared to the results obtained previously where only short fibers have been used. The improved tensile and flexural properties were attributed to the continuous nature of the fiber reinforcement and the increased proportion of fibers in the loading direction. The improved impact properties were attributed to a larger surface area for fiber-matrix debonding and for subsequent sliding and fiber pull-out mechanisms to act on, allowing more energy to be absorbed. Coating cryogenically ground ENR50 particles with PHBV powder successfully inhibits the self-healing nature of ENR-50, preventing particles from coalescing and overcoming problems in mechanical mixing, compounding and molding. Cryogenic grinding, followed by powder impregnation and subsequent compression molding is an effective route to the production of high-mechanical-property biocomposites based on renewable resources for high-obsolescence applications such as plastic casings for consumer electronics.

Keywords—Natural fibers, natural rubber, polyhydroxyalkanoates, unidirectional.

I. INTRODUCTION

THE realization of the impacts of disposed plastics on the environment has come a long way. Disposal of synthetic polymer matrix composites is difficult due to different disposal requirements of different components [1]. There is an improper assignment of durable materials such as synthetic polymers and their composites to applications which have a short-term life [2]. As oil prices continue to be volatile, dependence on petroleum for polymers is increasingly becoming an issue [3]. To tackle these issues, the field of renewable resource based polymers and composites, known as "green composites", was born [1].

Poly(hydroxybutyrate) (PHB) is the most extensively studied member of a family of bacterial polyesters known as PHA. These polymers are produced by many microorganisms as a carbon and energy store [4] and the properties of PHB are comparable to those of isotactic polypropylene (iPP) [5]. PHB has a few limitations regarding processability and brittleness which can be overcome by copolymerizing with hydroxyvalerate (HV) to form PHBV.

Most research on PHBV/natural-fibre composites has used short fibres or random mats as reinforcing agents [6], [7]. UD natural fiber fabrics have only started emerging recently [8]. Subsequently, little work has examined biopolymer/UD natural fibre composites. However, findings have shown that tensile strengths of up to 240 MPa are attainable, in the case of UD flax/PLA composite [8], which exceed those of 3003-H14 aluminium and AM100A casting magnesium [9].

Impact toughness is a major challenge for PHBV biocomposites due to the inherent brittleness of PHBV, which is further embrittled after reinforcement. Much research has been conducted to improve this by blending PHBV with other biopolymers [6], [10]-[12]. Poly(butylene adipate-co-terephthelate) (PBAT) is a flexible biodegradable polymer often used to toughen PHBV, but it is petroleum based which does not strictly make it green [6]. Natural rubber can be a suitable alternative to PBAT that offers renewability, toughness and biodegradability. Parulekar and Mohanty [13] showed that blending PHB with ENR with 50% epoxidation (ENR50) improves impact toughness from 23-124 J/m in the presence of a maleated rubber compatibilizer.

In this work, composites of PHBV and UD flax were prepared. PBAT and ENR50 were used as toughening agents and the effects of UD flax, PBAT and ENR50 on tensile, flexure and impact properties of the composites were examined.

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II. Experimental

A. Materials

PHBV (trade name Y1000) was obtained from Tianan Biologic Material Co. This commercial grade of PHBV has 3 mol.% HV in its composition [4] and has a melt flow index of 2.5 g/10 min at 170 °C [3]. PBAT (Ecoflex C1200 F) was obtained from BASF. ENR50 was obtained from Industrial Organics, Australia. Quasi-unidirectional flax (trade name FlaxPly) was obtained from LINEO, Belgium.

B. Cryogenic Grinding of PBAT and ENR50

PBAT pellets and pieces of ENR50 about 5 mm cubed were cryogenically ground separately using a Spex Freezer Mill at 10 Hz for 3 cycles with 2 min cooldown time and 2 min time per cycle. For ENR50, 0.1 g PHBV powder was added into the grinding vial per 1 g ENR50 to allow the ground rubber powder to be coated with PHBV whilst still at cryogenic temperature.

The ground toughening agents (TA) were manually mixed with the matrix PHBV powder by shaking in a box in a 70:30 PHBV:TA ratio by weight.

C. Compression Moulding

UD composite plaques measuring 200 x 200 mm were prepared by laying up alternating layers of the mixed powder with layers of UD flax oriented in the axial (0 °) direction. Four and eight layers were used to produce 1.5 mm and 3 mm thick plaques respectively. The layup was hot pressed at 180 °C and 1 MPa for 12 min. The volume fraction of the UD flax in all composites was 30 vol%.

Three types of plaque were prepared: PHBV/UD flax (A), PHBV/PBAT/UD flax (B) and PHBV/ENR50/UD flax (C).

D. Tensile Testing

Tensile testing of the composites was performed according to ASTM D3039 using an Instron 5982 electromechanical universal testing machine. Parallel sided specimens measuring 182 x 15 mm were tested at a crosshead displacement rate of 5 mm/min. Samples were conditioned prior to testing according to ASTM D618. A mechanical extensometer with a gauge length of 50 mm was used to measure the strain up to 0.6% strain for modulus calculation. Samples were tabbed with 3 layers of emery paper to obtain fracture within the gauge length. The tensile modulus was determined as the chord modulus using the procedure given in ASTM D3039. A minimum of 5 specimens were tested for each of the three materials.

E. Flexural Testing

Flexural testing was carried out using the three-point bending method conducted in accordance with ASTM D790 using an Instron 5565 Universal Testing Machine, with specimen dimensions 50 x 12.7 x 1.5 mm and a span length of 25 mm, giving a span-to-depth ratio of 16:1. Specimens were conditioned according to ASTM D618 before testing. The tangent modulus method was used to obtain the flexural modulus of the samples. A minimum of 5 specimens were tested for each of the three materials.

F. Impact Testing

Charpy notched-impact testing was conducted according to ASTM D6110 using a Toyoseiki Charpy impact tester with 1.96 J energy capacity, using specimens having dimensions of 124 x 12.7 x 3 mm. Samples were conditioned according to ASTM D618 prior to testing. A minimum of 5 specimens were tested for each sample.

G. SEM

The fracture surfaces of failed tensile specimens were examined using a Hitachi S3400 SEM operated at 10 kV. The samples were sputter-coated with gold before being examined.

III. Results and Discussion

A. Coating Cryoground ENR50 with PHBV Powder

In initial cryogrinding trials of ENR50, it was found that the ground particles adhered to one another as they warmed to room temperature and, over time, the particles began coalescing into a solid mass. This self-healing phenomenon of natural rubber has been reported previously by [14] which attributed it to inter-diffusion of the polymer chains across the interface of adjoining particles, essentially "sewing" the rubber back together. This problem was overcome by adding 0.1 g PHBV powder per g of ENR50. This resulted in the cryoground ENR50 particles being coated with sufficient PHBV powder to prevent them from sticking back together as they warmed to room temperature.

B. Tensile Properties

The tensile strength and modulus of the PHBV/30% UD flax composite made without any toughening agent (A) were 189.56 MPa and 17.46 GPa, as given in Fig. 1, respectively. Neat PHBV (N) (grade Y1000, containing 3% HV) used in our work has been reported to have tensile strength 31.7 ± 0.3 MPa and modulus 1.68 ± 0.036 GPa respectively [4]. From these results, it can be seen that the addition of UD flax fibres improved the tensile strength of PHBV by 500% and the tensile modulus by 940% (Fig. 1).
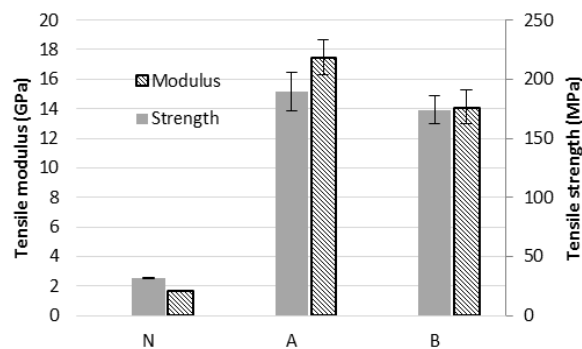

Fig. 1 Tensile strengths and moduli of neat PHBV (N), PHBV/UD flax samples with no toughening agent (A), and with the addition of 30% PBAT to the PHBV matrix (B): Error bars represent one standard deviation

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The addition of 30% PBAT to the PHBV matrix resulted in a 19% decrease in tensile modulus of the flax composite, Fig. 1. There were no statistically significant changes in the tensile strength. The reduction in modulus is attributed to the lower modulus of the elastomeric PBAT phase which allows the PBAT/PHBV to strain more at the same load than the neat PHBV, resulting in a lower modulus in the composite. The absence of any change in the strength is attributed to these properties being dominated by the fibres. The strain to failure was mostly unaffected by UD fibre addition and by subsequent addition of PBAT. The fibres carry most of the load and had a lower strain to failure than the matrix, regardless of whether it was toughened or not. Once the fibres failed, the load could no longer be carried by the matrix alone and failure of the composite occurred.

C. Flexural Properties

The flexural strength and modulus of the 30% UD flax composites made with PHBV without any toughening agent (A) were 209.76 MPa and 14.16 GPa, respectively, Fig. 2. Neat PHBV with 2% HV (1% less HV than used in present study) has been reported to have a flexural strength and modulus of 28.2 ± 1.1 MPa and 1.28 ± 0.12 GPa, respectively [16]. Based on the data, and neglecting the difference in the HV content of the PBAT, the addition of the UD flax can be seen to have improved the flexural strength by 640% and the flexural modulus 10-fold.
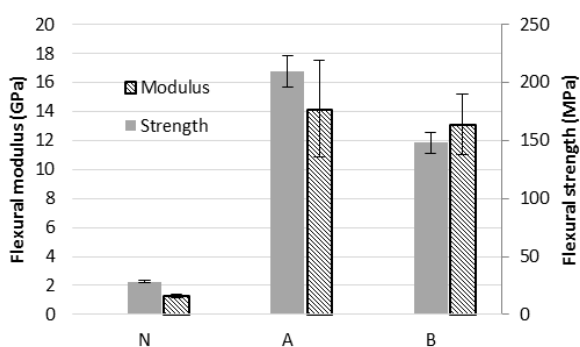

Fig. 2 Flexural strengths and moduli of neat PHBV (N), PHBV/UD flax samples with no toughening agent (A), and with the addition of 30% PBAT to the PHBV matrix (B). Error bars represent one standard deviation

The addition of PBAT reduced the flexural strength by 30% but had no significant effect on the flexural modulus. The reduction in flexural strength is consistent with findings of Yu and Li [15] who reported a 26% reduction with the addition of PBAT for PLA/ramie composites. They attributed the reduction in flexural strength to the presence of the more ductile PBAT phase affecting properties as per the rule of mixtures.

D. Impact Properties

Fig. 3 shows the impact resistance of the samples. The notched charpy impact resistance of PHBV/UD flax oriented at 90° and 0° was 2.86 and 42.92 kJ/m², respectively. The notched charpy impact resistance of PHBV/UD flax 0°/PBAT

was 33.66 kJ/m². The notched charpy impact resistance of neat PHBV (2-3 mol% HV) was 1.06 kJ/m² which is consistent with the values of 0.8 and 0.85 kJ/m² obtained by [16] and [17], respectively. The addition of the UD flax fibres improved the impact resistance by 170% when the fibres were in the 90° orientation (i.e., parallel to the notch direction), while the improvement was nearly 40-fold when the fibres were in the 0° orientation (i.e., perpendicular to the notch direction). The 0° value of 42 kJ/m² compares favourably with reported values of 41.3 kJ/m² for polycarbonate/ABS blend [18] and 32 kJ/m² for neat ABS [19].
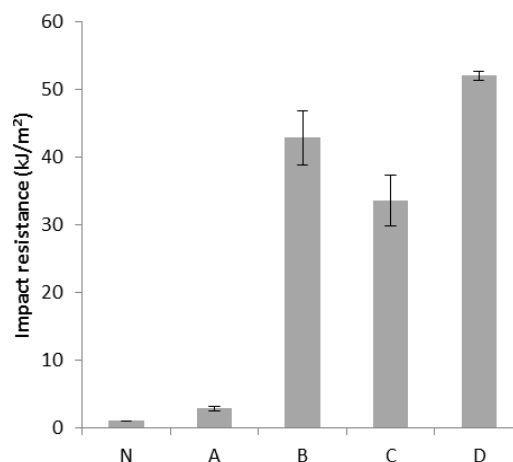

Fig. 3 Impact resistance of neat PHBV (N), PHBV/UD flax oriented at 90° (A), PHBV/UD flax oriented at 0° (B), PHBV/UD flax 0°/PBAT (C), and PHBV/UD flax 0°/ENR50 (D). Error bars represent one standard deviation

The improvement of impact strength with the addition of fibres and the effect of fibre orientation are well documented [20]. In the 90° orientation, there are no fibres in the direction of maximum stress, while in the 0° orientation, all fibres are in the direction of maximum stress. Accordingly, for the 90° orientation, debonding between the fibre and matrix is the predominant mechanism acting to absorb the impact energy, while in for the 0° orientation, fibre pullout and fibre breakage mechanisms are also acting in addition to debonding (Fig. 4), resulting in substantially greater energy absorption. This was confirmed by SEM, with a gap between fibre and matrix allowing debonding and cavities where fibre bundles were formerly embedded.

PBAT addition likely reduced impact toughness due to better interfacial bonding at the PBAT/flax interface, reducing fibre pull-out. In contrast, ENR50 addition was observed to improve impact toughness of the PHBV/0° flax sample, and samples containing both flax and ENR50 had the highest impact toughness of all samples studied.

E. Morphology

The PBAT phase appears as a circular phase ~20 μm across in the matrix region of the composite (Fig. 5), showing heavy plastic deformation, stretching and cavities left behind by debonded particles, likely contributing to impact property improvements.

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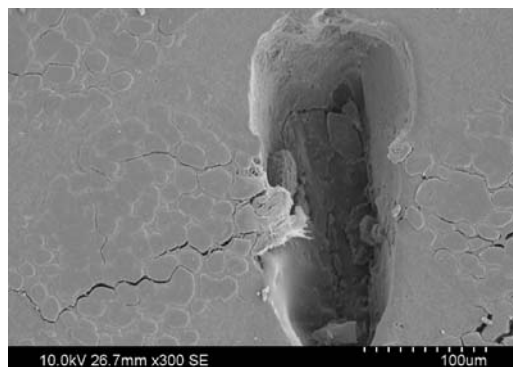Fig. 4 Tensile fracture surface showing fibre bundle pull-out observed under SEM

Fig. 7 Tensile fracture surface showing cavity left behind by ENR50 particle within PHBV matrix observed under SEM
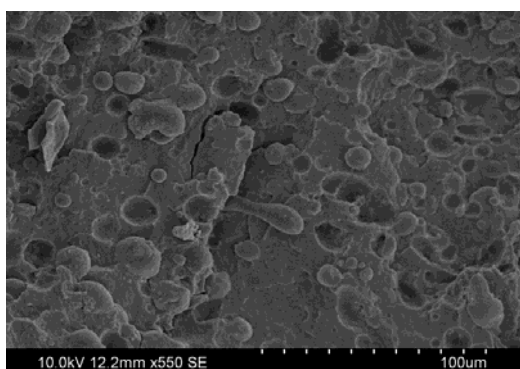
IV. CONCLUSION

PHBV/UD flax, PHBV/UD/PBAT and PHBV/UD/ENR50 composite samples were produced and characterized by SEM, tensile, flexure and impact testing techniques. Dramatic increases in mechanical properties of PHBV were observed due to incorporation of UD flax fibres. Further addition of PBAT reduced the property enhancements slightly, while PHBV/UD flax/ENR50 resulted in impact properties of PHBV beyond those of composites not containing any toughening agent, attributed to many more energy absorption mechanisms acting than composites containing no toughening agent. Further work will elucidate a clearer picture of the effects of ENR50 on the PHBV/UD flax system.

Fig. 5 Tensile fracture surface showing circular PBAT phase within PHBV matrix observed under SEM

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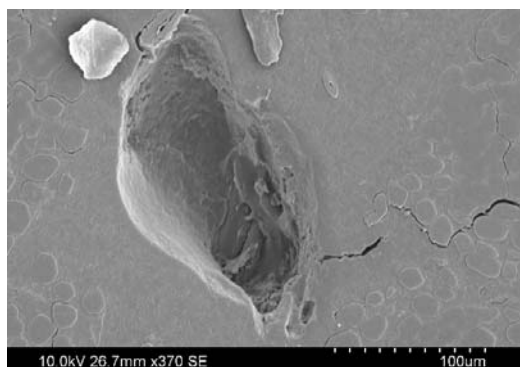
Fig. 6 Tensile fracture surface showing ENR50 particle within PHBV matrix observed under SEM

ENR50 particles are ~100 µm across and appear as regions with heavy plastic deformation within the composite (Fig. 6). The impact toughness improvement in Fig. 3 caused by ENR50 addition can be attributed to ENR50 particle debonding and pull-out mechanisms also acting in addition to flax fibre debonding and pull-out, contributing to energy absorption, as evidenced by cavities found within fractured samples where former ENR50 particles likely resided (Fig. 7).

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