Peroxide/Silane Crosslinked Poly(lactic acid) Hybrid Biocomposite Reinforced with Empty Fruit Bunch and Cotton Fibers for Hot-Fill Food Packaging

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A biocomposite manufactured from peroxide/silane crosslinked poly(lactic acid) reinforced with hybridized empty fruit bunch (EFB) oil palm and cotton fibers was investigated. Optimization of dicumyl peroxide (DCP) and the vinyltrimethoxysilane (VTMS) crosslink system by using the 2^k factorial design of experiment (DOE), with k = 2 was preliminary employed. There was no significant effect of the designed parameters, DCP(A) and VTMS(B), on the properties of the biocomposite. Concerning the environmental and economical aspects, the DPC and VTMS ratio was important. A crosslink agent content from 0.5 phr of DCP with 1 phr to 2 phr VTMS was recommended to manufacture a biocomposite with high heat distortion temperature (HDT) at above 100 °C and reasonable flow and mechanical properties. Also, the direct addition of the DCP/VTMS crosslink agent onto the PLA/rubber compound mixture and fed into a twin screw extruder for producing crosslinked PLA/EFB/cotton hybrid biocomposites were the optimized mixing methods. Shorter process line/time, ease of process steps, and reasonable engineering properties were justified. A HDT above 100 °C with a better toughness property of the biocomposite material was obtained. The PLA/PLA and PLA/ENR crosslinks *via* silane/moisture condensation during the sauna incubation was the prime explanation.

Keywords: Peroxide/Silane Crosslink; Sauna incubation; Biocomposite; Thermal and mechanical properties

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INTRODUCTION

Challenges for biocomposite studies, especially with a PLA-based matrix, have included toughness enhancement, weight reduction, and long-term property improvement. Nevertheless, the thermal property is also one of the main concerns. Recently, many types of coupling agents for the strong natural fiber/polymer matrix interfacial adhesion have been explored. The most commonly used are maleated polyolefins, isocyanates, and silanes. Generally, adding those coupling agents can achieve significant improvement in toughness of biocomposites (Bengtsson and Oksman 2006).

Crosslinking, either on fiber/polymer or polymer/polymer, is one of the research methods to improve the thermal and chemical resistance of polymers. There are three typical crosslink methods: (*i*) radiation, (*ii*) free radical initiation, and (*iii*) peroxide/silane condensation crosslinking. The peroxide/silane process is cost effective and easy to perform. Several research studies have focused on the use of the vinyl silane and free radical decomposed from peroxide as the precursors for the crosslink process. For example, in a linear low-density polyethylene (LLDPE), wood-plastic composite (WPC), the moisture-induced silane/peroxide crosslink technique had improved the physical properties of the WPC material (Kuan *et al*. 2006). Tensile and flexural strengths were significantly increased in the crosslinked WPC. The moisture-induced silane/peroxide crosslinking mechanism between polymer matrix and cellulosic fiber reinforcement was proposed as illustrated in Fig. 1 (Bengtsson and Oksman 2006). This process is normally succeeded by sauna incubation or curing. A similar outcome was found for WPC based on a poly(propylene)(PP)/ethylene propylene diene terpolymer (EPDM) blend (Zhou *et al.* 2009). Also, it was successfully used in high-density poly(ethylene)(HDPE), low-density poly(ethylene)(LDPE), and linear low-density poly(ethylene)(LLDPE)-based WPC (Bengtsson and Oksman 2006; Grubbström and Oksman 2009).

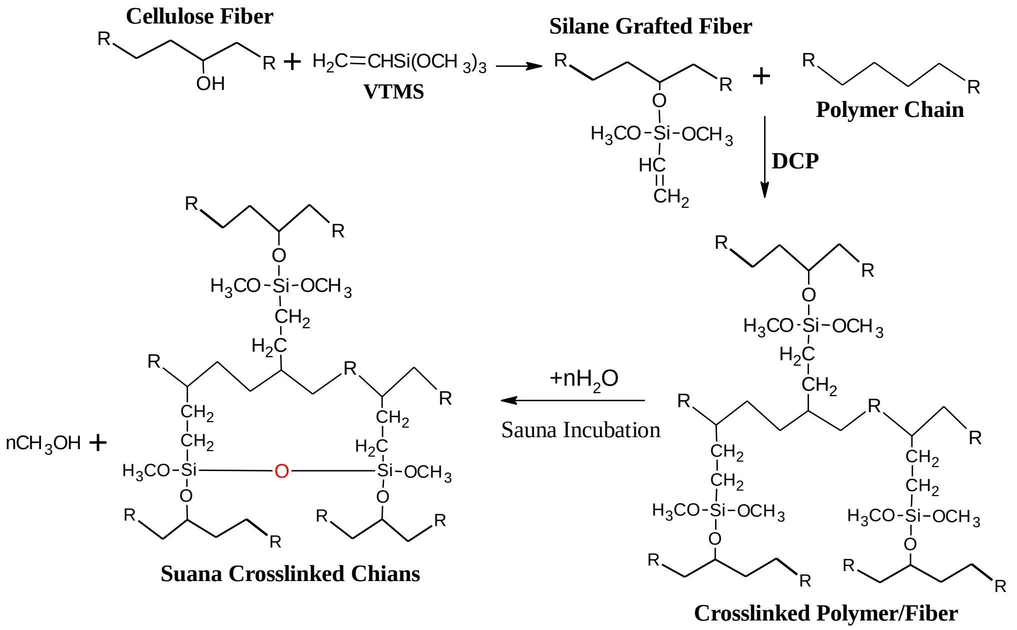

Fig. 1. Schematic illustration of the fiber/polymer crosslinking *via* peroxide/silane condensation

In bioplastics, such as poly(lactic acid) (PLA), the development of crosslinked poly(L-lactide) (PLLA) by grafting of vinyltrimethoxysilane (VTMS) onto PLLA using dicumyl peroxide (DCP) as a free radical initiator was investigated. The thermal stability, mechanical properties, and hydrolysis resistance of PLLA was improved. The T_g of silane/moisture induced crosslinked PLLA was increased with increasing the chain crosslinking density (Han *et al*. 2010). The purposed crosslink mechanism of the PLA is shown in Fig. 2.

The silane/water crosslinking of metallocene ethylene-octane copolymer (EOR) also has been reported. The fast crosslinking, high gel content, and hence reduction in the tensile strength and elongation at break was concluded (Sirisinha and Meksawat 2004). The enhancement of thermal stability and mechanical properties of PLA was attempted *via* chain crosslinking. A small amount of crosslinking agents comprised of triallyl isocyanurate (TAIC) and DCP was added to the molten PLA. The tensile properties and thermal stability of crosslinked PLA were superior to neat PLA. However, brittleness was evidenced with the establishment of a highly crosslinked structure (Yang *et al*. 2008).

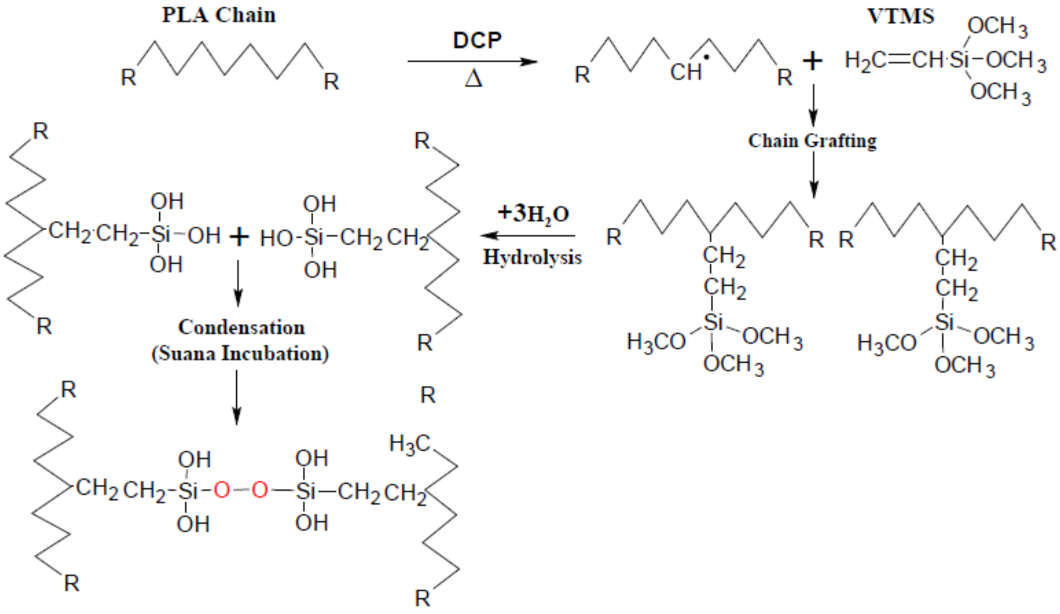

Fig. 2. Schematic illustration of the peroxide/silane crosslink mechanism *via* sauna incubation

Improvements in the mechanical and thermal properties of the biocomposites have been reported using different types of filler. A study of PLA-based composites reinforced with *Arundo donax* (AD) material showed that the tensile and flexural moduli greatly increased with increasing the AD content (Fiore *et al.* 2014). However, the glass transition temperature (T_g) and crystallization temperature (T_c) was decreased with increasing AD content.

Averous and Digabel (2006) explored the biopolymer, poly(butylene adipate-co-terephthalate) (PBAT), filled with lignocellulosic fibers (LCF) as a by-product from the wheat straw industry. The authors observed that filler content from 0 to 30 wt% enhanced mechanical properties, but T_g was reduced at higher filler content. The crystallinity of the matrix did not change with LCF content. Properties enhancement of bio-polyamides, PA10.10 and PA6.10, using rice hush ash (RHA) and modified nanoclay(MNC) was also recently published (Battegazzore *et al.* 2016). It was found that the Young's modulus was significantly improved, with a slight reduction in strength, by the addition of RHA and with the combined RHA/MNC fillers. The HDT was found to be increased with increasing the filler(s) loading.

In this publication, vinyltrimethoxysilane (VTMS)/dicumyl peroxide was employed as a crosslink system for the PLA reinforced with the combination (hybrid) of fibers of empty fruit bunch (EFB) oil palm and cotton fibers. A high heat distortion temperature (HDT), above 100 °C, without scarifying the mechanical properties of the obtained crosslinked PLA biocomposite, was the main target of this study. A high service temperature or hot fill food packaging, especially for the injection molding process, is the prime commercial interest. For the commercial scale-up interest, the ease of processing procedures was also verified.

EXPERIMENTAL

Materials

Table 1 summarizes the materials and their function for the manufacturing of biocomposites in this study. Poly(lactic acid) (PLA), 2002D, purchased from NatureWorks LLC (Blair, IA, USA) was used as the matrix. Vinyltrimethoxysilane (VTMS), A-171, available from Crompton Osi Specialty (Greenwich, CT, USA) was used as a coupling agent and also the sauna-induced crosslinking agent. Dicumyl peroxide (DCP) was supplied from Thai Poly Chemical Ltd. (Sumutsakorn, Thailand). The diglycidyl ether of bisphenol A (DGEBA) solid epoxy, YD-019, was obtained from Aditya Birla (Bangkok, Thailand) and used as the reactive compatibilizer. The epoxidized natural rubber (ENR50) with 50% by mol. of epoxide group, employed as the toughener, was supplied by San-Thap International Co., Ltd. (Bangkok, Thailand). Talc, Jetfine® 8CF, with the averaged particle size of 1.1 µm, was purchased from Imerys Talc Luzenac France (Luzenac sur-Ariège, France). Aliphatic polyester polyols, Rayelast® A8770, as a reactive plasticizer was purchased from IRPC Polyol Co., Ltd. (Bangkok, Thailand). The mixed powder between tris(2,4-di-tert-butylphenyl) phosphate, Irgafos 168, and octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, Inganox 1076, at 1:1 by weight was employed as a heat/processing stabilizer. They were supplied from Ciba Specialty Chemicals Corp. (Tarrytown, NY, USA). The oil palm empty fruit bunch (EFB) fiber from a local palm oil refinery (Suksomboon Palm Oil Industry, Chonburi, Thailand) was employed as the main reinforcement. The USA grade cotton pulp was kindly supplied from cotton yarn weaver (Bangkok Weaving Mill Ltd., Bangkok, Thailand). Those fibers were used either as single or hybridized (combination of two fiber types) forms.

Table 1. Materials and their Function in Biocomposites

Materials	Trade Name	Function
Poly(lactic acid)(PLA)	PLA 2002D	Polymer Matrix
Oil Palm Fiber	EFB	Reinforcement
Cotton	-	Reinforcement
Epoxidized Rubber	ENR50	Toughener
Solid DGEBA Epoxy	YD-019	Reactive Compatibilizer
Talc	Jetfine® 8CF	Filler
Dicumyl Peroxide	DCP	Free Radical Initiator
Vinyltrimethoxysilane	A-171	Coupling/Crosslink Agent
Polyester Polyols	A 8770	Reactive Plasticizer
Tris(2,4-di-tert-butylphenyl) phosphate	Irgafos 168	Heat/Processing Stabilizer
Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) proionate	Inganox 1076	Heat/Processing Stabilizer

Fiber preparation

For the preparation of EFB fiber, it was soaked in water overnight. Then, the excess water was squeezed out by manual screw thread driven plate compression. The moisture-depleted fiber was mechanically crushed and heat treated in an internal mixer chamber equipped with Banbury rotors, Haake Rheomix 3000P Model 557-1306, (Thermo Fisher Scientific Inc., Berlin, Germany), at 170 °C for 15 min. The fine crushed EFB was then mercerized twice using 3% w/v sodium hydroxide (NaOH) solution at 100 °C for 4 h. The heat/chemically-treated fined fiber was finally dried in vacuum oven at 105 °C for at least

4 h. The exact procedures described were also adopted for the cotton fiber treatment, but the concentration of NaOH solution was reduced to 2% w/v. Fine-ground EFB and cotton fibers were vacuum dried. Subsequently they underwent a silane treatment by mixing the liquid silane at 3.5 phr corresponding to the mixed fibers in the internal mixer chamber at 120 °C at the rotor speed of 100 rpm for 6 min.

Biocomposite compounding and specimen preparation

Figure 3 illustrates the schematic procedures for manufacturing the biocomposite specimens in this study. First, ENR50 was plasticated and kneaded on a two roll mill for a few minutes. The solid epoxy was incorporated onto ENR50 until a smooth milky rubber mixture was obtained. Then, the treated fragments of fiber(s) together with talc powder were gradually loaded into the rubber mixture. The rubber/fiber compound was obtained after a cutting/folding kneading action for at least 15 min. The resulting compound was then kneaded into an approximately 4 mm to 5 mm thick sheet, cut into small strips, and finally pelletized into granules. The PLA-based biocomposites were manufactured using the co-rotating intermeshing twin screw extruder, Brabender Model PL2100 (Brabender®GmbH & Co. KG, Duisburg, Germany), equipped with screws having the diameter of 25 mm and L/D = 20. The PLA and rubber compound pellets were vacuum-dried at 80 °C for 4 h. The dried PLA and rubber/fiber were coated with viscous liquid polyester polyols and heat/processing stabilizer powder in a high-speed mixing chamber. The material mixture was constantly fed into the twin screw device and melt mixed at the programmed temperature of 150 °C, 160 °C, 170 °C, 180 °C, and 190 °C from feeding to die zones and at a screw speed of 15 rpm. Finally, the composite strand was pelletized.

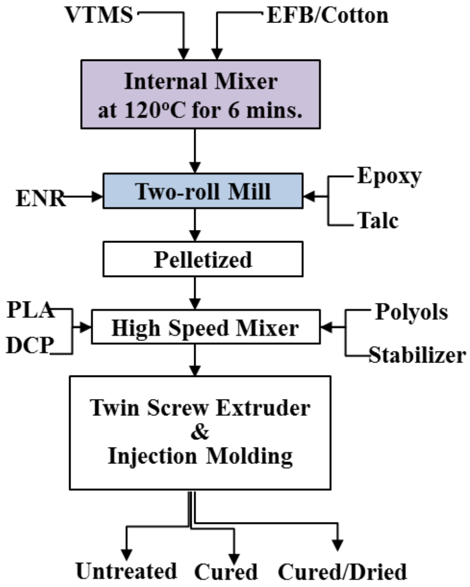

Fig. 3. Flow chart for manufacturing the biocomposite and its injection molded specimen

The test specimens were fabricated by injection molding. The composite pellets obtained from the above procedures were vacuum-dried at 80 °C for at least 2 h before undergoing injection molding. On the injection molding machine, CLF-80T (Chuan Lih Fa Machinery Works Co. Ltd., Tainan, Taiwan), the two plates mold having four cavities with edge gates was installed. The barrel temperatures for all four zones of the machine were equally set at 190 °C. The rectangular molding specimen with the dimensions, W × L × T, of 13 mm × 128 mm × 4 mm was obtained.

Typically, the injection molded composite test specimens were divided into three categorized of samples: (*i*) untreated, (*ii*) cured, and (*iii*) cured/dried samples. The "untreated" sample was annealed at room temperature for at least 24 h before testing. The "cured" specimen was obtained by placing the injection molded biocomposite in the oven saturated with water vapor at 60 °C for 12 h or *via* a sauna incubation process. The "cured/dried" sample was obtained by vacuum drying the sauna-cured sample at 80 °C for 4 h. This sauna conditioning is known as a way to accelerate the completion of the condensation reaction between the silane and water molecule or hydroxyl groups on the cellulosic fiber (Yu *et al*. 2010). In the final stage of this research study, the sauna-treated samples underwent vacuum drying at 80 °C for 4 h before testing. It was then named as the "dried cured" specimen.

Methods

The melt flow index (MFI) of the biocomposites was measured according to ASTM D1238 (2013), using the Kayeness Melt Flow Indexer (Dynisco, Inc., Franklin, Massachusetts, USA) at 190/10. The ASTM D790 (2010) three point bending flexural test was measured on a 5 kN UTM testing machine (Instron Model 5565, Norwood, Massachusetts, USA). An Izod mode impact strength, both notched and unnotched, measurement in accordance with ASTM D256 (2010), using the impact testing machine at 2.7 Joules impactor (Atlas Model BPI, Atlas Material Testing Technology LLC, Mount Prospect, Illinois, USA) was performed. The heat distortion temperature (HDT) was examined using an Atlas Testing Machine, Model HDV1 (Atlas Material Testing Technology LLC, Mount Prospect, Illinois, USA) and ASTM D648 (2007) and a 455 kPa standard load was followed. The morphology, by means of scanning electron microscopy (SEM), was investigated on the notched impact specimens. The SEM machine model JSM 6400 from JEOL Ltd. (Tokyo, Japan) was employed. The design of experiment (DOE) analysis with a degree of confidence at 95% ($\alpha = 0.05$) was performed by using Design Expert^{TM} Version 8 (Stat-Ease Inc., Minneapolis, Minnesota, USA).

RESULTS AND DISCUSSION

Design of Experiment (DOE)

The previous peer reviewed publication reported on the manufacturing and the biocomposite comprised of PLA matrix, ENR toughener, talc filler, epoxy compatibilizer, polyester polyols plasticizer, EFB/cotton hybridized fibers, and amino and epoxidized-type silane coupling agents (Meekum and Kingchang 2017). The PLA/EFB/cotton biocomposite showed outstanding thermal properties, a HDT above 100 °C, and reasonable mechanical properties. The content of the main ingredients corresponding to the PLA matrix were 50 phr of 25:75 hybridized EFB/cotton, 20 phr of talc, and 20 phr of ENR, respectively. The outstanding value of the HDT of the biocomposite material was partly contributed from the silane/polymer/fiber bonding *via* the condensation reaction, or sauna incubation, as demonstrated in Fig. 1.

With the scientific and commercial interests, the macro molecular crosslinking of the PLA matrix by the vinyl silane/peroxide system for manufacturing the biodegradable composite material was investigated and reported in this manuscript. Vinyltrimethoxysilane (VTMS), A-171, and dicumyl peroxide (DCP) were employed as the crosslink agents system. The PLA-reinforced EFB/cotton fiber biocomposite ingredients as mentioned earlier were adopted, as shown in Table 2. The optimization of the VTMS and DCP ratio was statistically evaluated by the 2^k factorial design of experiment (DOE). Thermal, HDT, rheological, MFI, and mechanical, both flexural and impacts properties, were measured and used as the design responses for the final statistical analysis. The amount of DCP and VTMS was statistically assigned as parameters A and B, respectively. The two levels, high (+) and low (-), of the designed parameters are shown in Table 1. For optimum randomization, each level was further divided into sub-levels. According to the rule of design, $2^2 = 4$, four design matrix formulas are constructed and illustrated in Table 2. The samples underwent randomized compounding in the twin screw at 190 °C and injection molding at 190 °C, and the molded samples were then conditioned. Table 3 shows the design responses after standard testing.

Table 1. DOE Design Parameters

Parameters	**Low Level (-1)**		**High Level (+1)**	
DCP (phr*)(**A**)	0.3	0.5	0.7	1.0
VTMS (phr*)(**B**)	3.0	5.0	8.0	10.0

*phr = part per hundred of resin(PLA)

Table 2. The 2^2 Factorial Design Matrix of the Biocomposite Formulations

Run	Design Parameters (g)		Biocomposite Ingredients (g)							
			Matrix			Fibers/Rubber Compound				
	(**A**) DCP	(**B**) VTMS	PLA	Polyols	Stab.*	ENR50	Cotton	EFB	Talc	Epoxy
#1	(+) 0.7	(+) 10.0	100	5	2	20	37.5	12.5	20	0.4
#2	(+) 1.0	(-) 3.0	100	5	2	20	37.5	12.5	20	0.4
#3	(-) 0.5	(+) 8.0	100	5	2	20	37.5	12.5	20	0.4
#4	(-) 0.3	(-) 5.0	100	5	2	20	37.5	12.5	20	0.4

* Stab. = Processing and thermal stabilizer

Through general observation, only the MFI of the obtained biomaterials were clearly changed with the given design parameters. The rest of the responses, HDT, impact, and flexural strengths, did not have the noticeable and statistical difference at the given level of VTMS/DCP ratio. Also, as expected, the sauna incubation, curing, and vacuum drying, curing/drying, of the samples, had a great effect only for HDT. A vast increasing in the HDT of the cured and cured/dried biocomposites was observed, which increased from a two digits HDT value, approximately 54 °C, to a three digits value, approximately 130 °C. Similar to those found when testing on the untreated samples, the mechanical properties did not have a huge change with the sauna treatment and after the removal of moisture residual from the sauna-cured sample.

Table 3. Results of the Designed Responses by Mean of MFI and HDT

Run	MFI* (g/10min)	HDT (°C)		
		Untreated	Cured	Cured/Dried
#1	4.59 ± 0.10	53.8 ± 0.3	130.1 ± 1.5	132.2 ± 1.7
#2	5.02 ± 0.31	53.6 ± 0.3	129.1 ± 1.6	129.5 ± 1.3
#3	4.49 ± 0.46	54.0 ± 0.5	127.8 ± 1.7	130.6 ± 1.7
#4	6.74 ± 0.30	54.1 ± 0.7	125.5 ± 2.5	127.2 ± 1.4

*Measured at 190 °C and 10.0 kg of standard load (190/10)

Run	Impact Strengths (kJ/m^2)					
	Notched			Unnotched		
	Untreated	Cured	Cured/Dried	Untreated	Cured	Cured/Dried
#1	6.66 ± 0.22	6.81 ± 0.24	6.79 ± 0.26	30.26 ± 3.77	26.77 ± 3.46	26.74 ± 1.79
#2	6.33 ± 0.16	6.72 ± 0.30	6.90 ± 0.31	28.40 ± 0.70	26.58 ± 2.82	26.90 ± 3.02
#3	6.72 ± 0.07	6.63 ± 0.34	6.80 ± 0.25	30.14 ± 2.31	28.59 ± 4.03	29.42 ± 3.12
#4	6.66 ± 0.16	6.93 ± 0.09	6.93 ± 0.12	30.39 ± 2.44	31.44 ± 3.84	30.27 ± 2.38

Run	Flexural Properties					
	Strength (MPa)			Modulus (GPa)		
	Untreated	Cured	Cured/Dried	Untreated	Cured	Cured/Dried
#1	80.16 ± 2.52	82.90 ± 2.93	82.10 ± 2.41	2.98 ± 0.04	3.03 ± 0.19	2.97 ± 0.16
#2	80.74 ± 1.28	84.41 ± 1.44	85.17 ± 1.53	3.06 ± 0.15	3.22 ± 0.16	3.20 ± 0.13
#3	84.82 ± 2.50	82.06 ± 0.85	83.71 ± 3.35	3.23 ± 0.40	3.11 ± 0.13	3.12 ± 0.13
#4	82.90 ± 2.20	83.04 ± 2.18	85.55 ± 1.41	3.16 ± 0.26	3.03 ± 0.20	2.93 ± 0.19

The obtained responses were considered in the DOE statistical analyses with a degree of confidence at 95% (α = 0.05) on Design Expert® Version 8 (Stat-Ease Inc., Minneapolis, Minnesota, USA), the analysis of variance (ANOVA), and the pareto charts conclusions. Results indicated that there were no absolute “significant” effects of DCP (A), VTMS (B), and the interaction between VTMS/DCP (AB), at the given designed content levels constructed in this study, on the MFI, HDT, impact strengths, and flexural properties, regardless of the sample conditionings (Kingchang 2011).

VTMS Contents and Comparison of Mixing Procedures

From the above DOE conclusion, the given designed contents of the DCP and VTMS crosslink system did not significantly affect the measured properties of the macro crosslinked PLA reinforced with the EFB/cotton hybridized fibers biocomposites.

Based on research curiosity and also due to environmental and economic concerns, the questions raised were; (*i*) what is the minimal ratio content between VTMS and DCP without ruining the outstanding HDT value of the macro crosslinked biocomposites, and (*ii*) how to minimize the procedures in the biocomposites manufacturing? The first question was both environmental and economical. Minimal DCP and VTMS ratio contents meant less chemical concentration involved in the production process and also a low unit cost of the biocomposite, consequently, by keeping the DCP content as low as 0.50 phr but varying the VTMS loading from 0 phr to 5 phr. According to the above DOE conclusion, the VTMS contents were also considered as low level. At a constant dosage of DCP, but with varied added VTMS (1 phr to 5 phr), five biocomposites compound formulations were tested as seen in Table 4.

As can be clearly visualized in Table 1, there were a number of chemicals in the biocomposite ingredients. Moreover, there were a vast variety of recipes of the physical forms that ranged from light liquid VTMS to high viscous liquid polyester polyols, and high dense power solid talc to low bulk density of pulp natural fibers. Therefore, feeding those chemicals into the twin screw extruder was one of the main obstacles. The single feeder became impossible. At the beginning stage of this work, an internal mixer and two-roll mill equipment were used to transform those chemicals into feedable materials. For example, as demonstrated in Fig. 2, sticky ENR rubber, loose pulp treated fiber, irregular flake solid epoxy, and fine talc powder were compounded onto the two-roll mill and then pelletized. The outcome of the process was a non-sticky hard rubber compound pellet. It can be dry-blended with PLA and finally coated with a high viscous polyester polyols liquid by using a high-speed mixer. The resulting mixture was feedable using the single screw feeder for the staved feeding twin screw extruder for good mixing. However, the procedures still involved many steps and equipment, was time consuming and, perhaps, high labor cost, if transferred to real commercial applications. This meant it was less economically feasible to commercialize this type of environmentally friendly material. Therefore, the above second question was justified. The preliminary modification to minimize the processing steps for manufacturing the macro crosslinked PLA/EFB/cotton biocomposites was established as the alternative method. Without doubt, the main objective was ease in the steps without ruining the main outstanding properties. Figure 4 illustrates the proposed alternative mixing procedures. The method #I was the normal practice for compounding the biocomposite described above and in the previous report (Meekum and Kingchang 2016). In this publication, the sample obtained by method #I was assigned as sample #I in this discussion. The alternate biocomposite manufacturing route for easing the processing steps was called method #II, and the obtained injection molding test specimen was assigned as sample #II. The main advantages of method #II over method #I were: (*i*) the heat/silane treatment of the hybridized fiber in the internal mixer chamber was omitted, and (*ii*) the highly viscous polyester polyols coated solid ingredients performed in the high-speed mixing chamber was finally coated with fine talc powder. The talc-coating procedure resulted in a loosely and free flowable solid mixture. It was easily and constantly fed into the twin screw extruder for melt compounding. Without the talc coating as conducted in method #I, sticky chunks of the solid mixture coated with the viscous polyester polyols were observed. Then, feeding the mixture into the twin screw mixing barrel using the single screw feeder was difficult. Fluctuation in the feeding rate and frequent blocking at the feed throat section of the twin screw were apparently experienced.

In addition, in relation to the chemical point of view, by pre-treating the fiber with VTMS in the internal mixer prior to mixing with other polymeric materials, as adopted in method #I and illustrated in Fig. 4, the fiber/polymer crosslinking was the most favored phenomenon. Alternatively, as performed in method #II, clear DCP/VTMS solution was incorporated with the polymer and rubber compound solid mixture. Therefore, the polymer/polymer crosslinking *via* the sauna incubation, as described in the reaction mechanism in Fig. 2, must be the most favored event.

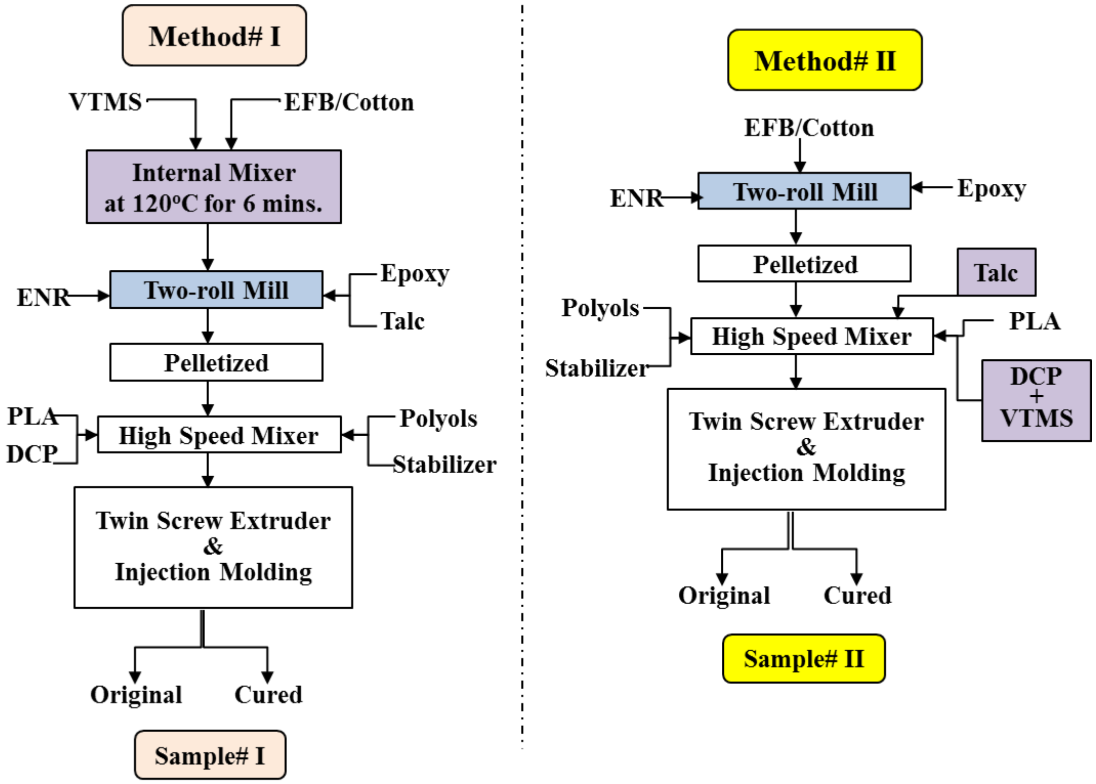

Fig. 4. Flow chart of biocomposite manufacturing process; Method # I and Method # II

After compounding the biocomposite formulations as shown in Table 4 *via* method #I and method #II, respectively, the biomaterials were injection molded into the test specimen at a processing temperature of 190 °C. Half of the molded samples were treated in the sauna oven for 12 h.

From the above DOE results, it was evidenced that there were no significant improvements on the vacuum drying of the sauna incubated samples. For that reason, the cured/dried samples were not analyzed in this experimental section. Only the untreated and cured test results were taken for discussion.

Table 4. Crosslinked PLA/EFB/Cotton Biocomposite Formulations with VTMS Contents

Formula	Biocomposite Ingredients (phr)									
	Crosslink Agent		Matrix			Rubber/Fibers Compound				
	VTMS	DCP	PLA	Polyols	Stab.	ENR	Cotton	EFB	Talc	Epoxy
VTMS#1	1.0	0.5	100	5	2	20	37.5	12.5	20	0.4
VTMS#2	2.0	0.5	100	5	2	20	37.5	12.5	20	0.4
VTMS#3	3.0	0.5	100	5	2	20	37.5	12.5	20	0.4
VTMS#4	4.0	0.5	100	5	2	20	37.5	12.5	20	0.4
VTMS#5	5.0	0.5	100	5	2	20	37.5	12.5	20	0.4

Table 5. MFI and HDT of Crosslinked PLA/EFB/Cotton Biocomposite and VTMS Contents Manufactured by Difference Methods

Formula	MFI (g/10min)		HDT (°C)			
			Untreated		Cured	
	Sample # I	Sample # II	Sample # I	Sample # II	Sample # I	Sample # II
VTMS#1	3.83 ± 0.28	3.27 ± 0.24	53.8 ± 0.3	54.3 ± 0.3	119.9 ± 4.2	126.5 ± 2.3
VTMS#2	3.53 ± 0.14	3.38 ± 0.22	53.4 ± 0.4	54.2 ± 0.3	120.5 ± 1.3	128.3 ± 2.9
VTMS#3	3.26 ± 0.32	3.41 ± 0.21	52.2 ± 0.8	53.8 ± 0.8	124.1 ± 4.2	129.2 ± 2.8
VTMS#4	4.98 ± 0.23	3.28 ± 0.21	52.7 ± 0.6	54.3 ± 0.3	128.9 ± 1.4	128.3 ± 2.1
VTMS#5	4.33 ± 0.20	4.32 ± 0.28	52.7 ± 0.3	53.7 ± 0.6	129.6 ± 2.0	127.9 ± 3.1

The MFIs of the DCP/VTMS crosslinked PLA-based biocomposite with increased VTMS loading from 0 phr to 5 phr are shown in Table 5. The MFI tended to be higher at high vinyl silane content. Meanwhile, in comparison between sample #I and sample #II at the given VTMS, a tiny degree of difference in the MFI was noticed. Within the standard deviation of MFI testing error, it could be generally stated that there was no significant difference in the compounding methods applied in this study.

Consideration of the measured HDT, again, the untreated samples showed an HDT of approximately 53 °C. The results did not depend on the silane dosing. After the sauna treatment, the HDT of the cured samples jumped to above 110 °C for both sample #I and sample #II. Moreover, in the cured sample #I, it was clearly seen that the HDTs gradually increased with an increase in the VTMS dosing. This observation enriched the mechanism of the macro chain crosslinking and fiber/polymer interfacial bonding induced by silane/moisture condensation reaction. In comparison between the HDT of the biocomposite obtained from method #I and method #II, at low VTMS contents, it was clearly noticed that method #II offered superior HDT compared to method #I, especially for the cured samples. In fact as stated above for the difference in terms of chemical aspects between method #I and method #II, the fiber/polymer crosslink was favored relative to method #I but the polymer/polymer crosslinking was likely to take place in method #II. Therefore, it could be tentatively stated that the superior HDT was most likely driven by the PLA/PLA crosslinked chain, especially at low VTMS contents. At high VTMS loading, the excess silane could do both functions, fiber/polymer, and polymer/polymer crosslinking.

In Table 6, for the given methods and conditioned samples, the tendency of both notched and unnotched impact strengths with the increased dose of VTMS on the biocomposites was difficult to rationalize. The impact strengths were minimally enhanced with increased VTMS loadings. Within the standard deviation of testing error, the conclusion could be made that the of impact strengths of the crosslinked PLA/EFB/cotton biocomposites do not depend on the VTMS usage. However, by comparison, especially between the notched samples, it was clearly seen that the impact strengths of the crosslinked hybridized biocomposite obtained from method #II were superior to the samples obtained from method #I.

Table 6. The Impact Strengths of Crosslinked PLA/EFB/Cotton Biocomposite and VTMS Contents Manufactured by Difference Methods

Formula	Impact Strength (kJ/m^2)			
	Notched			
	Untreated		Cured	
	Sample # I	Sample # II	Sample # I	Sample # II
VTMS#1	6.58 ± 0.51	7.53 ± 0.11	6.45 ± 0.24	7.53 ± 0.13
VTMS#2	6.97 ± 0.36	7.77 ± 0.16	6.76 ± 0.08	7.93 ± 0.33
VTMS#3	6.70 ± 0.13	7.60 ± 0.30	6.73 ± 0.41	8.09 ± 0.50
VTMS#4	6.98 ± 0.33	7.91 ± 0.26	6.75 ± 0.16	8.16 ± 0.25
VTMS#5	6.53 ± 0.25	7.98 ± 0.18	6.84 ± 0.34	8.43 ± 0.31

Formula	Impact Strength (kJ/m^2)			
	Unnotched			
	Untreated		Cured	
	Sample # I	Sample # II	Sample # I	Sample # II
VTMS#1	27.78 ± 2.46	28.46 ± 1.41	27.42 ± 0.59	29.38 ± 4.06
VTMS#2	32.59 ± 3.36	32.88 ± 2.52	28.73 ± 1.10	29.81 ± 4.89
VTMS#3	33.41 ± 2.26	31.76 ± 1.39	30.08 ± 4.03	32.39 ± 3.47
VTMS#4	33.99 ± 3.21	33.58 ± 5.47	30.67 ± 0.89	32.54 ± 1.14
VTMS#5	30.45 ± 2.46	32.20 ± 4.42	30.58 ± 4.61	29.34 ± 1.27

The better impact toughness of sample #II can be explained, again, by the polymer/ polymer direct crosslink of the peroxide/silane *via* the sauna treatment. In fact, there are not only PLA chains in the matrix phase, but the ENR chains are also present. Therefore, during the crosslink reaction, free radicals could undergo an initiation reaction with the vinyl segments of the ENR backbone. The resulting silane-grafted rubber would finally undergo crosslink during the sauna incubation. The crosslinked rubber chains would enhance the impact toughness properties of the biocomposites. In contrast, as mixing in method #I, the crosslink structures would be mainly present between the fiber and polymer. Hence, the toughening enhancement *via* the rubber crosslinking would not occur.

Table 7. Flexural Properties of Crosslinked PLA/EFB/Cotton Biocomposite and VTMS Contents Manufactured by Different Methods

Formula	Flexural Properties			
	Strength (MPa)			
	Untreated		Cured	
	Sample # I	Sample # II	Sample # I	Sample # II
VTMS#1	84.98 ± 1.92	82.25 ± 3.09	84.43 ± 3.21	83.84 ± 1.84
VTMS#2	81.61 ± 2.01	80.41 ± 3.12	81.60 ± 2.83	83.34 ± 2.97
VTMS#3	78.36 ± 1.63	78.26 ± 3.15	80.38 ± 0.79	81.19 ± 0.64
VTMS#4	77.11 ± 2.40	78.33 ± 1.46	80.40 ± 1.60	81.77 ± 0.92
VTMS#5	76.63 ± 2.23	77.69 ± 1.76	77.60 ± 2.09	79.24 ± 1.38

Formula	Flexural Properties			
	Modulus (GPa)			
	Untreated		Cured	
	Sample # I	Sample # II	Sample # I	Sample # II
VTMS#1	3.27 ± 0.24	2.86 ± 0.18	3.32 ± 0.10	2.88 ± 0.12
VTMS#2	3.24 ± 0.07	2.99 ± 0.25	3.12 ± 0.08	2.78 ± 0.11
VTMS#3	2.95 ± 0.28	2.83 ± 0.22	3.02 ± 0.11	2.77 ± 0.08
VTMS#4	3.03 ± 0.07	3.00 ± 0.14	2.82 ± 0.08	2.72 ± 0.08
VTMS#5	2.94 ± 0.17	2.98 ± 0.05	2.83 ± 0.08	2.64 ± 0.06

The flexural strength and modulus of the hybrid biocomposite, as reported Table 7, revealed that the flexural characteristics were decreased by increasing the silane contents, in both mixing methods. Moreover, at all given VTMS contents, the sauna-curing had a marginally superior effect on the flexural properties. It seemed that the fractional degree of improvement on the test's value was likely and proportionally directed to the VTMS content. The decreasing trend of the three point bending flexural properties at high vinyl silane dosing would indicate that the more silane present the more network structures both fiber/polymer and polymer/polymer linkages were formed. Consequently, the brittleness of the thermoset polymer in the matrix phase would be increased. Generally, at the given VTMS added, the flexural strength of the biocomposite prepared by method #II was superior to the method #I. In contrast, the opposite trend was found for the flexural modulus. Typically, a high flexural strength and modulus is characteristically normal of the brittle thermosets. *Vice versa*, a high flexural strength, but low modulus is commonly observed in tough thermoplastics. Within the flexural indicators found in this work, it could be concluded that the sample #IIs were tougher than the sample #Is. As stated in the above conclusion, the crosslinked ENR rubber chains, most likely occurring in method #II, would supplementary enhance the toughness properties of the biocomposites.

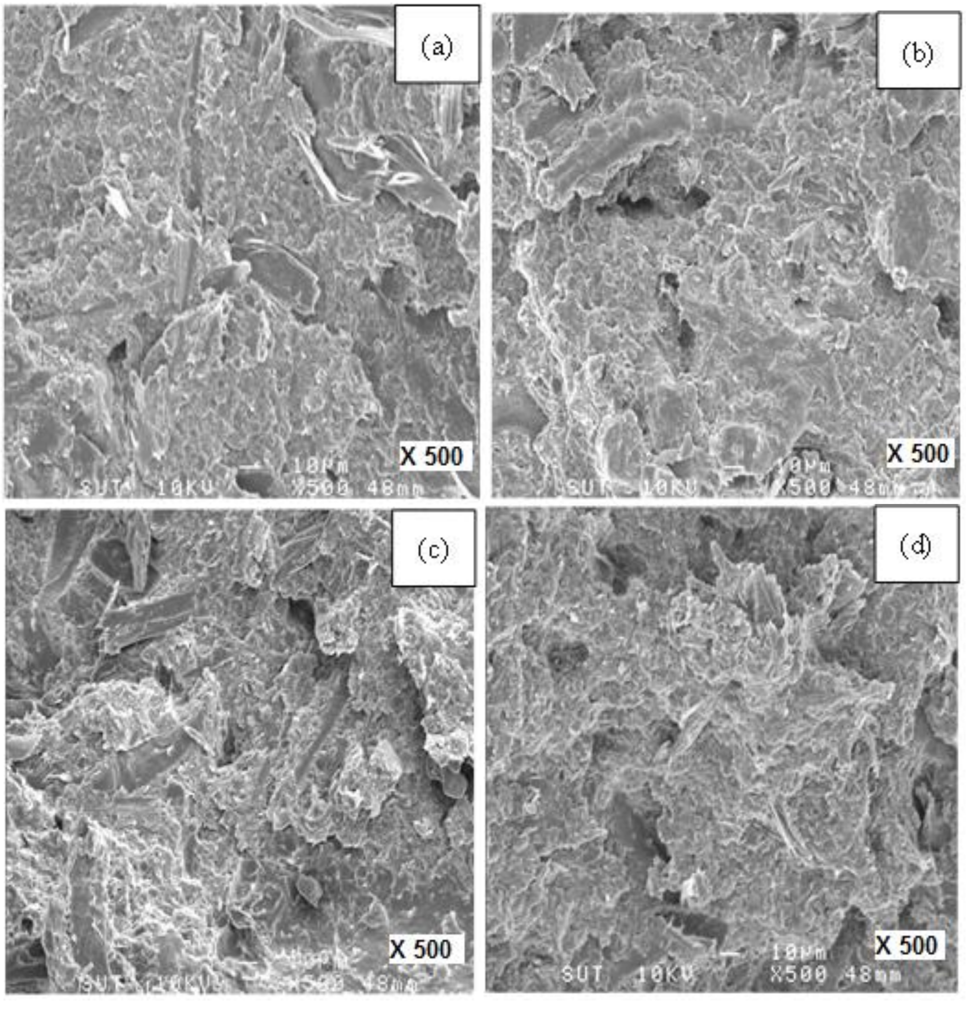

Fig. 5. SEM photographs of the crosslinked PLA/EFB/cotton hybridized biocomposite with 5 phr of VTMS dosing; (a) sample # I (untreated), (b) sample # II (untreated), (c) sample # I (cured), and (d) sample # II (cured) (X500)

Figures 5 (a) through 5 (d) illustrate the fractured surface SEM photographs of the crosslinked PLA/EFB/cotton hybridized biocomposites that were manufactured using 5.0 phr of VTMS and compounded by method #I and method #II, respectively. By employing the mixing method #I, the fractured surface of the untreated and cured samples, as shown in Fig. 3s (a) and (c), were almost identical. The improvement in fiber/matrix interfacial adhesion that resulted from the sauna treatment was not clearly observed. These SEM images could be used to reinforce the above impact test results that there were no significant impact enhancement through the sauna treatment of the sample. The similar SEM evidence was also found within the samples mixed by method #II. However, by careful SEM observation of the samples prepared by method #I and method #II, the differences on the broken traces at the matrix phase are clearly visualized. The rougher fractured surface was seen on the method #II samples, both untreated and cured, in which the crosslink agents, DCP/VTMS, were directly added onto the PLA/ENR rubber compound solid mixture. Commonly, a rough fractured surface is evidence that can confirm the high toughness properties of polymeric materials. Therefore, with the SEM investigation taken into consideration, it could strongly strengthen the above conclusion that, with the presence of peroxide/silane and compounding the biocomposites by method #II the polymer/polymer and polymer/rubber crosslinking formed as proposed in the previous work (Han *et al*. 2010). Such networks enhanced the fracture toughness of the biocomposite. *Vice versa*, the PLA/fiber crosslinking *via* a silane/peroxide reaction, that principally occurred by biocomposites compounding employed in method #I, would enhance only the polymer/fiber adhesion (Kuan *et al*. 2006). However, it was not sufficient for enhancing the toughness of the biocomposite material.

From the results manifested in this study, two statements can be drawn about the DCP/VTMS ratio content and compounding methods. For environmental and economic considerations, without ruining the outstanding HDT and mechanical properties, the minimal DCP and VTMS ratio of 0.5 phr to 1 to 2 phr can be recommended as the peroxide/silane crosslink system. The method #II mixing route, in which the DCP/VTMS crosslink reagents were directly added onto the PLA/ENR rubber compound, was preferred. Favorable properties of the biocompositesly were tentatively attributed to the levels of polymer/polymer and polymer/ENR crosslinks. The direct mixing *via* method #II shortened the working procedures in the manufacturing process and achieved better properties. The ease of machining and avoiding the need for an internal mixer in method#II, for the manufacture of biocomposites, was also beneficial in term of costs and energy savings.

CONCLUSIONS

1. In the manufacturing process of the crosslinked poly(lactic acid) (PLA) composites reinforced with empty fruit bunch (EFB) and cotton, the design of experiments (DOE) study concluded that the ratio of dicumyl peroxide (DCP) and vinyltrimethoxysilane (VTMS) in the ranges considered did not have a significant effect on the assigned responses.
2. Regarding the environmental and economical aspects, minimization of the VTMS dosage to 0.5 phr of DCP can be recommended. Without ruining the high HDT at above

100 °C and maintaining reasonable flow and mechanical properties, a VTMS content at 1 phr to 2 phr can be recommended.

3. Justification of the mixing methods for producing the crosslinked PLA/EFB/cotton hybridized biocomposites was established. Taking the process line/time and engineering properties into consideration; shorter, easier to process, and better properties of the obtained biocomposites, the production method by the direct addition of the DCP/VTMS crosslink agent onto the PLA/rubber compound, mixture and feeding into twin screw extruder for melt mixing was chosen. A HDT above 100 °C resulted in an improved toughness of the biocomposite material. The PLA/PLA and PLA/ENR crosslinks *via* the silane/moisture condensation during the sauna incubation was the prime explanation for the effects.

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