The Effect of Dynamic Vulcanization on the Mechanical and Thermal Properties of Stereocomplex PLLA/PDLA/rubber Blends

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Abstract. This study investigated the influence of dynamic vulcanization of stereocomplex PLA/PDLA (ST) containing various types of rubbers by using dicumyl peroxide (DCP) as a vulcanizing agent. In this work, natural rubber (NR), isoprene rubber (IR), silicone rubber (SI), acrylic rubber (AR), thermoplastic copolyester (TPE) and thermoplastic polyurethane (TPU) were selected. Here, 5 wt% of PDLA, 15 wt% of rubber and 2 wt% DCP as an initiator were melt-blended with PLA in an internal mixer at 180 °C and 50 rpm. It was found that the addition of DCP in (NR and IR) led to a significantly increase in the impact strength and % elongation at break. On the other hand, for the rubbers that do not have double bonds in the main chain (SI, AR, TPE and TPU), the addition of DCP led to a decrease in impact strength and % elongation at break compare to the case without DCP due to the lack of double bonds to react with DCP. For the effect of DCP on the rubber dispersion, it was found that the addition of DCP on the NR and IR could improve the interface compatibility of the rubber and PLA leading to smaller average rubber domain sizes than without DCP. For other types of rubbers, the average rubber domain sizes were bigger with poorer interface compatibility than without DCP. For the effect of DCP on the crystallinity, it was found that the addition of DCP could increase the crystal density and could consequently reduce the crystal sizes of the ST/rubber blends.

1. Introduction
PLA has been used in a broad range of medical applications, including drug delivery systems and tissue engineering [1-5]. However, the major deficiencies of PLA that limited its wider range of applications are low thermal resistance and high brittleness. Many researches have attempted to improve the thermal properties of PLA. A few studies have focused on the addition of inorganic fillers which act as heterogeneous nucleation sites for PLA crystals. Urayama et al. (2003) [6] found that talc was the most effective nucleating agent for PLLA. Even though the addition of a nucleating agent could enhance the crystallization rate of PLA, it decreased its toughness. One of the interesting methods to induce crystallization of PLA without introducing alien inorganic components is by using stereocomplex crystals formed by the enantiomeric blends of PLLA and PDLA. Ikada et al. (1987) [7] reported that the 50:50 blend of PLLA and PDLA produces a stereocomplex with the melting temperature (T_m) around 230 °C, which is 50 °C higher than the melting points of its homocrystal counterparts. Yamane et al. (2003) [8] studied the effect of PDLA on the thermal property of PLLA. They found that a small amount of PDLA could significantly enhance the crystallization of PLLA by forming stereocomplex crystallites in the PLLA matrix. The stereocomplex structure with small
amount of PDLA (1-5 wt%) could improve the heat tolerance, tensile strength and Young’s modulus of PLA. For the improvement in toughness of PLA, citrate ester, triacetin, poly(ethylene glycol) (PEG) and other small molecules have been reported as efficient plasticizers for PLA [9-13]. However, blends of PLA with plasticizers caused a blooming problem when used at high concentration. The elastomers such as commercial natural and synthetic rubbers, as well as thermoplastic elastomers are better choices for improving the toughness of PLA because it is extremely tough and easy to process without a blooming problem. Bitinis et al. (2011) found that the optimal NR content to improve the brittleness of PLA was 10 wt%, where the tensile tests of the samples showed a drastic increase in the average elongation at break from 5% to 200% [14]. Kowalczyk and Piorkowska (2012) researched mechanisms of plastic deformation in biodegradable poly(lactide/poly(1,4-cis-isoprene) blends and found that incorporation of only 5 wt% of the poly(1,4-cis-isoprene) rubber could significantly increase the strain at break by 3 fold and impact strength by 1.81 fold, respectively [15]. Petchwattana and Covavisaruch, (2014) studied the toughness improvement of PLA/rubber wood sawdust composites by using acrylic core-shell rubber (CSR). They found that 5% of CSR could improve the impact strength of the composite by more than five times with improved tensile elongation at break [16]. Rui-lei et al. (2014) studied the improvement in toughness of PLA by melt blending it with bio-based polyurethane elastomer (TPU). They found that 15 wt% of TPU had the highest improvement in impact strength from 4 kJ/m² to 9 kJ/m² [17].

In our group, we found that the improvement in toughness and impact strength by adding rubbers came with the sacrifice of lower thermal resistance. It seems that less attention has been paid to resolve both problems simultaneously. Because most rubbers and polymer were not naturally compatible and they required one or more steps to make them compatible, the dynamic vulcanization using peroxide as crosslink agent is a simple technique that has been widely applied. The free radicals obtained from decomposed peroxides could promote chain scission, branching, crosslinking or any combination of the three, which affect the mechanical and thermal properties of polymers. For decades, dynamic vulcanized of various polymer/rubber systems [18-29] have already been investigated. They suggested that dynamic vulcanization could lead to fine morphologies and better interfacial interaction [30-36]. For PLA, Rytlewski et al. (2011) [37] studied the influence of DCP content on thermal and mechanical properties of PLA. They found that the only 0.2 wt% of DCP led to higher % crystallinity and adding of DCP (above 0.4 wt%) caused crosslinking of PLA and led to the decrease in molecular weight due to decomposition and degradation processes. Moreover, the high content of DCP led to a significant decrease in the tensile strength and impact strength. Daosheng et al. (2014) [38] studied the use of 1.5 wt% DCP in PLA/NR blend at the PLA:N R ratio of 60:40. They found that DCP led to an increase in impact strength from 5 kJ/m² to 40 kJ/m² compared to neat PLA and an increase in % elongation at break from 30% to 120%. Moreover, the addition of DCP could increase the percent crystallinity of PLA/NR from 9.71% to 15.44% compared to neat PLA. Nevertheless, there is only one research article reported on the use of DCP in the PLA/PDLA stereocomplex system. Wan-jie et al. (2017) [39] investigated the effect of dynamic vulcanization using DCP in the PLLA/PDLA/bioelastomer (BE) blends. They found that the addition of DCP (0.1 wt%) in PLLA/BE enhanced the impact strength from 50 J/m to 600 J/m and they also found that the addition of PDLA (only 10 wt%) in the blend(70%PLLA/20%BE10%PDLA) had the best impact strength and excellent heat resistance. In this paper, the effect of dynamic vulcanization using dicumyl peroxide (DCP) as a cross-linking agent has been applied to various rubber-toughened stereocomplex PLA/PDLA systems. The rubbers used in this study included natural rubber (NR), isoprene rubber (IR), acrylic rubber (AR), acrylic core-shell rubber (CSR), thermoplastic polyester (TPE) and thermoplastic polyurethane (TPU). The effect of DCP on the crystallization, morphology, and mechanical properties of the blends has been systematically investigated.
2. Materials and Methods

2.1 Materials
Polyactic acid, PLA (4043D) used in this study was produced by NatureWorks Co. Ltd., USA. Poly (D-lactide) (PDLA) grade D100H with Mₘ = 40-45 kg/mol was purchased from Sulzer ChemTech Co. Ltd. PLA and PDLA were dried at 70°C for 24 hours in a hot air oven before use. Polyisoprene (IR) grade IR2200 and acrylic rubber (AR) grade ACRON 801 were obtained from Innovation Group Co. Ltd., Thailand. The thermoplastic polyester (TPE) grade ARNITEL EM 400 and thermoplastic polyurethane (TPU) grade WHT-1195IC were purchased from Ableone Engineering Co. Ltd., Thailand. Liquid silicone rubber (SI) grade RTV S815 was purchased from Super-Silicone and Resin Art Co. Ltd., Thailand.

2.2 Preparation of the rubber-toughened PLA/PDLA blends
The melt blending of PLA/PDLA with a rubber was carried out in an internal mixer at 180 °C with the rotor speed of 50 rpm. The ratio of PLA to PDLA was 95:5 by weight and the rubber content was fixed at 15 wt%. The amount of DCP was fixed at 2.0% by weight of the rubber. The mixing began by feeding PLA and PDLA into the internal mixer, which was set at 180 °C. The specified amount of rubber and DCP were added at 2 and 5 minutes, respectively, while the total mixing time was 12 minutes. The blend sample was compression molded at 190 °C for 15 minutes before further characterization. Here, the compound of PLA with PDLA is denoted as ST a and the blend of ST with xx rubbers is denoted as ST/xx. In addition, the blend of ST/xx with DCP is called ST/xxD.

2.3 Characterization
2.3.1 X-ray diffraction (XRD). XRD is primarily used for distinguishing between amorphous and crystalline portions of a material and for quantifying the percent crystallinity of a sample. Wide-angle X-ray diffraction (WAXD) measurements of a compression-molded specimen were carried out with a DX-1000 X-ray diffractometer (Dandong Fanyuan Instrument Co. LTD, China) using a Cu Kα radiation source (λ = 0.154 056 nm, 40 kV, 25 mA) in the scanning angle range of 20 = 5°-40° at a scan speed of 3°/min. The percent crystallinity of the homocrystals (%X hc) and stereocomplex crystals (%X sc) were calculated using the following equations:

\[ X_{hc} (\%) = \frac{I_{hc}}{I_{hc} + I_{isc} + I_{tamor}} \times 100 \]  \hspace{1cm} (1)

\[ X_{sc} (\%) = \frac{I_{sc}}{I_{hc} + I_{isc} + I_{tamor}} \times 100 \]  \hspace{1cm} (2)

where \( I_{hc} \) is the integrated intensity of homocrystals, \( I_{sc} \) is the integrated intensity for the stereocomplex crystallites and \( I_{tamor} \) is the integrated intensity of the amorphous portion.

2.3.2 Differential scanning calorimetry (DSC). The thermal properties of PLA and ST/rubber blends were investigated by a METTLER TOLEDO (DSC 3) differential scanning calorimetry (DSC) at the heating rate of 10 °C/min from 50 to 230 °C.

2.3.3 Mechanical properties. Tensile tests were performed according to ASTM D 638 type I on an Instron machine Model 5969, Instron Engineering corporation USA, at 25°C, with the cross-head speed of 5 mm/min. Dumbbell-shaped specimens were cut from the compression-molded sheet prepared at the pressure of 1500 psi and 190 °C. At least five specimens of each sample were tested to determine the mean value of the results. The notched Izod impact tests were measured according to ASTM D256 by the Rasil impactor using the pendulum energy of 2.75 J at 25 °C. For this measurement, the samples were cut, notched, and kept in desiccators overnight before the tests.

2.3.4 Morphology of the blends by SEM. The size and dispersion of rubber domains in the ST matrices were observed on the freeze-fractured surfaces of the samples using a scanning electronic microscope (SEM) (Camtrad, JEOL MX2000 operated at 5-15 keV). The fractured surfaces after impact tests of
selected samples were also observed by SEM to investigate the fracture behavior of the blends. All samples were coated with gold before SEM analysis.

3. Results and Discussion

3.1 Characteristics of ST and ST/rubber blends

In this part, the stereocomplex formation of PLA/PDLA was confirmed by XRD and DSC. The XRD profile of PLA and ST in Figure 1 illustrated that, even though the PDLA content was only 5 wt%, the stereocomplex crystals were successfully formed. The characteristic of ST peaks were observed at the 2θ of 12.0°, 20.9°, and 24.0°, which were assigned to the (110), (300)/(030), and (220) planes of stereocomplex crystals [40]. On the other hand, the characteristic peaks of PLA homocrystals were at the 2θ of 14.8°, 16.9°, 19.0°, and 22.5° corresponding to the α or β-form of PLA homocrystals[16]. The amorphous portion of the blend was indicated by the underlying broad peak. From the DSC pattern in Figure 2, the characteristic of stereocomplex crystals was indicated by the high melting point peak at around 220 °C, which could pose a potentially improved heat tolerance of the sample.

![Figure 1. Wide-angle X-ray scattering profiles of PLA and ST](image1)

![Figure 2. DSC heating curves of PLA, PDLA and ST](image2)

3.2 The effect of DCP on mechanical properties

In this section, the effect of dynamic vulcanization was investigated on rubber-toughened stereocomplex PLA/PDLA systems by using 2.0 wt % of DCP as a radical initiator. The rubber blends with PLA were categorized by the double bonds in rubber main chains. NR and IR were classified as unsaturated rubbers, whereas SI, AR, TPE and TPU were classified as saturated rubbers. The effect of DCP on the impact strength, % elongation at break and tensile strength of ST/rubber blends are demonstrated in Figures 3-4, respectively. It can be seen that the addition of DCP in PLA or ST led to decreased impact strengths, which was from 27 J/m to 22 J/m for neat PLA and from 31 J/m to 28 J/m for ST. This was probably because high DCP content could cause a chain scission reaction in PLA chains [17]. For the ST/rubber blends, it was found that DCP could significantly improve the interfacial adhesion between unsaturated rubbers (NR) and (IR) and PLA matrix as observed by
smaller rubber domain sizes (Figure 5 and 6) leading to improved impact strength, tensile strength and % elongation at break of the blends (Figures 3-4). This was probably because DCP could easily react with the double bonds in the rubber chains and thus provide improved linkage between the rubbers and PLA. However, for the blends of ST with saturated rubbers (SI, AR, TPE, and TPU), the addition of DCP led to significant decreases in the impact strength, tensile strength and % elongation at break with increased rubber domain sizes. This finding is consistent with a previous work, which reported that the reaction of DCP in miscible blends tended to induce phase separation, where the dispersed domain sizes increased from nanometer range to sub micrometer range [41]. However, in case of PLA/TPU, Shi et al. (2014) [42] reported that the addition of DCP at the lower content of 0.2 wt% could improve impact strength by nearly 3 times of the unmodified PLA/TPU blend with a decrease in rubber size.

**Figure 3.** The impact strength of the ST/rubber blends without and with DCP.

**Figure 4.** % Elongation at break and Tensile strength of ST/rubber blends without and with DCP.
3.3 Effect of DCP on thermal properties

The crystallization behaviors of ST/rubber blends with DCP were compared to those without DCP by XRD technique. The XRD profiles of the blends are not shown and the percent crystallinities of the blends are summarized in Table 1. For neat PLA, it was found that crystalline peaks could not be detected from XRD (Figure 1). This is probably because the PLA sample used in this work was processed the same way with the PLA/rubber blends without annealing to control the similarity in their process conditions and cooling pattern. It was found that the addition of DCP into neat PLA, ST, and all ST/rubber blends could lead to significant increases in the percent crystallinities of both of homo and stereocomplex crystallize. In particular, the percent crystallinity of ST with DCP increased by 62.7%. With the presence of unsaturated rubbers, the percent crystallinity of ST/NR and ST/IR increased by 12.8% and 47.4%, respectively. Whereas, for the blends with saturated rubbers, the percent crystallinity of ST/SI, ST/TPE and ST/TPU increased by 18.5%, 32.8% and 56.1%.
respectively. For ST/AR, the percent crystallinity did not increase much with the presence of DCP as its original value was already high. These results indicated that the DCP could contribute to improvement in the crystallization of PLA phase, possibly due to the enhanced chain mobility or improved heterogeneous nucleation effect [43]. In addition, according to Scherrer equation [44], it was found that the relative intensity of the blends with DCP was higher than the blends without DCP indicating that the crystal sizes of ST/rubber blends with DCP were smaller than those without DCP.

Table 1. The percent crystallinity calculated from XRD profile

| Formulation | %Xc (Homo) Without DCP | %Xc (Homo) With DCP | %Xsc (Stereocomplex) Without DCP | %Xsc (Stereocomplex) With DCP |
|-------------|------------------------|---------------------|-----------------------------|-----------------------------|
| ST          | N/A                    | N/A                 | 4.13                        | 6.72                        |
| ST_NR       | N/A                    | 1.11                | 3.98                        | 4.49                        |
| ST_IR       | N/A                    | 2.09                | 3.86                        | 5.69                        |
| ST_SI       | N/A                    | 3.07                | 4.64                        | 5.50                        |
| ST_AR       | N/A                    | 2.97                | 4.89                        | 4.92                        |
| ST_TPE      | N/A                    | 2.69                | 4.03                        | 5.35                        |
| ST_TPU      | N/A                    | 2.96                | 3.49                        | 5.45                        |

* N/A = the crystals were not detectable.

4. Conclusions
The dynamic vulcanization of stereocomplex PLA/PDLA in the presence of various rubbers was successfully prepared in an internal mixer by using 2 wt% DCP as a radical initiator. From the results, the addition of DCP in unsaturated rubber blends led to a significant increase in the impact strength, tensile strength and % elongation at break with smaller rubber domain sizes. This is probably because the addition of DCP into unsaturated rubbers could improve phase interaction and crosslink the rubber. On the other hand, for saturated rubber blends, the addition of DCP led to decreases in impact strength, tensile strength and % elongation at break with increased rubber domain sizes. On the other hand, saturated rubbers already had excellent phase interaction without DCP as indicated by originally very small rubber domain sizes. The addition of DCP led to poorer phase interactions leading to bigger average rubber domain sizes. For crystallization properties, the addition of DCP in ST/rubber blends could increase the % crystallinity and reduce the crystallite size of both homo and stereocomplex crystals in the blends.

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