Characterization of polylactic-epoxidized natural rubber/modified cellulosic fiber biocomposites with different silane coupling agents

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Abstract. A purpose of this research was to investigate a potential of two differently modified cellulosic fibers for applying as reinforcing fillers in polylactic acid (PLA) and modified epoxidized rubber (ENR) base of biocomposites. Coupling agents including 3-(trimethoxysilyl) propyl methacrylate and (3-aminopropyl) trimethoxysilane were used in order to modify cellulosic fibers. These fibers were compounded with PLA-modified ENR (modified by bisphenol A diglycidyl ether) in an internal mixer and fabricated to composite sheets using a compression molding, respectively. The formulations of biocomposites were designed by weight ratio of PLA (85%): modified ENR (5%): the cellulosic fiber (10%). According with the results of mechanical property analysis of their biocomposites, the modifications of cellulosic fibers with both silane types significantly improved flexural, hardness and impact properties of PLA-modified ENR based biocomposites. However, the methacrylate-silane modified cellulosic fiber provided the greatest increase in flexural properties while the amino-silane modified cellulosic fiber resulting in the highest value of hardness and impact resistance of all biocomposites. Oil absorption test of biocomposites was also investigated in this research in order to evaluate its possibility to use under oily environment. After 168 hours of experiment, the amino-silane modified composite exhibited the highest oil absorption among all materials. This result indicated the most improvement of hydrophobicity of modified cellulosic fiber by (3-aminopropyl) trimethoxysilane.

1. Introduction
A decade ago, polylactic acid (PLA) based cellulose fibre biocomposite has been considerably interested and widely developed as a new sustainable material with aiming to substitute polyolefin based cellulose biocomposite [1]. Due to full biodegradation and 100% renewable material resources, this make it expected to remedy the pollution from plastic waste as confronting nowadays [2]. Nevertheless, a problem of using cellulose fibre incorporating into PLA is due to a poor interfacial adhesion between fibre and matrix which determines thermal, mechanical properties, moisture absorption and also life time of service [3]. Hence, overcoming of this drawback by fibre surface modification is usually processed in order for improvement of the compatibility [4].

This work was aimed to solve these problems by developing a new biocomposite of cellulose fibre/modified epoxidized rubber (ENR)/PLA. Two different types of silane: 3-(trimethoxysilyl) propyl
methacrylate and (3-aminopropyl) trimethoxysilane were used to treat cellulose fibres prior applying as reinforcing fillers in the biocomposites.

2. Experimental

2.1. Material
PLA grade of 3052D was supplied by the NatureWorks, USA. Chopped cellulose fibre and ENR 25% were kindly provided by local companies, Thailand. Bisphenol A diglycidyl ether was used to modify ENR. (3-Aminopropyl)trimethoxy silane 97% concentrations, 3-(Trimethoxysilyl) propyl methacrylate 98% concentrations were purchased from SigmaAldrich. Acetic acid and ethanol of commercial grades were also used.

2.2. Methods
2.2.1. Fiber treatment. Silanization of cellulose fibre was taken place according to the previous work [5]. Two different types of silane were supplied as reactants to improve compatibility of cellulose fibre and matrix phases.

2.2.2. Modified ENR. Bisphenol A diglycidyl ether was compounded together with ENR by a two-roll mill machine for 5 min.

2.2.3. Compounding and fabrication of the biocomposite. Biocomposites of PLA/modified ENR/cellulosic fibre were formulated by ratio of 85% :5%: 10% by weight. 3 different types of fibres as following: 1) unmodified cellulose, 2) methacrylate silanized cellulose and 3) amino silanized cellulose were compounded with PLA and modified ENR in the internal mixer. The compounding process was operated for 3 min, 60 rpm under temperature of 180°C. After that, the compounded biocomposites were granulated and transferred to a compression molding unit for fabrication of biocomposite sheets. The fabrication process was carried on under a condition of 180°C, pressure of 200 kgf/cm². The biocomposite sheets as obtained were kept in a desiccator for further testing in the next step.

2.2.4. Mechanical properties and oil swelling tests. In order to investigate the effect of different types of silanes onto the biocomposite performances, the mechanical testing of charpy impact test (unnotched specimen), flexure test was employed accordance with ASTM D256 and ISO 178, respectively. Hardness test was also characterized using a mode of shore A. Oil swelling test was performed accordance with ASTM D543-06. All test results were recorded and analysed followed to a statistical method.

3. Results and discussion
Figure 1 presents a comparison of hardness and impact resistance among all biocomposites. The highest value of both tests as observed in an amino silanized cellulose biocomposite could confirm a good internal interaction, probably due to a crosslink interaction between amine groups of the amino silanized cellulose and epoxy group of modified ENR. In which fibre dispersion and loading transfer from matrix to fibre was improved, these sequentially resulted to improve impact property. Meanwhile, the hardness and impact resistance of a methacrylate silanized cellulose biocomposite was also showing a better reinforcement than that of an unmodified biocomposite. This emphasises the potential of methacrylate silane treatment for improvement of fibre – matrix interaction.

Figure 2 presents and compares the flexural strength and modulus of all biocomposites. The methacrylate silanized cellulose biocomposite remarkably showed the best of all. This could be attributed by a good interfacial adhesion of the modified cellulose with PLA and ENR phases. Due to reactive groups of methacrylate silane possessing of ester and ethylene groups, these could produce the bond with carbonyl or α-carbon on backbone chain of PLA. In consequence, the reinforcement ability by loading transfer from PLA matrix to the cellulose was mostly improved.
Figure 1 Impact resistance and hardness of biocomposites

![Impact resistance and hardness of biocomposites](image1)

Figure 2 Flexural strength and flexural modulus of biocomposites

![Flexural strength and flexural modulus of biocomposites](image2)

Figure 3 presents the oil absorption test in all biocomposites. After 168 hours of the experiment, cellulose modified with amino-silane demonstrated the most oil absorption of all materials. This is evidenced to confirm the improved hydrophobicity of this biocomposite due to a covalent bonding interaction between amine groups of the modified cellulose and epoxy groups of modified ENR. Actually, the ENR is a hydrocarbon compound which could easily introduce hydrophobic fluid like a cook oil to be absorbed while cellulose fibre performing against it because of hydroxyl groups. Hence, the most oil absorption is a crucial evidence to confirm the substantial improvement of hydrophobicity by surface alteration of (3-Aminopropyl)trimethoxy silane.

![Oil absorption in biocomposites](image3)

Figure 3 Oil absorption in biocomposites.

Figure 4 presents the SEM images of fracture cross section of biocomposites. It is clear that both types of silanized cellulose showed a better adhesion relative to the unmodified fiber. Sequentially, the loading transfer from matrix to fiber was improved with increasing the mechanical properties as described earlier.
Figure 4 Cross section of fractured biocomposite (900X): (a) unmodified cellulose, (b) methacrylate silanized cellulose, and (c) amino silanized cellulose.

4. Conclusions
The modification of cellulose with 2 different types of silane provides the mechanical properties of biocomposites in different ways. Treatment of cellulose with (3-Aminopropy)trimethoxy silane could considerably improve the hardness and impact resistance. Meanwhile 3-(Trimethoxysilyl) propyl methacrylate results in the best of flexural strength and modulus. Furthermore, the most oil absorption of amino silanized cellulose biocomposite indicates the predominance of hydrophobicity.

5. References
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