Reactive Compatibilization of Short-Fiber Reinforced Poly(lactic acid) Biocomposites

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ABSTRACT: Poor interfacial adhesion between biobased thermoplastics and natural fibers is recognized as a major drawback for biocomposites. To be applicable for the large-scale production, a simple method to handle is of importance. This work presented poly(lactic acid) (PLA) reinforced with short-fiber and three reactive agents including anhydride and epoxide groups were selected as compatibilizers. Biocomposites were prepared by one-step melt-mixing methods. The influence of reactive agents on mechanical, dynamic mechanical properties and morphology of PLA biocomposites were investigated. Tensile strength and storage modulus of PLA biocomposites incorporated with epoxide-based reactive agent was increased 13.9% and 37.4% compared to non-compatibilized PLA biocomposite, which was higher than adding anhydride-based reactive agent. SEM micrographs and Molau test exhibited an improvement of interfacial fiber-matrix adhesion in the PLA biocomposites incorporated with epoxide-based reactive agent. FTIR revealed the chemical reaction between the fiber and PLA with the presence of epoxide-based reactive agents.

KEYWORDS: Biocomposite, poly(lactic acid), Reactive agent, in situ compatibilization, interfacial adhesion

1 INTRODUCTION

Biocomposites based on biodegradable polymers and natural fibers have caught much attention in the last few decades due to less environmental impact with being fully biodegradable and more sustainable in terms of renewable resources. Among the biodegradable polymers, aliphatic poly(lactic acid) (PLA) is one of the most popular ones. PLA is eco-friendly, has a good processability in most equipment [1], high mechanical strength and high modulus, therefore PLA has the potential to replace the applications in some conventional plastics such as PET and PS. PLA has been reported as a matrix for several lignocelluloses reinforcing fibers such as kenaf [1-3], flax [4-6], abaca [7], jute [8, 9], coir [10], miscanthus [11], ramie [9, 12], bamboo [13, 14], coconut [13], vetiver [13] and wood pulp [15]. Natural fibers have many advantages such as light weight, renewability, biodegradability, and non-hazard are readily available at the relatively low cost compared to synthetic fibers [6, 15].

Using Bleached Kraft Pulp (BKP), especially Eucalyptus for PLA composites, has not yet been reported. Bleached Kraft Pulp is interesting in term of cost-effective cellulose fiber resource, which widely used in papermaking [16].

The advantages of Bleached Kraft Pulp are its whiteness, high purity of cellulose and aspect ratio with a uniform diameter at about 20 μm and length within 1 mm compared to wood pulp [17].

However, the poor interfacial adhesion between natural fiber and polymer matrix was commonly found in biocomposites systems [18], resulting in the unsatisfactory mechanical properties, which further limited their practical use. To overcome the weak fiber-polymer matrix adhesion; there are several existing approaches, including the surface modification of either polymer (e.g. grafting reaction) or fibers (e.g. silane coupling) or both polymers and fibers (e.g. the addition of some compatibilizer compounds). However, such methods are suitable mostly for polymer blends, time-consuming, and difficult to scale up for industrial production. The treatment prior to melt blending is not practical and costly. Therefore, based on these aspects, the concept of the reactive processing is introduced and applied for the biocomposite processing. The reactive processing is a cost-effective manufacturing technique with the possibility of increasing the level of interfacial adhesion [19]. The reaction occurs in situ during the melt processing.

Although a few types of the multifunctional reactive agents have been employed for either blends or

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composites of polyesters for different purposes including the use of multifunctional epoxides as thermal degradation control for PLA/nanoclay [20], anhydride as a chain extension for PET [21], diisocyanate as a chain extender for PET/PC recycling [22], and carbodiimide as a compatibilizer for PLA/cellulose biocomposites [15], for PLA and BKP biocomposites, the systematic approach for investigating the interfacial adhesion between two phases using various multifunctional reactive groups is still lacking.

In our previous works, Joncryl® or peroxide was used as the *in situ* compatibilizers for natural fiber to produce PLA and PBS biocomposites by one-step melt-mixing method [23]. Alternatively, A. Awal and colleagues studied thermorheological and mechanical properties of cellulose reinforced PLA biocomposites and reported that the addition of multifunctional bioadimide as a reactive agent could improve the adhesion between fibers and matrix [15]. Therefore, this work introduced the different types of reactive agents including multifunctional epoxides, reactive terpolymer (maleic anhydrides or epoxides) as in situ compatibilizers in the processing of PLA biocomposites. Maleic anhydride or epoxy based multifunctional group was highly reactive with hydroxyl groups (OH) in cellulose structure and formed carbon-carbon bond to the polymer chain [20, 24]. The bleached eucalyptus pulps (short fiber) with high cellulose compositions were used as a reinforcement incorporated with reactive agents for the PLA biocomposites. The influence of reactive agents on the morphology, mechanical and dynamic mechanical properties of PLA biocomposites were investigated and discussed. Furthermore, Molau test together with FT-IR technique was performed to examine the compatibility of biocomposite and verify the possible reactions of PLA, fibers and reactive agents.

2 EXPERIMENTAL

2.1 Materials

Poly(lactic acid) (PLA), 3052D injection grade was purchased from NatureWorks® LLC (USA). Bleach Eucalyptus Kraft Pulps (BEKP) were kindly provided by SCG Packaging PLC., Thailand. The average length and diameter of BEKP were 0.538 mm and 13.90 µm, respectively, which were analyzed by Fiber Quality Analyzer (FQA) assisted by SCG packaging PLC. The chemical compositions of the BEKP fibers were 83-86% α-cellulose, 12-15% hemicellulose, 1.5% lignin and less 0.5% extractives, which were analyzed according to Technical Association of the Pulp and Paper Industry (TAPPI) standard T 223 cm-01, T 236 om-99, T 203 cm-99 and T 222 om-02. An epoxy-based chain extender Joncryl® ADR-4368F (designated as CEGMA) was obtained from BASF Chemical Co., Ltd Thailand. A reactive terpolymer (ethylene, acrylic ester, and glycidyl methacrylate) Lotader® AX8900 (designated as EAGMA), and a random terpolymer (ethylene, acrylic ester and maleic anhydride) Lotader® 4210 (designated as EAMAH) were kindly supplied by 2 A.M. Connection Co. Ltd., Thailand. The chemical structures of three reactive agents were presented in Figure 1.

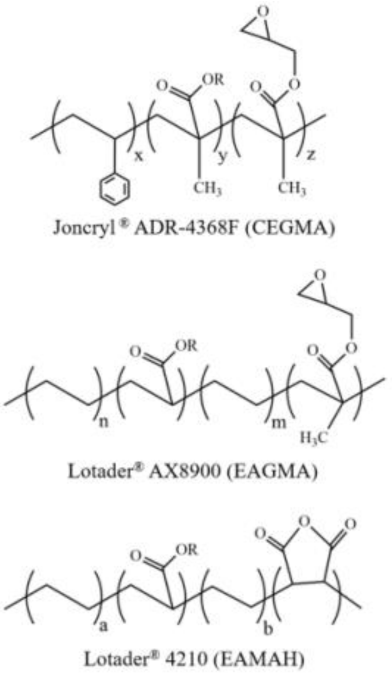


Figure 1 Chemical structures of three reactive agents used in this work.

2.2 Preparation of PLA Biocomposites

Eucalyptus paper pulps were first dried and ground to obtain short fibers using a high-speed grinder, with the rotation speed of 28,000 rpm. Prior to melt mixing, PLA was dried at 60°C in a vacuum oven for 6 h whereas the fibers were dried overnight at 80°C. PLA with 10 wt% of eucalyptus fibers loading (referred as PLA/FB10) without reactive agents was first prepared in an internal mixer (Chareon tut CO. LTD., model MX 105-D40L50) with the rotational speed of 60 rpm and the temperature of 190°C. Three Multifunctional group compounds such as multi-epoxide groups (designated as CEGMA) and two reactive terpolymers containing epoxide (designated as EAGMA) and maleic anhydride groups (designated as EAMAH) were selected as reactive compatibilizers in PLA biocomposites. The concentrations of 0.5 phr and 1.0 phr of each reactive agent were added along with 10 wt% fiber to produce PLA biocomposites. PLA biocomposites specimens were prepared and referred as PLA/FB/CEGMAx, PLA/FB/EAGMAx and PLA/FB/EAMAHx, where *x* stands for the contents of reactive agents in phr for chain extender containing epoxide groups, terpolymers containing epoxide groups and terpolymers containing maleic anhydride groups, respectively.

2.3 Testing and Characterizations

2.3.1 Tensile Testing

The obtained PLA biocomposites and neat PLA were molded into tensile specimens at 190°C and 1,000 psi pressure for 1 minute after pre-heating for 4 min using the compression molding machine (Chareon tut CO. LTD.). Tensile properties were determined using a universal testing machine (Instron 5969) in accordance with ASTM D638, specimen type V, 5 KN load cell. The testing was carried out under ambient conditions using a cross-head speed of 1 mm/min. All the reported values were obtained by averaging over five specimens.

2.3.2 Dynamic mechanical analysis (DMA)

DMA specimens were prepared by compression molding at 190°C and 1,000 psi pressure for 1 minute after pre-heating for 4 minutes and then laser-cut to rectangular dimensions of 10×1.16×40 mm^3. Dynamic mechanical properties of PLA biocomposites were examined by using an ANTON PAAR, Modular Compact Rheometer (MCR302) equipped with rectangular fixtures (SRF) holder under the DMTA torsion mode at a frequency of 1 Hz. A temperature sweep was carried out from 30°C to 110°C at a heating rate of 3 °C/min.

2.3.3 Field Emission Scanning Electron Microscopy (FE-SEM)

The tensile fractured surface morphology of PLA biocomposite specimens was characterized by Field Emission Scanning Electron Microscope (FE-SEM) (TESCAN MIRA3 LMH Schottky) at an accelerating voltage of 5 kV. Prior to observations, the samples were sputter coated with a thin layer of gold to avoid charging.

2.3.4 Molau Test

Molau test was performed by dissolving 0.5 g of PLA biocomposite samples in 10 mL chloroform and thoroughly shaking. The solutions were left to stand for 48 h at room temperature before the visual observation recorded by a digital camera.

2.3.5 Fourier Transformation Infrared Spectroscopy (FTIR)

The fibers in each sample of Molau test was precipitated and PLA solution was removed. Each precipitated fiber sample was transferred to 50 mL chloroform and stirred to ensure the complete removal of PLA. The insoluble fiber was collected via filtration by vacuum suction. Afterward, the extracted fibers were dried in an oven at 60°C for an hour for complete solvent removal. Finally, the filtered fiber samples in comparison with pristine fibers were analyzed by using FT-IR spectrometer (VERTEX70) at a resolution of 4 cm^{-1} with background and sample 32 scans in the spectral range of 4000-400 cm^{-1}.

3 RESULTS AND DISCUSSION

3.1 Mechanical Properties

The averaged stress-strain diagrams of neat PLA and PLA biocomposites with and without reactive agents were shown in Figure 2. It was seen that all PLA biocomposites showed a stiffer and more brittle behavior than neat PLA. The summary of mechanical properties of PLA biocomposites with and without 0.5 phr or 1.0 phr of reactive agents were shown in Table 1. It was found that the tensile strength of PLA with 10 wt% fibers loading without reactive agent (PLA/FB10) was slightly increased about 7.4% compared to neat PLA. A. Awal and colleagues reported that the tensile strength of PLA/wood fiber biocomposites was increased because of the reinforcement of fibers and the addition of bioadimide even improved the tensile strength of wood fiber reinforced PLA biocomposites due to the better interfacial adhesion within PLA and wood fiber [15]. The tensile strength of PLA biocomposites with EAGMA and EAMAH was slightly higher than non-compatibilized PLA biocomposite (PLA/FB10) whereas the tensile strength of PLA biocomposites with CEGMA showed the greater improvement than non-compatibilized PLA biocomposite. The increase of the tensile strength was more pronounced for PLA/FB/CEGMA1.0, which was corresponded to 22.4% and 13.9% higher than that of neat PLA and non-compatibilized PLA biocomposite, respectively, indicating a better interfacial adhesion within PLA and fiber. In case of Young's modulus, all PLA biocomposites possessed the higher Young's modulus when incorporating 10 wt% fiber with and without reactive agents compared to neat PLA, suggesting the better transfer of stress to the added fibers [25] (except the addition of EAMAH). Young's modulus of the PLA biocomposites was greatly improved due to the presence of the fiber that caused the stiffening effect obtained from the decrease in the mobility of the polymer matrix chains [26-28]. Although it was known that the improvement of the quality of the polymer interface did not significantly affect Young's moduli or stiffness of the materials [29], the addition of 0.5 phr EAMAH in PLA biocomposite showed the lowest Young's modulus value, which was decreased by 7.3% compared to non-compatibilized PLA biocomposite. In case of elongation at break, it was noticed that the elongation at break of non-compatibilized PLA biocomposites was slightly lower than neat PLA. However, the incorporation with 0.5 phr of all reactive agents showed a slight increase in the elongation at break compared to non-compatibilized PLA biocomposite. The presence of 0.5 phr of CEGMA demonstrated a large improvement in the elongation at break, which was 16.1% higher than non-compatibilized PLA biocomposite. This might be due to the fact that all reactive agents contained acrylic ester acted as a soft segment of their molecule. In addition, the incorporation of CEGMA could change the molecular weight distribution of PLA matrix due to the chain extension effect [30], which might lead to the improvement of the elongation at break.

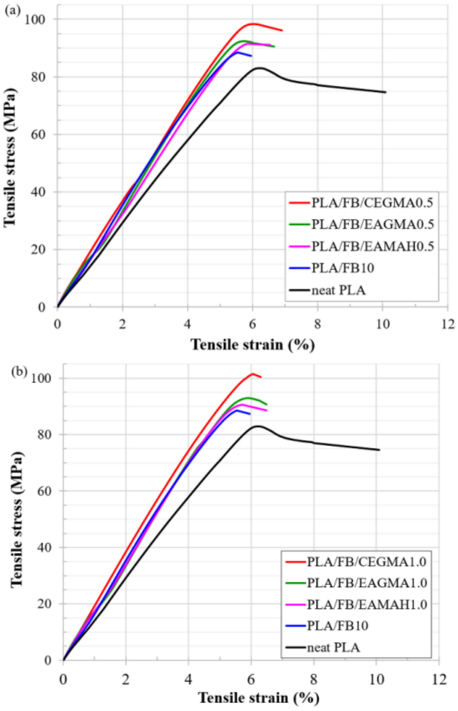


Figure 2 Tensile stress-strain diagrams of neat PLA and PLA biocomposites with and without reactive agents 0.5 phr (a) and 1.0 phr (b).

Table 1 Summary **of** mechanical properties of neat PLA and PLA biocomposites with and without reactive agents.

Sample codes	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
neat PLA	82.86 (4.79)	1603 (30)	10.09 (1.73)
PLA/FB10	89.03 (2.66)	1948 (23)	5.95 (0.29)
PLA/FB/CEGMA0.5	99.05 (3.62)	1941 (26)	6.91 (0.64)
PLA/FB/CEGMA1.0	101.44 (3.76)	1961 (20)	6.31 (0.38)
PLA/FB/EAGMA0.5	92.67 (2.40)	1937 (23)	6.65 (0.62)
PLA/FB/EAGMA1.0	92.09 (2.57)	1927 (31)	6.47 (0.71)
PLA/FB/EAMAH0.5	93.80 (6.46)	1805 (47)	6.54 (0.63)
PLA/FB/EAMAH1.0	91.16 (5.46)	1875 (30)	6.49 (0.41)

The standard deviation of samples were shown in parentheses.

3.2 Dynamic Mechanical Properties

The temperature dependence of storage moduli of neat PLA and PLA biocomposites with and without reactive agents were presented in Figure 3. In the glassy region (from 30°C to 50°C), all PLA biocomposite samples displayed the higher values of storage modulus (G') than that of neat PLA. The storage modulus of PLA with 10 wt% fiber loading was increased by 60% compared to that of neat PLA (1,564 MPa) due to the reinforcement effect. It was observed in Figure 3(a) that PLA biocomposites incorporated with 0.5 phr of all reactive agents had a higher storage modulus than non-compatibilized PLA biocomposite. The addition of CEGMA into PLA and fibers exhibited higher storage modulus than EAGMA and EAMAH, respectively. However, in the case of adding 1.0 phr of the anhydride-based reactive agent, the storage modulus was comparable to non-compatibilized PLA biocomposite. Upon increasing the temperature, it was seen that the storage modulus of neat PLA and all PLA biocomposites dropped at around 65°C, which corresponded to their glass transition temperature. As the temperature continued to increase, the storage moduli decreased as PLA matrix became soft at higher temperatures. In the rubbery region (from 75°C to 90°C), all PLA biocomposites exhibited significantly higher storage modulus than that of neat PLA, especially for the addition of the epoxide-based reactive agent. From Figure 3(b), the storage moduli of neat PLA and PLA incorporated with 1.0 phr EAGMA started to increase at about 98°C while the other PLA biocomposites started to increase at slightly lower temperature. These storage moduli were recovered due to the cold crystallization of PLA tested specimen in DMA temperature sweep [31].

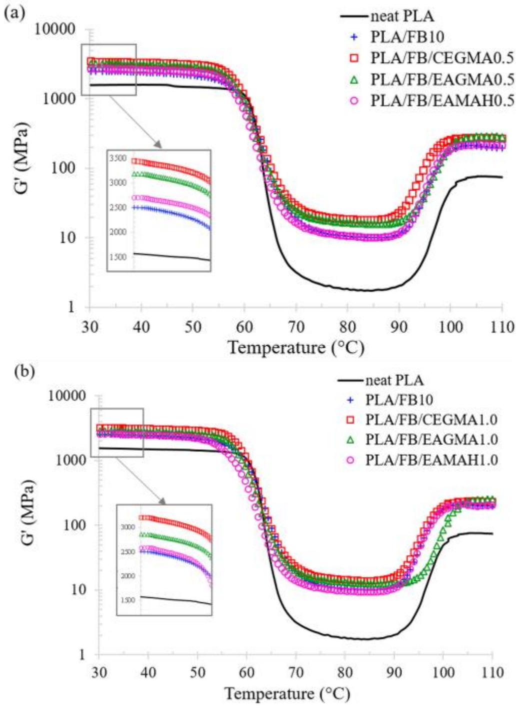


Figure 3 Storage modulus of neat PLA and PLA biocomposites with and without reactive agents 0.5 phr (a) and 1.0 phr (b).

Figure 4 depicted the curves of damping or tan δ, which was defined as the ratio of the loss to the storage modulus. The loss and storage modulus were referred as an ability for dissipating energy (viscous phase) and storing mechanical energy (elastic phase), respectively [32]. In the transition region, composites had essentially lower tan δ than neat PLA because the addition of fibers increased the mobility of the amorphous phase in the polymer matrix [32, 33]. For composites, tan δ was affected by the distribution of fibers, a concentration of shear stress, viscoelastic energy dissipation as well as the fiber and matrix interfacial adhesion [34, 35]. Therefore, tan δ peak height might be used in order to investigate the interfacial adhesion between fiber and polymer matrix [36-40]. As reported elsewhere [37, 39-41], the higher tan δ values indicated a weak interfacial adhesion whereas the lower tan δ values indicated a good interfacial adhesion due to a reduction in mobility of the polymer chain. From Figures 4(a) and 4(b), the tan δ curves of all PLA biocomposites with reactive agents shifted toward lower values than non-compatibilized PLA biocomposite, implying the better interface between the components compared to non-compatibilized PLA biocomposite. However, the incorporating of 0.5 phr anhydride-based reactive agent showed the similar tan δ value to non-compatibilized PLA biocomposite.

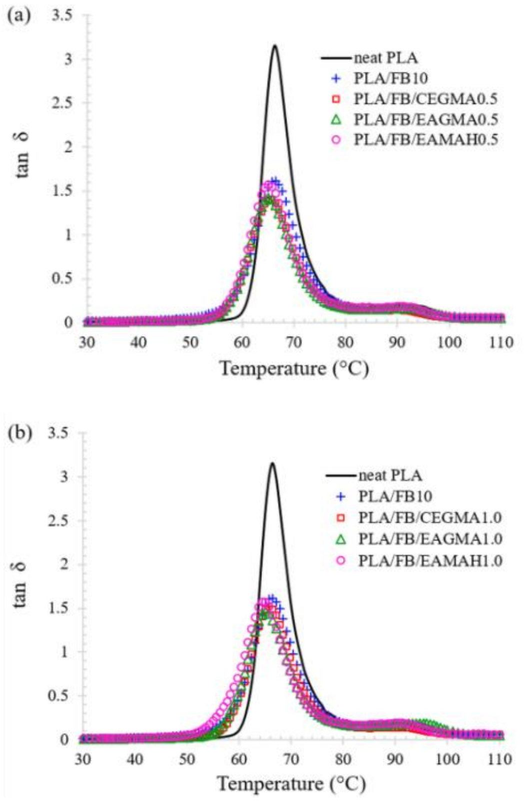


Figure 4 Tan δ of neat PLA and PLA biocomposites with and without reactive agents 0.5 phr (a) and 1.0 phr (b).

One of the parameters used to evaluate a degree of interfacial adhesion between fiber and polymer matrix due to the reduction of molecular mobility of polymer around the fiber surface compared to the matrix is called an adhesion factor (A). The adhesion factor (A) was determined using Equation (1) [41], where V_f was the volume fraction of the fiber (0.1), $\tan\delta_c$ was the relative damping of the PLA biocomposites and $\tan\delta_p$ was the relative damping of the pure PLA. The relative damping of the materials was determined by the maximum tan δ peak [39]. The results were presented in Table 2.

$$A = \left(\frac{1}{1-V_f}\frac{\tan\delta_c}{\tan\delta_p}\right) - 1 \qquad (1)$$

As seen in Table 2, PLA/FB/CEGMA0.5 and PLA/FB/EAGMA0.5 showed the lowest adhesion factor, which implied the strong interfacial adhesion between the fiber and PLA matrix. Furthermore, the effectiveness of stress transfer between the PLA and filler could be demonstrated by effectiveness coefficient parameter (C) [41]. The effectiveness coefficient was defined as the ratio of storage modulus of the composite in the glassy region and the rubbery region in relation to the pure resin [41]. The effectiveness coefficient (C) was computed using Equation (2) [41], where G'_g and G'_r were the storage modulus in the glassy region and rubbery region, respectively.

$$C = \frac{G'_g/G'_r\,(composite)}{G'_g/G'_r\,(resin)} \tag{2}$$

Table 2 Tan δ peak values, Adhesion factor (A) and Effectiveness coefficient (C) parameters of neat PLA and PLA biocomposites.

Sample codes	Max tan δ peak value	Adhesion factor (A)	Effectiveness coefficient (C)
neat PLA	3.15	0	1.00
PLA/FB10	1.61	-0.43	0.27
PLA/FB/CEGMA0.5	1.40	-0.50	0.21
PLA/FB/CEGMA1.0	1.52	-0.46	0.25
PLA/FB/EAGMA0.5	1.43	-0.50	0.22
PLA/FB/EAGMA1.0	1.46	-0.49	0.25
PLA/FB/EAMAH0.5	1.57	-0.45	0.29
PLA/FB/EAMAH1.0	1.57	-0.45	0.30

From Table 2, PLA/FB/CEGMA0.5 exhibited the lowest C, which indicated the most effectiveness of stress transfer from PLA matrix to the fiber, similar to PLA/FB/EAGMA0.5 while PLA/FB/EAMAH1.0 showed the highest C compared to all PLA biocomposites. For the comparison, the incorporation the epoxide-based reactive agent exhibited more improved interfacial adhesion or compatibility between PLA and the fiber than the anhydride-based reactive agent. This could result from reactive epoxide group, which was more selective to the fiber and PLA system.

The changes introduced by reinforced filler into the structural properties of the polymeric matrix could be studied from Cole-Cole analysis [42]. The shape of Cole-Cole curve (plotted loss modulus G'' *vs.* storage modulus G') reflected the homogeneity of the system [43, 44]. The homogeneous materials showed the perfect semicircle curve while the composite systems showed the imperfect semicircle curve [42]. The elliptical or imperfect semicircle curve denoted the good adhesion between the filler and the polymer matrix [42]. In Figure 5, the Cole-Cole characteristics of all PLA biocomposites revealed the semicircles. It was also reported that the compatibility of polymer blends was represented by the slope of the curve in the low G' region [43]. At the beginning of the curve, the nearer the slope approached 2 referred a better compatibility of the blend [43]. The calculated slope of all PLA biocomposites was lower than 2, but PLA/FB/CEGMA showed the nearest slope to 2 as seen in Figure 5. Therefore, it was implied that the addition of CEGMA in PLA biocomposite could lead to the improvement of compatibility between the fiber and PLA. The better compatibility of these PLA biocomposites samples could be confirmed by SEM, Molau test, and FT-IR.

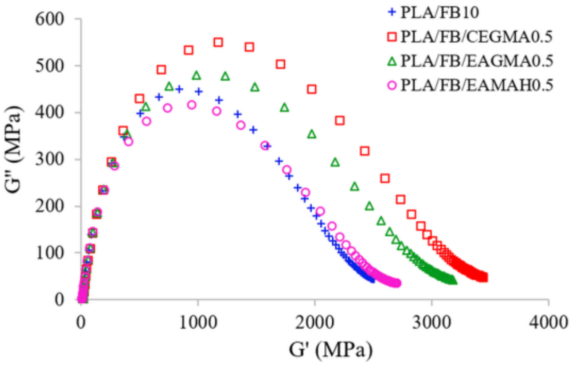


Figure 5 Cole-cole plot for PLA biocomposites with and without reactive agents 0.5 phr.

3.3 Morphology of PLA Biocomposites

Field emission scanning electron microscopy (FE-SEM) micrographs of the tensile fractured surface of PLA biocomposites with and without reactive agents were depicted in Figure 6. The micrograph of non-compatibilized PLA biocomposite in Figure 6(a) exhibited the remaining pores due to the pull-out of fibers and the space between the fiber and PLA matrix, suggesting a lack of interfacial adhesion. Figure 6 (b, b', c, and c') showed the micrographs of PLA biocomposites incorporated with epoxide-based reactive agents. The fibers breakage and disappearance of space between PLA and fibers were observed rather than pullout, indicating better interfacial adhesion between the fibers and PLA matrix. Whereas the micrographs of PLA biocomposites incorporated with the anhydride-based reactive agent showed the smooth of the fiber without the remaining pores as seen in Figures 6 (d, d'). Figure 6a, which indicates the pullout of the fiber from the PLA matrix. From FE-SEM results, it could be concluded that PLA biocomposites with epoxide-based reactive agents helped to promote the better interfacial adhesion, essentially resulting in more efficient transfer of stress from the PLA matrix to the reinforcement than that with the anhydride-based reactive agent. R. Gunti and colleagues reported that the fiber reinforced PLA composites had exhibited fiber breakage rather than pullout due to the better stress transfer between fiber and matrix [45]. The results were in good agreement with the improved mechanical properties of the PLA composites with the epoxide-based reactive agent (CEGMA) discussed earlier.

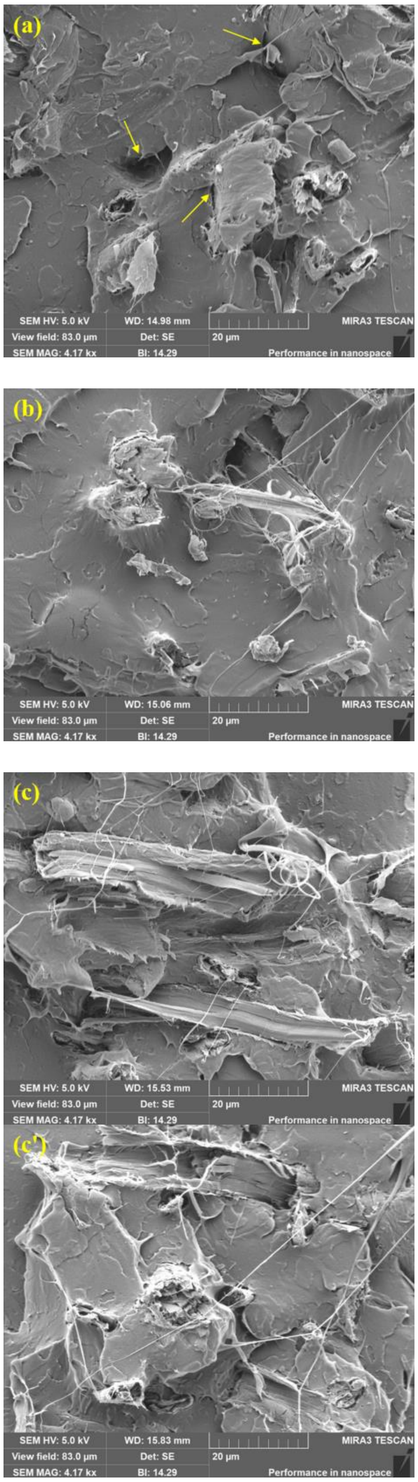


Figure 6 FE-SEM micrographs of tensile fractured surface of PLA biocomposites; PLA/FB10 (a), PLA/FB/CEGMA 0.5 phr (b) and 1.0 phr (b'), PLA/FB/EAGMA 0.5 phr (c) and 1.0 phr (c'), PLA/FB/EAMAH 0.5 phr (d) and 1.0 phr (d').

3.4 Molau Test of PLA Biocomposites

In order to investigate any changes in physical properties due to interfacial bonding or compatibility in PLA biocomposites with and without reactive agents, Molau test of these PLA biocomposites compared to neat PLA were presented in Figure 7. It was observed that neat PLA could be dissolved completely in chloroform, thus a transparent solution was obtained. In the case of non-compatibilized PLA biocomposite (PLA/FB10), the phase separation was clearly noticed. The lower layer contained the insoluble fiber and the upper layer was the PLA solution, indicating the lack of interaction between the fiber and PLA. When 1.0 phr of EAGMA or EAMAH was used as reactive agents for PLA biocomposite, more turbidity of the solution was observed even though the phase separation was still observed. The addition of CEGMA in PLA biocomposite exhibited the most turbid solution. This indicated that the addition of CEGMA could lead to some chemical reactions between fibers and PLA. A. Mujica-Garcia and colleagues also used the Molau test to study the interfacial interaction between PLA matrix and CNC. They observed that CNC of both neat CNC and mixture of CNC/PLA solutions precipitated, but the suspension of functionalized CNC in the CNC-g-PLLA solution was maintained stable, as a consequence of the well-done functionalization [46].

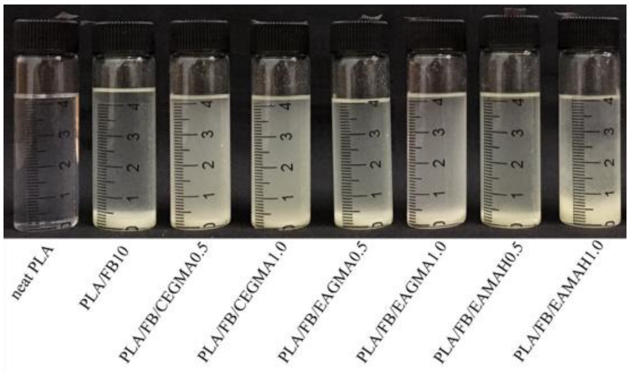
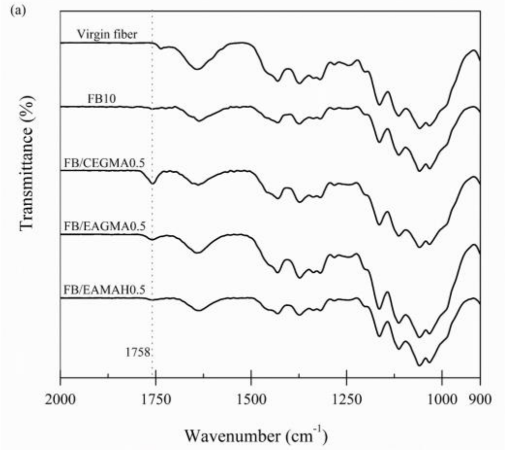


Figure 7 Photographs obtained by Molau test of neat PLA and PLA biocomposites with and without reactive agents (0.5 phr and 1.0 phr).

3.5 Characterization of Compatibilized PLA Biocomposites

The interaction between the fiber and PLA within the biocomposites was analyzed by FTIR. Figure 8 illustrated FT-IR spectra of virgin fiber and the precipitated fibers of PLA biocomposites with and without reactive agents. The intensity of the broad peak at 3480 cm^{-1}, which assigned to the -OH stretching of cellulose fibers in all samples, was unchanged (data not shown). Considering the characteristic at peak 1758 cm^{-1}, it was assigned to the remaining carbonyl groups (C=O) of PLA chains in precipitated fibers. It was clearly seen that the peak was disappeared at 1758 cm^{-1} for virgin fiber, fibers without reactive agents (PLA/FB10) and fibers with 0.5 phr EAMAH (PLA/FB/EAMAH0.5). On the other hand, the strong peak at 1758 cm^{-1} for precipitated fiber sample of CEGMA was indicative of a strong interaction between the fiber and PLA matrix. A. Mujica-Garcia and colleagues reported that FTIR spectrum of CNC-g-PLLA was the presence of the peak at 1753 cm^{-1}, corresponding to the stretching frequency of the carbonyl group in PLA and/or lactic acid oligomers, which confirmed the success of the grafting procedure [46]. It suggested that CEGMA was significantly improved the interfacial adhesion between the fiber and PLA matrix. Since CEGMA had multiple reactive epoxide groups, CEGMA might be chemically reacted with hydroxyl groups in fiber and also the PLA chain ends (-OH and -C=O groups) during melt processing, resulting in the significant increase in the compatibility between the fiber and PLA matrix. However, this was the first evidence, the chemical reaction between the fiber and PLA needed to be clarified. Furthermore, the weak peak at 1758 cm^{-1} for precipitated fiber sample of EAGMA or 1.0 phr EAMAH was observed. Similarly, EAGMA could improve the interfacial adhesion between the fiber and PLA matrix but not as much as CEGMA. In contrast, the addition of anhydride-based reactive agent as much as 1.0 phr would result in the improved interaction between the fiber and PLA matrix.



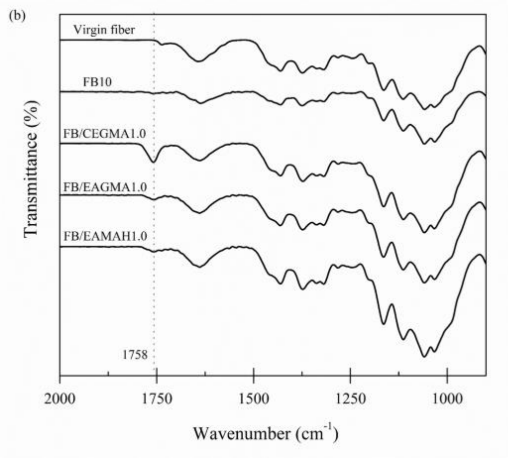


Figure 8 FT-IR spectra of virgin fiber and fibers with and without reactive agents 0.5 phr (a) and 1.0 phr (b) after dissolving from PLA biocomposites.

4 CONCLUSION

The *in situ* reactive compatibilization of short-fiber reinforced PLA biocomposites were successfully prepared by melt-mixing. Multifunctional group reagents such as CEGMA, EAGMA, and EAMAH were selected as reactive compatibilizers for PLA biocomposites. The influence of reactive agents on mechanical, dynamic mechanical properties and morphology of PLA biocomposites were investigated. The following conclusions could be drawn from this study:

1) PLA biocomposites loaded with 1.0 phr of CEGMA provided the most improvement of tensile strength about 22.4% and 13.9% compared to neat PLA and non-compatibilized PLA biocomposite, respectively. However, the effect of different reactive agents was not so dominant in terms of Young's modulus. The presence of all reactive agents also improved the elongation at break of PLA due to the existing acrylic ester in their molecules.

2) The storage modulus of PLA biocomposites showed the most increased when loading 0.5 phr of CEGMA followed by EAGMA and EAMAH, respectively.

3) The adhesion factor and effectiveness of the PLA biocomposites revealed that the interfacial adhesion of PLA/fiber was improved with the addition of the epoxide-based reactive agent (CEGMA and EAGMA).

4) The FE-SEM micrographs of PLA biocomposites incorporated with epoxide-based reactive agents (CEGMA and EAGMA) displayed fibers breakage and continuous matrix, indicating a better interfacial adhesion between the fibers and PLA matrix.

5) Molau test confirmed that epoxide-based reactive agent, CEGMA, enhanced the interaction between the fiber and PLA matrix.

6) FTIR spectra revealed that carbonyl groups appeared in precipitated fibers samples of epoxide-based reactive agents (CEGMA). However, the chemical reaction between the fiber and PLA would be further clarified.
7) The present results indicated that CEGMA was the most effective compatibilizer for PLA biocomposite.

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