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TENSILE PROPERTIES AND MORPHOLOGY OF PLA/KENAF FIBER COMPOSITES TOUGHENED WITH ETHYLENE ACRYLIC COPOYMER

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ABSTRACT

Composites from poly(lactic acid) (PLA) and kenaf bast fiber (KF) were prepared using an internal mixer and compression molding. The weight percent of the fiber was fixed at 40 wt %. The biodegradable composites were prepared with different amounts (0 to 40 wt %) of a commercially available ethylene acrylate copolymer impact modifier (IM). The tensile properties of the composites were examined in relation to their morphology. With increasing IM content, the PLA/KF composites showed some improvements in the elongation at break indicating the toughening effects of the impact modifier. In contrast, the tensile strength and tensile modulus decreased with the increase in the IM content. Scanning electron microscopy (SEM) examination on the composite fractured surfaces revealed the formation of a ductile material (flexible interface) partially around the embedded fiber. In addition, matrix drawing or shear yielding was also observed. Formation of the flexible interface and improved deformability of the PLA matrix may have contributed to the positive improvement in the elongation at break impact but negative improvements in the tensile strength and modulus of the composites. Other toughening mechanisms observed via SEM were fiber debonding and fiber pull-out.

Key words: Poly(lactic) acid, kenaf bast fiber, impact modifier, mechanical properties, morphology.

INTRODUCTION

PLA currently is the most widely used biodegradable polymer in many industrial applications. This is due to its good mechanical properties, processabilities and biocompatibility. At 2.2 US$/kg PLA [1] is seen as an expensive polymer as compared to traditional major petroleum based plastics. One of the way to reduce the cost while simultaneously extend the range of PLA properties, is to blend PLA with natural fibers. Generally, the addition of natural fibers has been found to increase strength and stiffness of the composites [2, 3]. The impact strength, however, was drastically reduced and the composites were found to be more brittle than the pure PLA [4]. This is because PLA itself is a brittle material as its glass transition temperature (55 to 65^{o}C) is well above the room temperature. PLA/natural fiber composites therefore are not suitable for some potential applications that require high impact performance and good low-temperature impact such as automotive components. A conventional approach to improve impact performance of a composite is to incorporate an impact modifier within the matrix as part of the formulation prior to compounding. This approach aims to improve the toughness of the polymer matrix. There are many commercially available impact modifiers for PLA. Some examples include impact modifiers like Biostrength™ 130 and Biostrength™ 150 from Arkema, Paraloid™ BPM-500 from Rohm and Haas and Biomax® Strong 100 from DuPont [5].

In this work biodegradable composites of PLA and kenaf bast fiber (KF) were manufactured using an internal mixer and compression molding. KF loading was fixed at 40 wt.% The effects of adding a commercially available impact modifier ethylene acrylate copolymer impact modifier, Biomax® Strong 100 from DuPont at different amounts (based on the total weight of PLA and the impact modifier) on the mechanical properties of the composites were investigated. Morphological examination of the composite fractured surfaces was carried out via a scanning electron microscopy to explore relationships between the phase microstructure and tensile properties of the composites.

MATERIALS AND METHODS

The materials used in this study were PLA, KF and an impact modifier (IM). Semi-crystalline PLA Grade 2002 D (4% D-lactide, 96% l-lactide content, molecular weight 121, 400 g/mol, MFR 6.4

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g/10 min) was purchased from Natureworks™ in pellet form. Its glass transition temperature is about 63°C and melting temperature 160°C. KF was supplied as short fiber bundles by Forest Research Institute of Malaysia (FRIM). Average length and diameter of the fibers were approximately 1.53 ± 1.17 mm and 70.91 ± 19.73 µm, respectively. IM, which is ethylene acrylate copolymer, was obtained from DuPont with the grade name of Biomax® Strong 100. It is a rubbery material with a glass transition temperature and melting temperature of -55 and 72°C, respectively. Its elongation at break is 950%.

Prior to blending, PLA, KF and IM were dried in a vacuum oven at 80°C for 4 h. PLA and IM at varying weight ratios were first melted in a Haake Rheomix Polydrive R 600/610 internal mixer (Haake Technik GmbH, Vreden, Germany) equipped with two counter-rotating blades and then mixed with KF (40 wt.%). The amounts of IM were 0, 10, 20, 30 and 40 wt.% based on the total weight of PLA and IM. Melt-mixing was performed at 190°C for 15 min at a rotor speed of 50 rpm. Compositions of the composites prepared are given in Table 1. Plates of 1 mm thickness were prepared by melt pressing chips of the composites on a Kao Tieh GoTech compression molding machine at 190°C. Test samples for tensile (narrow section: 50 mm x 6 mm x 3 mm) were cut from these plates by using a dumbbell cutter.

Table 1. Compositions of the studied materials.

Materials	Matrix (wt %)		KF (wt %)	Impact modifier[a] (wt %)
	PLA	PP		
PLA	100	-	-	-
PLA/KF	60	-	40	-
PLA/10IM/KF	54	-	40	10
PLA/20IM/KF	48	-	40	20
PLA/30IM/KF	42	-	40	30
PLA/40IM/KF	36	-	40	40

[a] The amount was based on the total weight of PLA and IM.

Tensile tests were performed at room temperature on an Instron 3366 testing machine (Instron Corp., Norwood, MA) according to ASTM D 638. The capacity of the load cell was 10 kN while the crosshead speed was set at 5 mm/min. At least five samples were tested for each reported value.

The morphology of the tensile fractured surfaces of the composites was examined by a Ziess Supra 35VP scanning electron microscope (Carl Zeiss, Oberkochen, Germany) at an acceleration voltage of 10 and 15 kV. The composite fractured surfaces were mounted on aluminum stubs using double sided tape and then sputter coated with gold for 1 min at 1.4 V using an Polaron SEM coating unit E5150 (Polaron Equipment Ltd, East Sussex, UK) to minimize electron charging effects during examination.

RESULTS AND DISCUSSION

Tensile Properties

Tensile properties of PLA and all the composites including PP/KF composites are shown in Table 2. Addition of KF reduced the tensile strength of PLA by 47% from 47 to 25 MPa. This was observed despite of relatively good adhesion between KF and PLA as observed from the SEM micrograph (see hereafter). Both the tensile strength and modulus of PLA/KF composites decreased with the addition of IM. Linear variations between both properties with impact modifier content with high coefficient of determination (R-squared) values of 0.985 and 0.977 (Figs. 1(A, B)) were observed respectively for the tensile strength and the tensile modulus of PLA/IM/KF composites. With the addition of 40 wt% IM the tensile strength and modulus of the composite decreased by 68 and 70 %, respectively. The decrease in the tensile break and tensile modulus was expected and can be attributed to the rubbery behaviour of the impact modifier and its low mechanical properties [6] and reduced crystallinity of the PLA matrix [7]. PLA/IM/KF composites with 10 and 20 wt% IM showed comparable elongation at break with that of PLA/KF composite. Significant increase in the property by 34 and 96% was observed when the amounts of IM in the composites were 30 and 40 wt%, respectively (Table 1). A linear variation between the elongation at break with impact modifier content with very high R-squared value of 0.999 (Fig. 1(C)) was observed suggesting that the elongation at break is a function of impact modifier content when the IM content is beyond 20 wt %. The changes in the tensile properties were linearly related to the amount of IM suggesting softening effect of the PLA matrix in the presence of IM. The similar patterns of changes in the tensile properties of impact modified composites were reported by other researchers for different matrices and fillers [6].

Table 2. Mechanical properties of PLA/KF composites[a].

Materials	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)	Notched impact strength (kJ/m^2)
PLA	46.92±1.48	2.12±0.13	3.18±0.19	7.83±1.07
PLA/KF	25.39 ±5.16	3.61±0.47	0.84±0.17	6.27±0.69
PLA/10IM/KF	21.83±2.22 (-14.02%)	3.34±0.12 (-7.48%)	0.85±0.03 (+1.19%)	6.78±0.10 (+8.13)
PLA/20IM/KF	16.15±2.16 (-36.39%)	2.43±0.33 (-32.67%)	0.88±0.08 (+4.76%)	7.47±0.95 (+19.14%)
PLA/30IM/KF	13.90±2.07 (-45.25%)	1.95±0.26 (-45.98%)	1.29±0.32 (+53.57%)	8.38±1.18 (+33.65)
PLA/40IM/KF	8.03±0.53 (-68.37%)	1.09±0.11 (-69.81%)	1.65±0.19 (+96.43%)	11.03±0.83 (+75.92%)

[a] Numbers in parentheses are percent change of the property as compared to PLA/KF composite.

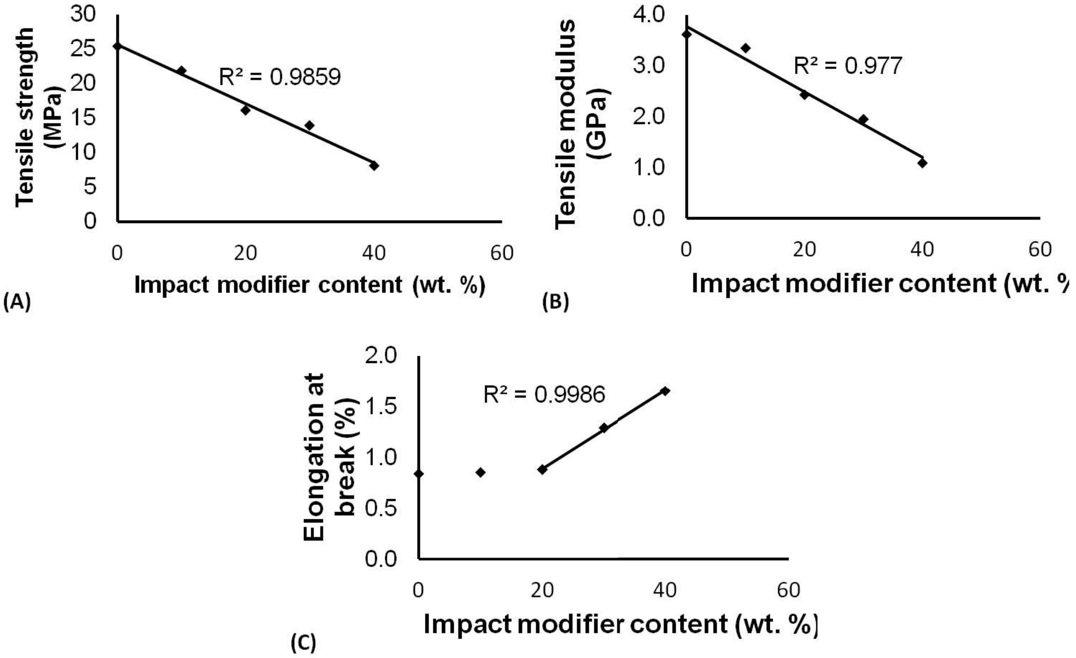

Fig. 1. **(A) Tensile strength, (B) Tensile modulus and (C) Elongation at break of PLA/KF and PLA/IM/KF composites.**

Scanning Electron Microscope

Fig. 2 shows the SEM micrographs of the tensile fractured surfaces of PLA/KBF composites with different amounts of IM. Short pulled-out of fibers with barely noticeable gaps around the fibers and fiber breakage (indicated by the arrows) were observed in the SEM micrograph of the composite without IM (Fig. 2(A)) suggesting some degree of interaction between PLA and KF and that in some places the interface was stronger than KF. The interaction between KF and PLA can be attributed to the formation of hydrogen bonds between the hydroxyl groups of KF and the terminal hydroxyl [4, 8] or carboxylic groups [9] as well as the carbonyl groups of the ester groups of PLA. In spite of these observations, the tensile strength of PLA/KF composite is lower than the unfilled PLA (Table 2) and this is probably due to low average fiber aspect ratio (lower than the critical fiber aspect ratio) in the composite. The initial aspect ratio of the fibers was about 21. The fibers might have undergone fiber length degradation during compounding. This may reduce the fiber aspect ratio resulting in poor reinforcing effect of the fibers. Stark and Rowlands [10] compared the effect of softwood flour particles and hardwood fibers on strength properties of WPC made with polypropylene in a mold-injection process. They concluded that it is not the particle length that affects strength properties, but rather the *L*/*D* (aspect ratio) value. Strength and rigidity of the composites were found to increase with increasing *L*/*D* ratio. Individual separation and dispersion of KF in the form of single fibers (as circled) were also observed (Fig. 2(A)). Some of the fibers might have undergone fiber opening process or fibrillation during the compounding.

Microstructure showing KF embedded in the PLA matrix was observed in the micrographs of fractured surfaces of the composites with IM (Figs. 2(B – E)). With increasing IM content, KF was found to be partially coated with relatively increasing amount of plastically deformed material. IM has epoxy functional groups that can react with the hydroxyl groups of KF. Both PLA and IM then can interact with KF during compounding. Following SEM observations of Figs. 2 (A-E), it is suggested that IM has greater affinity for the hydroxyl groups of KF than PLA. A number of ‘strings’ linking the KF surface to IM suggesting good adhesion between the two can be seen (as circled) in Fig. 2(E). During compounding some of IM domains from the surrounding resin might have migrated towards KF, pulling together the PLA macromolecules closer. This is possible as the epoxy functional groups of IM can also interact with the functional groups (hydroxyl and carboxyl groups at the chain ends) of PLA [11, 12]. This leads to the formation an interface which is a hybrid mixture of PLA and IM or toughened PLA phase partially around the fiber surface. The addition of IM therefore can be suggested to modify the interface in the boundary regions between PLA and KF. Sui and co-workers [13] also reported a similar morphology in short glass fiber-reinforced nylon 6, 6 composites (with rubbery inclusions) as indicated by back-scattered electron imaging (BEI) images obtained under SEM. They observed a mixture of rubbery and nylon concentrating around the fiber diameter. This interface is probably too soft to facilitate efficient stress transfer (4) from the PLA matrix to the fiber and to restrain the segmental mobility of the PLA molecules in the vicinity of the fiber. This reduces the reinforcing efficiency of the fiber, KF, in the composites. With increasing IM content, more of IM domains might have migrated to the fiber surface and the interface then might have become increasingly softer and more flexible. In addition to low mechanical properties of the impact modifier and reduced crystallinity of the PLA matrix, this may explain the increasingly decrease in the tensile strength as well as modulus of PLA/IM/KF composites with the increase in the IM content (Fig. 1(B)). Based on the tensile strength results, the interface formed was probably weak and as results some fibers were debonded and also pulled-out from the matrix (Figs. 2 (A-E)). Ductile tearing of the flexible interface during the tensile loading is clearly observed in Fig. 2(E).

Brittle fracture surface with less pronounced plastic deformation was observed on the fractured surface of PLA/KF composite (Fig. 2(A)). In contrast, a large amount of plastically deformed material was observed on the fractured surfaces of PLA/IM/KF composites (Figs. 2(B-E)). The presence of plastic deformation in the form of matrix drawing or shear yielding due to rubber cavitations of the impact modifier domains dispersed in the matrix phase is believed to be the main mechanism for the deformability of the composites. Plastic deformation of the PLA matrix was not effectively suppressed by the rigid PLA matrix due to the flexible interface formed between the fiber and the matrix. As a result, massive plastic yielding was introduced in the PLA matrix. Plastic deformation of the PLA matrix became more apparent when the impact modifier content in the composites was equal to or more than 20 wt %. It is, however, very difficult to see IM domains from the micrographs because of the low magnification (100 X) used during the SEM examination.

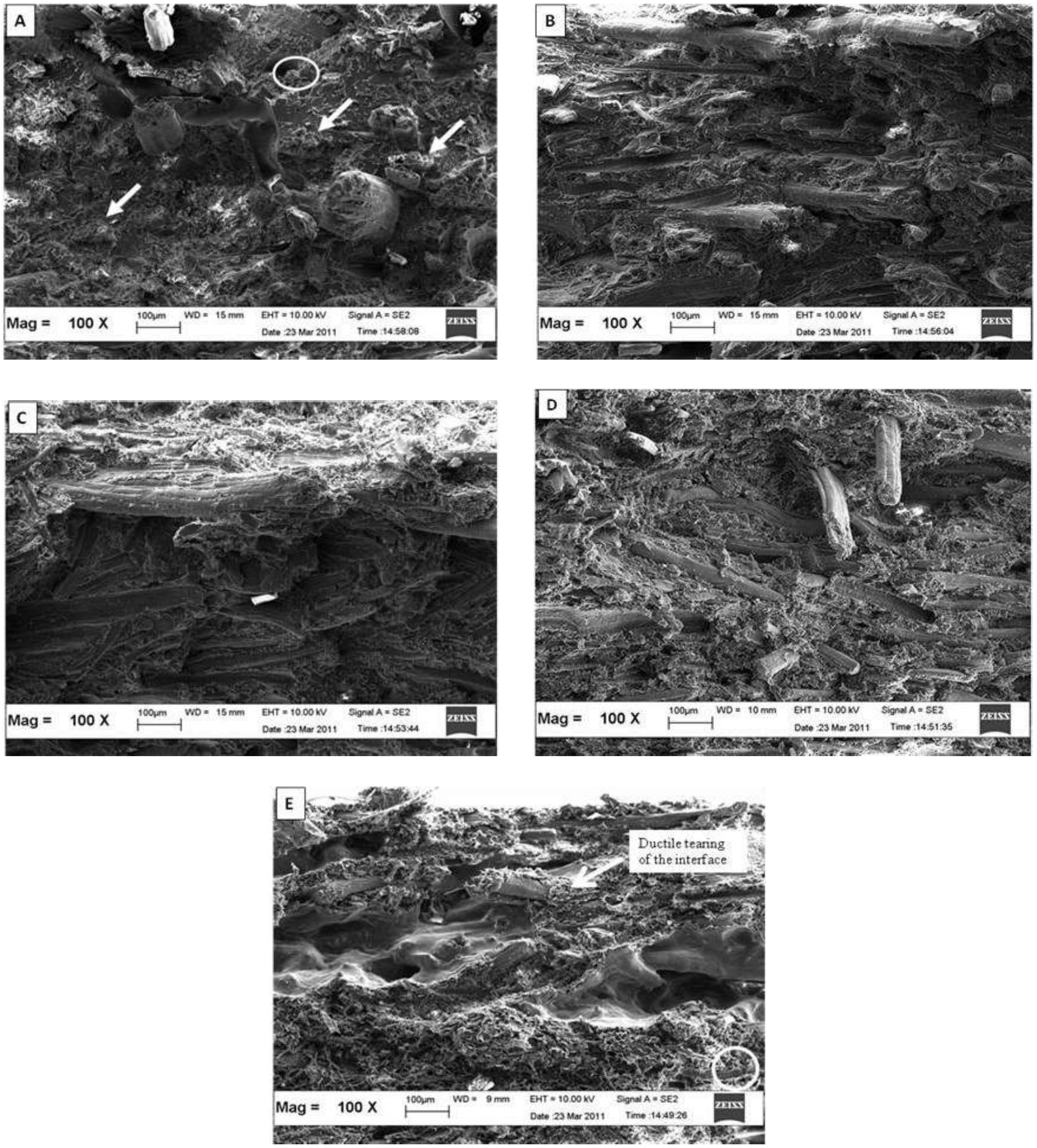

Fig. 2. **SEM micrographs showing fracture surfaces of A) PLA/KF, B) PLA/10IM/KF, C) PLA/20IM/KF, D) PLA/30IM/KF, and E) PLA/40IM/KF composites.**

CONCLUSIONS

Impact modifier had a negative effect on the tensile strength and modulus but a positive effect on the elongation at break of PLA/KF composites. Linear variations of these properties with IM content with high R-squared values were observed. Addition of IM modified the interface in the boundary regions between the PLA matrix and KF. Embedded fiber coated with a ductile matrix phase (flexible interface) was observed on the fractured surfaces of PLA/IM/KF composites as observed via SEM. The negative impact on the tensile strength and modulus was due to the softening of plastic the PLA matrix and the flexible interface formed due to the addition of IM in PLA/KF composites.

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