



Properties Enhancement of Biocomposite Based on Poly (Lactic Acid) and Banana Fiber

Muhamad Hilmi Basri^a, Zurina Mohamad^{a,*}, Azman Hassan^b, Ashish Kumar^a

^aDepartment of Bioprocess and Polymer Engineering, Faculty of Engineering, School of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310, Skudai, Johor, Malaysia.

^bCentre for Advanced Composite Materials, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia.
r-zurina@utm.my

A preliminary investigation was done in this study to determine the maximum loading of banana fiber (BF) in poly (lactic acid) (PLA) matrices. The weight percent of BF were varied from 0,10,20 wt% and were blended using a co-rotating twin screw extruder. The morphological and mechanical aspect of this particular biocomposite were studied. The tensile modulus showed a steady increment up to 20 wt% of BF but the tensile strength, elongation at break and impact strength were reduced with the addition of BF. The compatibilizer, Joncryl was added to the biocomposite, to remedy the deteriorated mechanical properties incurred by the PLA/BF biocomposite. Incorporation of Joncryl proved to improve the mechanical properties of the biocomposite. The compatibilized PLA/BF biocomposite, both at 10 and 20 wt% BF contents shown a drastic improvement of 19 % and 9 %, in term of its impact strength, compared to the uncompatibilized counterpart. The Scanning Electron Microscopy (SEM) micrograph obtained for uncompatibilized PLA/BF biocomposite showed some interfacial gap presence, specifically at the interfacial area while for the compatibilized biocomposite, the gap appeared to be smaller and lesser. The Fourier-transform infrared spectroscopy (FTIR) analysis revealed that there was an interaction between an epoxy group of Joncryl with the carboxyl group of PLA and hydroxyl group of BF. This was proved by the formation of a new peak at the wavelength of $1,747.4\text{ cm}^{-1}$ and $1,711.8\text{ cm}^{-1}$ that further justified the properties enhancement experienced by the compatibilized biocomposite.

1. Introduction

Awareness to reduce the global environmental impact has always been a pivotal factor in the development of newer materials. As the world's population continues to grow, so does the amount of solid waste that people produce, especially the plastic waste. The main problem with plastic waste was it took a very long time, even thousands of years to degrade. In light of potential catastrophe caused by this undegradable waste, there has been an interest on maximising the usage of biodegradable material. Poly (lactic acid) (PLA) was one of the biodegradable material. PLA is an aliphatic thermoplastic polyester obtained by either ring-opening polymerization of cyclic lactide dimer or by condensation of lactic acid (Jacobson et al.,1999). It is an auspicious polymer with inherent biodegradability character, offers good aesthetics and strength, easy processability and non-toxicity. Even though PLA has many desirable properties, it does have several impediments that restricted its usefulness in certain applications. The poor toughness, low heat deflection temperature and high cost, in particular, have limited the application of PLA in various industries (Zurina et al., 2018). To expand the applicability, many research studies have been conducted on modification of PLA by blending with other biodegradable polymers. Unfortunately, the fabrication method of blending with others biodegradable polymer will result in high cost. The more approvable method was to produce biocomposites based on biodegradable polymers, filled with natural fibers to reduce the cost as well as to enhance the mechanical properties without compromising the green composite image. However, the incompatibility of hydrophilic fiber with hydrophobic PLA will result in ineffective stress transfer between them, that leads to poor mechanical properties of the composites. Previous studies have shown various modification techniques such as solvent extraction and utilization of several compatibilizing agents that have been implemented by numerous researchers around the world (Rakesh et al., 2010). It was found out that these treatments can

improve the compatibility between the PLA matrix and BF, thus, enhance the mechanical properties of the biocomposite. According to Jandas et al. (2011), a 17% improvement in tensile strength of biocomposite was observed when BF was treated with 3-aminopropyltriethoxysilane (APS). Plackett et al. (2003) also came out with a similar pattern, whereby BF treated with silane-based coupling agent shown a significant, 20% more enhancement in term of tensile strength compared with untreated BF. Dupraz et al. (1996), in his earlier research, did mention regarding the mechanism and chemical reaction involved between the natural fiber and silane-based coupling agent that ultimately enhance the mechanical properties of the natural fibre itself. The silane-based compatibilizer has the ability to interact with both polylactic chain and natural fibre hydroxide group, providing a pivotal role in term of compatibility between PLA and BF. This enhancing effect does not limit to tensile strength alone but rather, influencing others mechanical properties as well, such as impact and the flexural strength. Usually, the impact and flexural strength do experience enhancement up to a certain level when the biocomposite was treated with a various type of compatibilizing agent. In a similar fashion, this research hopes to utilize the new type of additive named Joncryl that will act as a compatibilizer. Joncryl contains multifunction epoxy that can react with OH group from BF and COOH group from PLA. These reactions expected to improve the interfacial bonding between BF and PLA matrix. Joncryl consist of the tailored styrene-acrylic oligomer with epoxy and its physical characteristics were listed in Table 1. Joncryl was commonly used in as the chain extender in a recycling process of condensation plastics but for this research, Joncryl was used as a compatibilizer. This deviates from its original function that adheres short molecular chain together (form the same type of material), after being subjected through chain scissoring that typically occurs in the recycled plastic extruding process. It is interesting to see the effectiveness of Joncryl, whether it can provide the same kind of mechanical interlocking needed to combined different type of material together. This novel approach might offer a new vibrant in term material blending itself, offering a new possibility to create a smart biocomposite. A material that has superior properties but still retaining its biodegradability aspect.

Table 1: Physical characteristic of Joncryl® ADR

Parameter	Value
Specific gravity, 25 °C	1.08
Molecular weight, Mw	~6800 g/mol
Number average molecular weight, Mw	3000
Glass transition temperature, °C	54
Epoxy equivalent weight	285 g/mol

2. Materials

The polymer used in this study was poly (lactic acid) (PLA), Natureworks grade 3051D with average molecular mass, $M_n = 175,000$ g/mol, bought from NatureWorks® LLC (Minnetonka, MN, USA). Banana fiber (Musa sepeintum) used was bought from Siddhi Vinayak Enterprises, Jaipur, India, with a density of 1.35 g/cm³ and Joncryl ADR-4368-CS (powder) was bought from BASF Corporation (Kanagawa/Japan)

3. Methodology

3.1 Fabrication of PLA/Banana Fibre treated with Joncryl composite

The compositions of all samples are listed in Table 2. PLA/BF and PLA/BF with Joncryl was fabricated at a different weight percent (wt%) using co-rotating twin-screw extruder (5&15 Micro Compounder DSM Xplore Model 2005) with 50 rpm of the rotor speed, at 170 °C. Joncryl was used as additives to enhance the compatibility between PLA and BF.

Table 2: Formulation of PLA/BF and PLA/BF treated with Joncryl.

Formulation	PLA (wt%)	BF (wt%)	Joncryl(phr)
PLA	100	-	-
BF10	90	10	-
BF20	80	20	-
PLAJ	100	-	1
BF10J	90	10	1
BF20J	80	20	1

4. Characterization

The tensile test was performed using an Instron Universal Testing Machine Model 5582 and the test was carried out according to ASTM D638. The impact strength was tested at ambient condition according to ASTM D256 and the average energy value obtained before sample deformation opted as impact strength. Scanning Electron Microscopy (SEM) was used to observe the Morphological aspect of the composite was investigated using a scanning microscope (Leo Supra, 50 VP, Carl Zeiss, SMT Germany) under conventional secondary electron imaging condition at accelerating voltage of 15 kV. Fourier-transform infrared spectroscopy (FTIR) analysis of the composite was carried out using Thermo Nicolet 6700 FTIR spectrometer, Thermofisher, USA.

5. Result and discussion

5.1 Mechanical properties

The mechanical properties of both PLA/BF and compatibilized PLA/BF with Joncryl were tabulated in Table 3. The impact strength recorded for pristine PLA was 315.08 J/m. Incorporation of BF at various loading from 10 wt% to 20 wt% resulted in a consistent decrement of the impact strength. Impact strength recorded for BF10 was 148.64 J/m, showing a significant 53 % decrement compared with pristine PLA. With the increased of BF content to 20 wt%, the impact strength decreased further to 101.75 J/m, 68% decrement compared to the pristine PLA. The incompatibility between BF and PLA matrix does prevent an effective stress transfer between the matrix and fiber, thus, lowering the amount of force that can be absorbed by the composite before its deformed. Low amount of force absorbs before deformation can also be defined as low impact strength since the impact strength often describes as the capability of materials to withstand a sudden applied load, that expressed in terms of energy. The similar declining trend can be observed for the compatibilized PLA/BF. The impact strength suffered decrement from 355.34 J/m (PLAJ) to 178.30 J/m (BFJ10) and finally 140.14 J/m (BFJ20). The compatibilized PLA/BF with Joncryl show higher impact strength compared with the uncompatibilized composites. For BFJ10, the composite shows an improvement of 19 % while for BFJ20 the composite shows an increment of 9 %, compared to the uncompatibilized composite. This proved that the addition of Joncryl imparts a positive effect on impact strength of the PLA/BF composite.

Table 3: Impact Strength and Tensile properties of PLA/BF and PLA/BF treated with Joncryl.

Formulation	Impact Strength, J/m	Tensile modulus, MPa	Tensile Strength, J/m	Elongation at Break, %
PLA	315.08 ± 26.74	1117.56 ± 30.31	57.34 ± 1.71	6.70 ± 1.04
BF10	148.64 ± 18.47	1173.99 ± 24.92	53.06 ± 1.48	6.55 ± 0.39
BF20	101.75 ± 15.82	1342.21 ± 28.92	52.79 ± 1.35	6.54 ± 0.95
PLAJ	355.34 ± 52.91	1078.05 ± 22.58	56.67 ± 3.32	6.87 ± 0.45
BF10J	178.30 ± 24.47	1116.26 ± 18.33	50.25 ± 1.68	6.66 ± 0.72
BF20J	111.14 ± 10.27	1233.81 ± 25.07	38.86 ± 1.12	4.79 ± 0.77

The tensile modulus increased with the addition of banana fibers loading. In BF10 composite, the tensile modulus increased up to 1173.99 MPa, compared with 1117.56 MPa recorded for the pristine PLA. Increased in BF loading (20 wt%) gives an increment of 14.33%, making the tensile modulus to 1342.21 MPa. Tensile modulus usually correlated with material stiffness. The addition of fiber, typically, will amplify the material stiffness since the fiber will fill up all the free volume in the matrix, producing a densely pack and harder materials. A substantial increase trend in term of tensile modulus also recorded for both compatibilized composite at 10 wt% and 20 wt% BF loading, from 1116.26 MPa to 1233.81 MPa.

The 7.5 % and 8% decrement in tensile strength were recorded for both uncompatibilized biocomposites with 10wt% and 20% BF loading, in comparison with pristine PLA. The tensile strength recorded for BF10 was 53.01 MPa while 52.80 MPa for BF20. This behavior was primarily attributed due to the poor interfacial adhesion between the PLA matrix and banana fiber. The quality of a fiber-reinforced composite is highly dependable on the fiber–matrix interfacial bonding since a well-formed adhesive bond will promote a better stress transfer from matrix to the fiber. A good interfacial adhesion between the matrix and fiber can be considered as the most crucial factor in order to improve the mechanical strength of the composites. Addition of Joncryl was expected to improve the tensile strength, however, the result shown was rather contradicted. For BFJ10, the tensile strength still suffered a marginal decrement of 5% when compared with BF10. Further decrease in tensile strength also recorded for BFJ20. The tensile strength recorded was 38.86 MPa, a staggering decrement of 26.3 % compared with BF10. The declining pattern in term of tensile strength proved the mechanism of Joncryl. It doesn't really improve the compatibility between the polymer matrix and fiber like typical coupling agent does, instead, it reduces the brittleness and act as an impact modifier. At higher fiber content (20 % BF loading), fiber agglomeration takes place, resulting in poor stress transfer across the

interface. This ultimately leads to microcrack formation, which results in a staggering drop in tensile strength value. The elongation at break of virgin PLA was found to be 6.7 %, which decreased slightly to 2.9 % and 2.4 % with the incorporation of 10 % and 20 % of BF loading respectively. The compatibilized composite BFJ10 shows a slight improvement in term of the elongation at break (6.7 %) compared with uncompatibilized BF10 composite but suffered a marginal decrement for BFJ20 composite. This again proved that Joncryl does impart flexibility to the composite and reduce the brittleness nature of PLA matrix. However, the threshold limit for optimum loading must be taken into consideration, since it can trigger fiber agglomeration that lowered the mechanical properties of the composite, thus preventing the effectiveness of Joncryl.

5.2 Morphological analysis

The SEM micrograph of uncompatibilized PLA/BF and compatibilized PLA/BF composites is shown in Figure 1. All images were taken from the impact fractured surfaces. All of the micrographs reveal that there was an interfacial gap between the matrix and banana fibre on the impact fractured surface of PLA/BF composites. The interfacial gap present indicates the lack of proper interaction and poor adhesion between BF and PLA matrix.

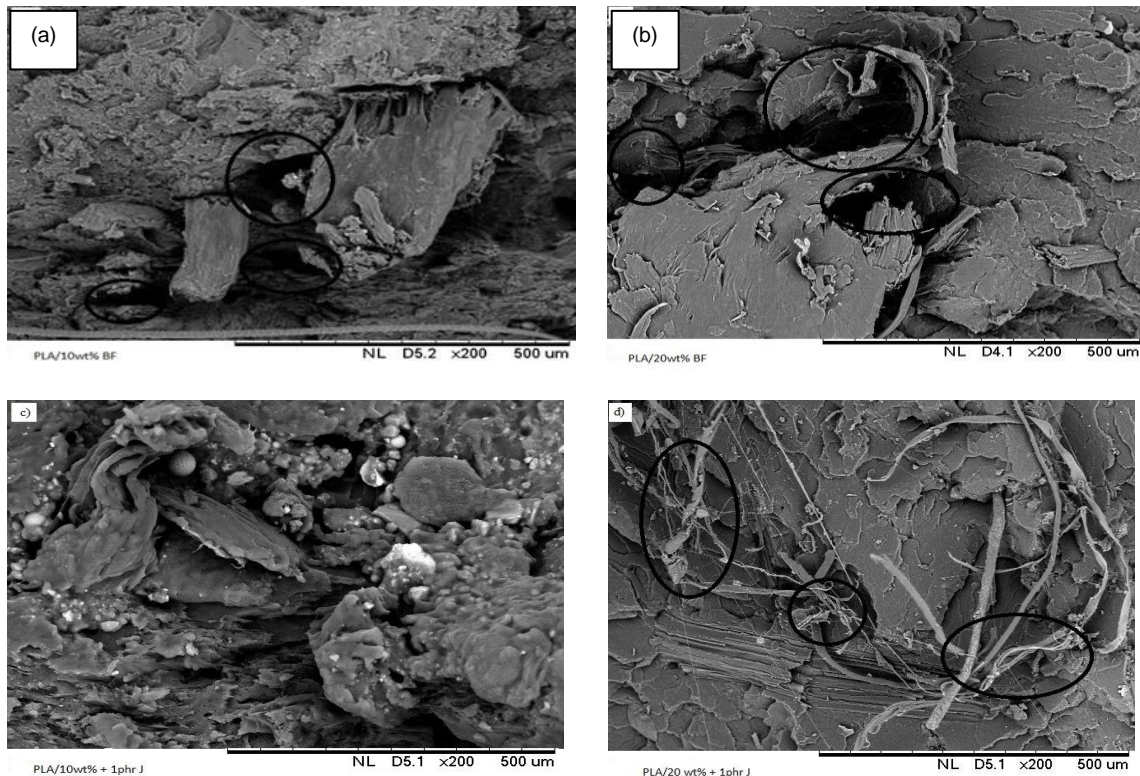


Figure 1: SEM micrograph of (a) PLA/10 wt% BF; (b) PLA/20 wt% BF; (c) PLA/10 wt% BF treated with 1 phr Joncryl; (d) PLA/20wt% BF treated with 1 phr Joncryl.

Closer examination of Figure 1a and 1b show that there is a big gap present, especially for the untreated biocomposite. The presence of the gap on the fracture surface is an indication of poor compatibility between PLA and BF could be the cause for the low impact and tensile strength value. On the other hand, for Figure 1c, BFJ10, the gap seems to be smaller and almost non-existent. The Joncryl seem to infiltrate the gap between the matrix and fiber, thus decreasing the fiber pullout on that area. This action seems to improve the wettability between PLA and BF matrix. The incorporation of Joncryl, seems to govern a better stress transfer between the matrix and fibre, thus enhanced the impact strength of the biocomposite due to its elastomeric nature. However, for Figure 1d, BFJ20, although the gap present is in a smaller size, similar to Figure 1c, the fiber seems to be agglomerate with each other. An agglomeration of fiber will lower the surface contact between fibre and matrix, resulting in a less effective interfacial bondage that dented the effective stress transfer between them, thus lowered the mechanical strength of the composite. This validates the results of the impact strength in mechanical properties where 10% BF loading display a higher impact strength compared to 20% BF loading when compatibilized with Joncryl.

5.3 Fourier-transform infrared spectroscopy (FTIR) analysis

The presence of a new chemical reaction formed at the interfacial area was examined using Fourier-transform infrared spectroscopy (FTIR) machine. The result was displayed in Figure 2. The absorption peak at $3,700\text{ cm}^{-1}$ denotes the stretching of free hydroxyl (O-H) group in banana fiber (BF) while the peak around $1,000\text{ cm}^{-1}$ shows O-H bending vibration of the fiber. For both uncompatibilized PLA/BF biocomposites, Figure 2a and 2b showed the absorption band at $2,851.7\text{ cm}^{-1}$, representing the stretch vibration of C-H bond inside the polymer matrix. The $1,454.1\text{ cm}^{-1}$ peak parallels to the CH_3 bending vibration of an alkyl group of PLAs whereas both peak at $1,127.3\text{ cm}^{-1}$ and $1,040.3\text{ cm}^{-1}$ represent C-O stretching vibration and O-H bending vibration related to the PLA matrix respectively.

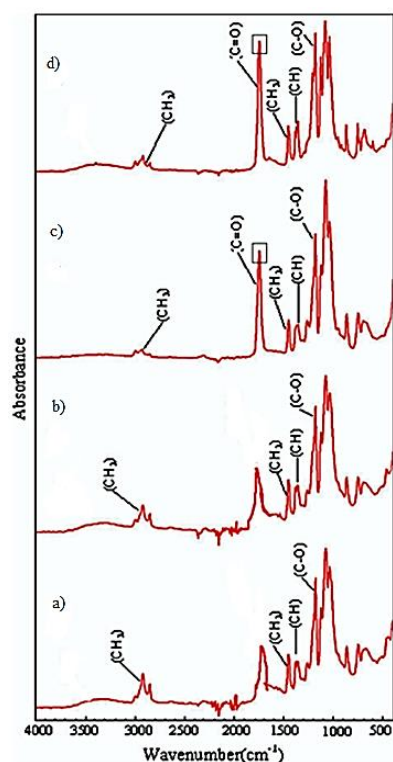


Figure 2: FTIR results for both compatibilized PLA/BF composite, (a) PLA/10wt% loading BF (b) PLA/20wt% (c) PLA/10wt% treated Joncryl (d) PLA/20wt% treated Joncryl

In the case of both compatibilized PLA/BF composite denoted by Figure 2c and Figure 2d a new peak at $1,747.1\text{ cm}^{-1}$ and $1,711.8\text{ cm}^{-1}$ were observed. These two peaks could very well represent the interaction between the epoxy group of Joncryl with the carboxyl group of PLAs. The possible chemical reaction and formation of these new peaks were illustrated in Figure 3.

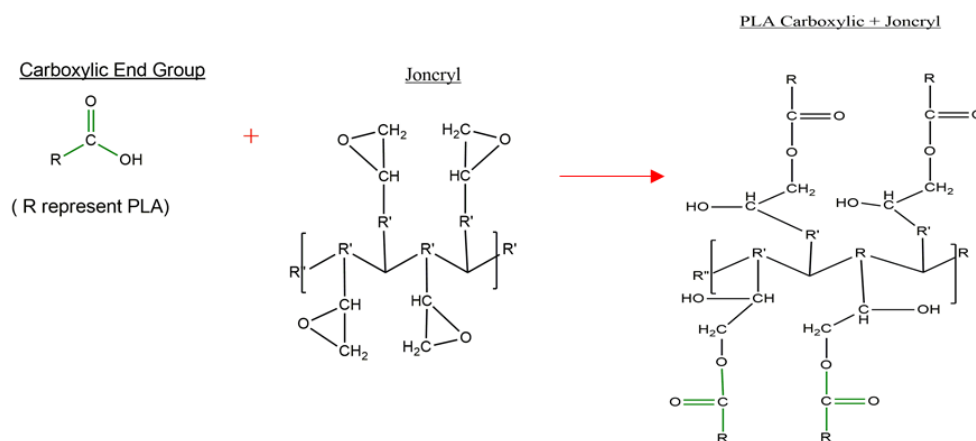


Figure 3: Possible chemical reaction between Joncryl and PL

The epoxide groups can react with the carboxyl end groups of PET and PBT. The excess epoxide groups will likely react with terminal hydroxyl groups and with the new hydroxyl groups formed from the joining of the epoxide and carboxyl groups (Bikiaris and Karayannidis, 1996). Since PLA fall into the same group of polyester, this means that similar reaction between the carboxyl group of PLA and epoxy group from Joncryl are possible. It was strongly justified by the formation of the new peak obtained in the FTIR spectra in Figure 2.

6. Conclusion

The addition of untreated BF has reduced the overall mechanical performance of the biocomposite. The addition of Joncryl improve few crucial mechanical aspects such as the impact strength and the elongation at break. Unlike typical compatibilizer that improved the interfacial adhesion by acting as a coupling agent between polymer matrix and fiber, Joncryl worked by imparting plasticizing or flexibility effect since its consist of the tailored styrene-acrylic oligomer with epoxy. This reduces the brittleness properties inherent by both PLA /BF composites. The enhancing mechanism of Joncryl however, only applicable up to a certain limit of BF loading. The optimum loading was determined to be 10 wt% of BF since the overall mechanical aspect deteriorate when approaching 20 wt% of BF. It was also established compatibilized biocomposite will give a better mechanical performance. The morphology analysis using SEM further illustrate that the compatibilized biocomposites have better impact strength since the gap presence at the interfacial area were smaller and lesser compared to uncompatibilized composites. Finally, the FTIR analysis established that there was an interaction between the epoxy group of Joncryl with carboxyl group from PLA and hydroxyl group in BF, proved by the formation of a few new peaks.

Acknowledgements

The author would like to thank the Universiti Teknologi Malaysia (UTM) and the Ministry of Education (MOE), Malaysia for funding this research under Fundamental Research Grant Scheme (FRGS/1/2017/TK05/UTM/02/4 / R. J130000.7846.4F978) and GUP grant No 13H29.

Reference

- Dupraz, A. M. P., Meer, S. A. T. V., De Wijn, J. R. D., Goedemoed, J. H., 1996, Biocompatibility Screening of Silane-treated Hydroxyapatite Powders, For Use as Filler in Resorbable Composites, *Journal of Materials Science: Materials in Medicine*, 7, 731-738.
- Bikiaris. D. N., Karayannidis G. P., 1996, Chain Extension of Polyesters PET and PBT with Two New Diimidodiepoxides, *Applied Polymer Science: Polymer Chemistry*, 34, 1337-1342.
- Plackett, D., Tom, L., Andersen, W., Batsberg, P., Lotte, N., 2003, Biodegradable Composites Based on L - Polylactide and Jute Fibres, *Composites Science and Technology*, 63, 1287-1296.
- Jacobson, S., Fritz, H. G., Degée, P., Dubois, P., Jérôme, R., 1999, Polylactide (PLA), A New Way of Production, *Polymer Engineering and Science*, 39, 1311-1319.
- Jandas, P.J., Mohanty, S., Nayak, S.K., 2011, Effect of Surface Treatments of Banana Fiber on Mechanical, Thermal and Biodegradability Properties of PLA/Banana Fiber Biocomposites, *Polymer Composite*, 32, 1689-1700.
- Rakesh, K., Mohammed, K. Y., Rajesh, D. A., 2010, Effect of Montmorillonite Clay on Flax Fabric Reinforced Poly Lactic Acid Composites with Amphiphilic Additives, *Composites Part A: Applied Science and Manufacturing*, 41, 1620-1627.
- Zurina M., Nur S.N.N., Norhayani O., Nurfairna B., Siti H.C.M., Mazura J., Rohah A.M., 2018, Properties Enhancement of Polylactic Acid Biocomposite, *Chemical Engineering Transactions*, 63, 361-366.