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ORIGINAL PAPER

Influence of mold temperature and annealing on the microstructure and mechanical properties of ESO-plasticized PP/CL composites

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ABSTRACT

Composites of polypropylene (PP) and calcium lactate (CL) with a constant weight percentage of 60% and 40%, respectively, were compounded with 3, 5 and 7 phr of epoxidized soybean oil (ESO) plasticizer using an internal mixer. The testing samples were prepared using an injection molding technique. The effects of the mold temperature and annealing treatment on the morphological and mechanical properties of PP-based composites using polarized optical microscopy (POM), differential scanning calorimetry (DSC), universal testing machines (UTM), and impact tester were performed. The results showed a remarkable increase in the elongation-at-break and impact strength, but a noticeable decrease in tensile strength and stiffness with increasing ESO contents. The experimental results also indicated that the higher mold temperature significantly improved the tensile strength and stiffness of samples due to an increase in spherulite size for neat PP, PP/CL composite and PP/CL composite with 3 phr of ESO. Additionally, annealing treatment enhanced the tensile and impact strengths of both neat PP and PP/CL composite, which was attributed to the increase in the crystal perfection and degree of crystallinity. These findings suggested that mechanical improvements using high mold temperature and annealing treatment were confined to the incorporation of an ESO plasticizer. The resulting performance of the plasticized PP composites after thermal treatment was described by two possibilities: the loss in the adhesion between the components and the migration of plasticizer. **Polyolefins J (2024) 11: 265-275**

Keywords: Polyolefins; structure-properties relations; crystallization; injection molding; polymer-matrix composite.

INTRODUCTION

Polymer composites are one of the most important engineering materials. The application of polymer composites has been widely used in various fields, such as automotives, food packaging, electronics, and aerospace [1]. Because of the growing environmental awareness, the use of synthetic filler-based composites is now critically considered. Due to its biodegradability, renewable filler-reinforced materials are becoming attractive. Hence, many researchers pay attention to the use of petroleum-based thermoplastic filled with

fillers extracted from natural and renewable resources. In general, the mechanical and thermal properties of commodity polymers, such as polypropylene (PP), polyethylene (PE), and polystyrene (PS), can be improved by incorporation of natural fillers. Diverse natural-based fillers have been integrated with petroleum-based thermoplastic, including biochar [2], sawdust [3], spent coffee grounds [1], coir fiber [4], microfibrous cellulose [5], hemp fiber [6], etc. Usually, when filler is added to a polymer matrix to enhance

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the stiffness and strength, the decrease in flexibility is unavoidable. To balance both mechanical properties, the addition of plasticizer is one of the most useful techniques. Due to its biodegradability, plasticizer deriving from renewable plants is employed as a beneficial choice, such as clove essential oil (CEO), linseed oil (LO), tung oil anhydride (TOA), epoxidized palm oil (EPO), epoxidized soybean oil (ESO). Among them, ESO is widely used due to its good compatibility with bioplastics like polylactic acid (PLA). The incorporation of ESO has been reported to improve the mechanical properties of the PLA composites, especially the flexibility [7-13]. The mechanical improvement by ESO is also possible in the petroleum-based thermoplastic matrix [14-15]. The use of combined ESO and TOA led to an increase in the impact resistance and revealed a rough fractured surface, implying the plasticization effect of the ESO and TOA [14]. Besides, EOS grafted with poly(12-hydroxysterate) (PHS) improved the compatibility between microcrystalline cellulose and PP, thus enhancing the mechanical properties [16].

Numerous studies have highlighted that the morphological structure, controlled by crystallization during processing, significantly influences the properties of polymers. The crystallization is determined by thermal conditions during injection molding [17,18]. The adjustment of the processing variables and their effects on the properties of polymer composites has been well-reported [19,20,21]. One key finding is that mechanical properties can be enhanced by optimizing mold temperature. The effect of mold temperature has been extensively explored by researchers, with studies showing a strong correlation between morphological structure and mechanical properties. These results consistently indicate that increased mechanical performance is associated with a higher degree of crystallinity and larger spherulite size [17,20,22-24,25,26]. Moreover, the mold temperature also influenced the form of spherulitic structure. At low mold temperatures, where cooling rates are rapid, the formation of a mesophase in PP can be observed [27]. On the other hand, the α form of PP appears at high mold temperature (slow cooling rate). In most cases, the mesophase provides a noticeable increase in ductility and flexibility while the α form contributes a distinct increment in stiffness and rigidity [27]. Furthermore, annealing is one of the most important methods to improve the performance of polymer after molding. This post-processing method is performed at the elevated temperature

between glass transition temperature (T_g) and melting temperature (T_m). Therefore, it has been reported that the annealing method can promote molecular chain relaxation and induce a change in morphological and mechanical properties of polymers [21,28-30,31,32, 33,34]. In previous work, the addition of calcium lactate (CL) produced by a fermentation of lactic acid in the production of PLA was shown to increase both tensile and flexural stiffnesses of PP. However, the reinforcement effect of CL is accompanied by a reduction in the flexibility of PP [35].

In this study, to balance the performance of material, plasticized PP/CL composites were prepared with the inclusion of the ESO. The synergistic effect of mold temperature and annealing treatment on the properties of plasticized PP/CL composites was elucidated. The mechanical properties of the plasticized composites were performed, and their thermal transition and morphology properties were also examined. The discussion focused on the interplay between the variant factors.

EXPERIMENTAL

Materials
Polypropylene (PP) with a melt flow index of 22 g/10 min (Moplen HP553R) was supplied by HMC polymers Co., Ltd. Calcium lactate (CL) was purchased by PURAC. Epoxidized soybean oil (ESO) was supported by Srithepthai Chemical Co. Ltd. Preparation of composites

From our earlier work [35], PP/CL composites showed an optimum mechanical property with the addition of 40 wt.% of CL and were chosen to use in this work. ESO was added at different phrs (3, 5, and 7 phr) to the PP/CL composites. The PP/CL weight proportion was maintained at 60/40 for all plasticizer contents. The number following the notation PP/CL/ESO indicates the percentage of ESO relative to the PP/CL content. The mixture was initially processed using an internal mixer (MX500, Chareon Tut, Thailand), with rotor speeds set to 60 rpm and a chamber temperature of 190°C for 25 min. Then, the compound was pelletized by a co-rotating twin screw extruder (CTED22L32, Chareon Tut, Thailand) at a rotating speed of 60 rpm. The temperature profile of the extruder was set at 180, 190, 200, and 210°C from the hopper to the die. Subsequently, the extruded materials were shaped into testing part by injection molding (60SE, JONWAI, Taiwan). The temperature

from the feed to the nozzle was set as 160, 170, 180, and 190°C. In the selected case, an annealing treatment was conducted at 120°C for 6 h in an oven (UF110, Memmert, Germany). The condition of the annealing treatment was chosen according to the literature [30]

Fourier transform infrared spectroscopy (FTIR)

The chemical compositions of the PP, CL, and ESO and interaction between them were investigated by FTIR (Frontier, Perkin-Elmer, USA). All spectra were recorded within a wavenumber in the range of 4000-500 cm^{-1}.

Melt flow index (MFI)

The melt flow index of all samples was accomplished according to ASTM standard D1238 using a melt flow indexer (MP1200, Tinius Olsen, USA). The testing weight of 2.16 kg was used and the temperature of 210°C was set.

Differential scanning calorimetry (DSC)

A thermal transition test was performed using differential scanning calorimetry (DCS25, TA Instruments, USA). A sample in the range of 5 to 10 mg was weighted and put in the aluminum pan. Two heating-cooling cycles from 0°C to 200°C with a heating and cooling rate of 10°C /min were operated under a nitrogen atmosphere. In order to get rid of the processing history, the sample was held at 200°C for 5 min. The degree of crystallinity (X_c) was calculated according to the following equation:

$$X_c(\%) = \left(\frac{\Delta H_m - \Delta H_c}{\Delta H_m^o \times w_{pp}} \right) \times 100$$

where ΔH_m^o is the melting enthalpy for theoretically 100% crystalline PP, ΔH_c is the enthalpy of the crystallization process, ΔH_m is the enthalpy of the melting process, and w_{pp} is the weight fraction of PP. In the work, a value of 209 J/g was taken as the ΔH_m^o [5].

Polarized Optical Microscope (POM)

A polarized optical microscope (DM2700M, Leica) was used to visualize the spherulite structure of the samples. Thin sections of 10 micrometers were sliced from the middle of the samples by using a rotary microtome (RM2235, Leica, Germany).

Mechanical properties test

Universal testing machine (Model 25ST, Tinius Olsen, USA) was used to perform the tensile testing in accordance with ASTM D638 using a 5 kN load cell and a crosshead speed of 50 mm/min. The tensile strength, Young's modulus, and elongation-at-break were measured and recorded. An impact testing machine (IT504, Tinius Olsen, USA) with a pendulum energy of 5.64 Jules was used to carry out the notched Izod impact testing according to ASTM D256. At least five specimens were tested for each measurement.

RESULTS AND DISCUSSION

The FTIR spectra of all samples are presented in Figure 1. The spectrum of neat PP can be observed at outstanding peaks, including 840 cm^{-1}, 1375 cm^{-1}, 2952 cm^{-1}, describing the stretching vibration mode of the C-CH_3 bond, symmetric bending vibration of the -CH_3 group, and asymmetric stretching vibration of the -CH_3 group), respectively, Furthermore, absorption peaks of 972, 997 and 1165 cm^{-1} which reveals the rocking vibration mode of the -CH_3 group are detected. All the preceding quoted absorption peaks are associated with the methyl group in the neat PP [36]. In addition, the symmetric bending, symmetric stretching, and asymmetric stretching of the -CH_2- group of neat PP are detected at the spectrum peaks, including 1455, 2838, and 2917 cm^{-1}, respectively [36]. In the case of PP/CL, the vibration of various C-O bonds is found at the absorption peaks near 1127, 1097, and 1046 cm^{-1}, and the carboxylate (COO-) groups are revealed at 1571 cm^{-1} [37-38]. For PP/CL/ESO, the prominent peaks at 1738 cm^{-1}, representing the C=O stretching of the ester group and the C-O-C asymmetric stretching vibration of the epoxy group have been discovered. Both characteristic peaks of the
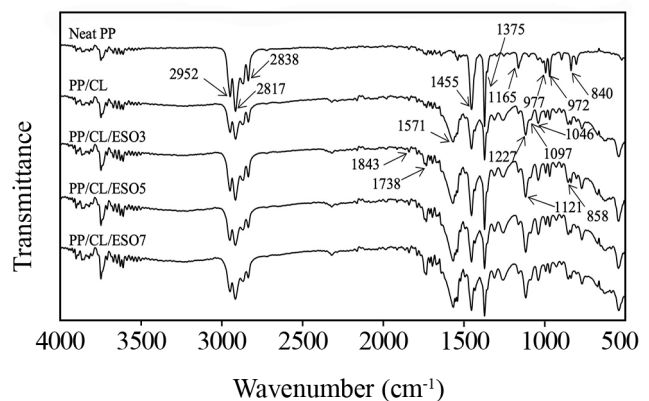

Figure 1. FTIR spectra of neat PP, PP/CL and PP/CL/ESO composites.

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ester and epoxy groups are the main functional groups of ESO [10,14-16]. Notably, with increasing content of ESO in the composite, the intensity of the absorption band assigned to ESO is gradually increased. The results indicate the addition of CL and ESO causes no additional significant absorption peaks, implying the absence of any strong chemical interactions in the PP/CL/ESO composite [12, 37].

Figure 2 shows the melt flow index of the samples, which implies the resistance of molten polymer flow. The addition of CL to PP clearly reduces the MFI as compared to neat PP. The decrease in the MFI corresponds to an increase in the viscosity of the PP/CL composite, which is due to the restriction of molecular chain mobility imposed by the CL particles. In contrast, the presence of ESO increases the MFI of PP/CL composites, indicating that the resistance of molecular chain mobility is reduced by the ESO segments. Additionally, the incorporation of higher ESO content increases the molecular chain mobility, leading to a reduction in flow resistance and, consequently, a decrease in viscosity. This is attributed of the plasticization effect of ESO, which reduces the number of loose attachments between the polymer chains such as van der Waals forces or crystalline structures. The plasticizer acts by lubricating the movement of the molecules and separating the polymer chain. This theory reduces internal resistance between the molecules and allows the polymer molecules to move freely, thus enhancing molecular mobility [39].

Figure 3 presents the DCS thermograms of the neat PP, PP/CL, and PP/CL/ESO composites. All the samples exhibit a similar endothermic peak around 164°C. As indicated in Table 1, the melting temperature remains unaffected by the amount of ESO added. According to Figure 3 and Table 1, the mold temperature appears
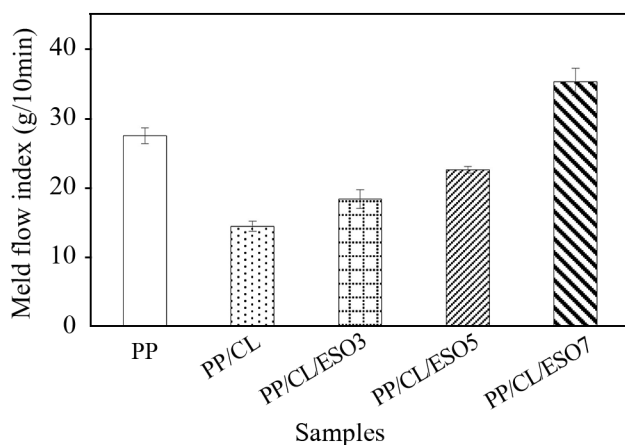
Table 1. Melting and crystallinity values of the PP/CL/ESO composites.

Samples	Mold Temperature (°C)	T_m (°C)	X_c (%)
Neat PP	40	164.5	42.6
	60	164.5	42.6
	80	164.7	42.5
Neat PP, annealing at 120°C for 6 h	80	164.7	47.2
PP/CL	40	165.0	39.1
	60	164.7	42.4
	80	164.5	37.7
PP/CL, annealing at 120°C for 6 h	80	164.7	42.8
PP/CL/ESO3	40	164.2	39.4
	60	164.1	38.2
	80	164.1	37.0
PP/CL/ESO3, annealing at 120°C for 6 h	80	164.1	41.5

to have an insignificant effect on both the melting temperature and the crystallinity. After annealing, the crystallinity of all samples increased, while the melting temperature remained unchanged. As shown in the table, annealing temperature at 120°C increased the crystallinity from 42.5 to 47.2%, 37.7 to 42.8%, and 37.0 to 41.5% for neat PP, PP/CL, and PP/CL/ESO, respectively. The increase in the crystallinity with annealing treatment was mentioned by several authors [31,33,34]. Annealing treatment provides an increase in the mobility of the polymer chains in the interface of the crystalline-amorphous regions and amorphous regions. Additionally, the segments of loose tie molecular chains may be induced to crystallize, which results in an increase in the lamellae thickness and the overall degree of crystallinity [31].

The polarized optical microscopy (POM) micrographs of neat PP, PP/CL, and PP/CL/ESO composites are demonstrated in Figure 4. The neat PP forms a well-defined Maltese cross pattern of spherulitic structure with a diameter ranging between 10 and 20 μm. Obviously, it can be observed that the presence of CL causes a huge decrement in the spherulite size of PP. This observation hints that CL agglomerates serve as nucleating sites for PP crystallization [35]. However, the spherulite size becomes larger with the incorporation of ESO as compared to PP/CL composite. This implies that the ESO hinders the crystallization of PP, which is in accordance with the DSC results.

The influence of mold temperature on the spherulitic structure is shown in Figure 5. For injection molding,
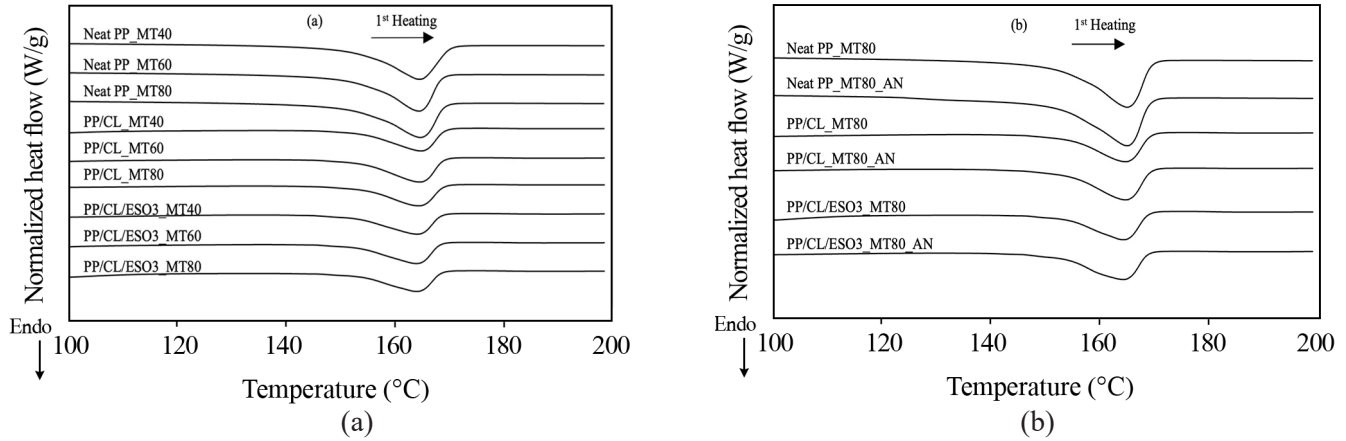

Figure 2. Melt flow index of neat PP and its composites.

Figure 3. DSC thermograms of PP/CL/ESO composites: (a) at different mold temperatures and (b) annealing.

the processing of the samples at a low mold temperature gives higher cooling rates then higher shear rates due to increased viscosity during the solidification [17-18]. For neat PP, by increasing the mold temperature, the spherulite size of PP increases. This is because the nuclei formation relies upon the degree of supercooling. At low degree of supercooling (high crystallization temperature), a small number of nuclei is formed and a large size of spherulite is observed [17, 21]. However, in the case of PP/CL and PP/CL/ESO composites, the formation of spherulite is more complicated. The effect of mold temperature on the spherulitic structure was difficult to observe. This

emphasizes the competitive effect of the presence of CL and ESO and having a high mold temperature.

The effect of the annealing treatment on the spherulitic structure is presented in Figure 6. When a sufficient annealing temperature and annealing duration are provided, there are multiple adjustment processes of microstructure, such as the perfection of crystals and the thickening of primary lamellae [29]. However, the annealing treatment has no effect on the spherulite size and no notable change in the spherulitic diameter, which is detectable after annealing in this work.

The tensile results of neat PP, PP/CL and PP/ CL/ESO composites are presented in Figure 7. To
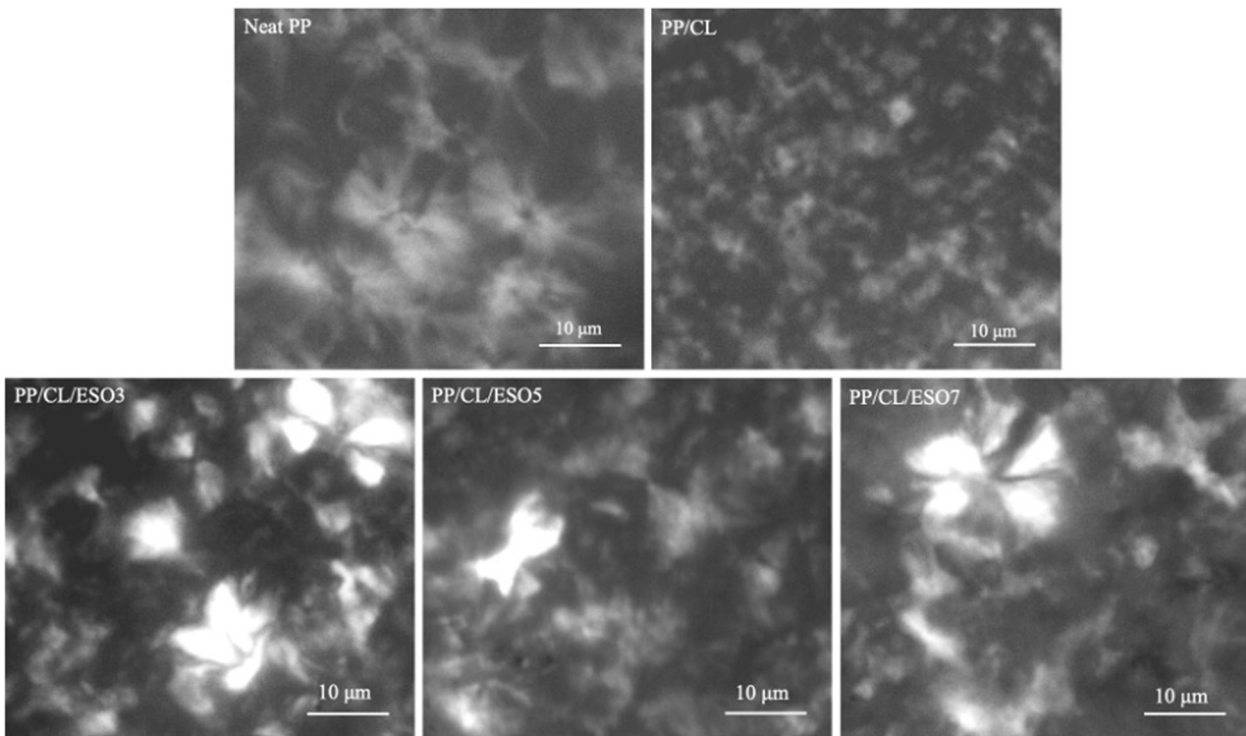

Figure 4. POM micrographs of neat PP and its composites.

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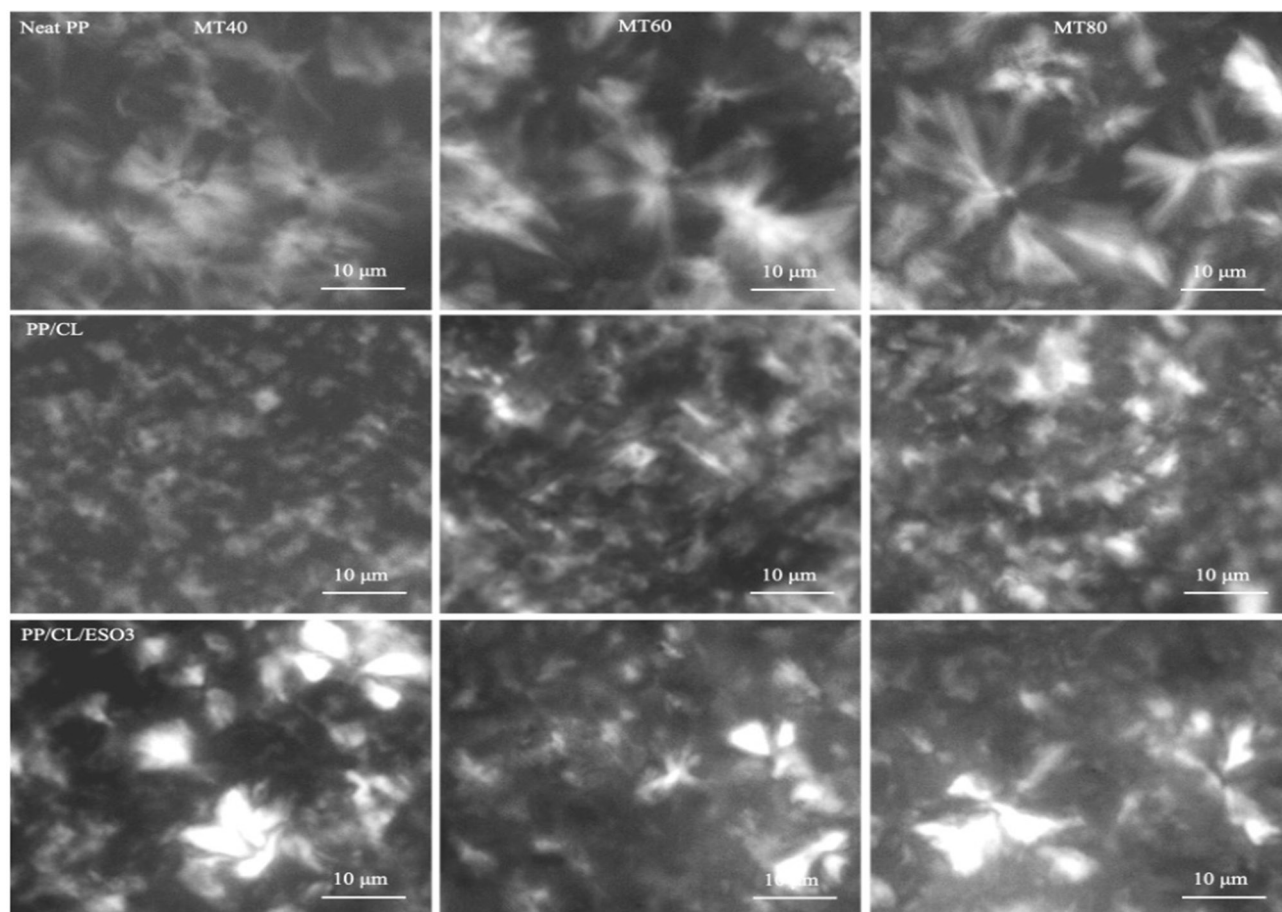
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Figure 5. POM micrographs of neat PP and its composites at various mold temperature.

elucidate the effect of ESO content on the mechanical properties of PP, the mold temperature of 40°C was focused. The neat PP exhibited a tensile strength of 29 MPa and a Young's modulus of 411 MPa. When

40 wt.% of CL was incorporated into the PP matrix, the tensile strength and modulus of the PP/CL were found to be 17 MPa and 756 MPa, respectively. The tensile strength of PP significantly decreased while the
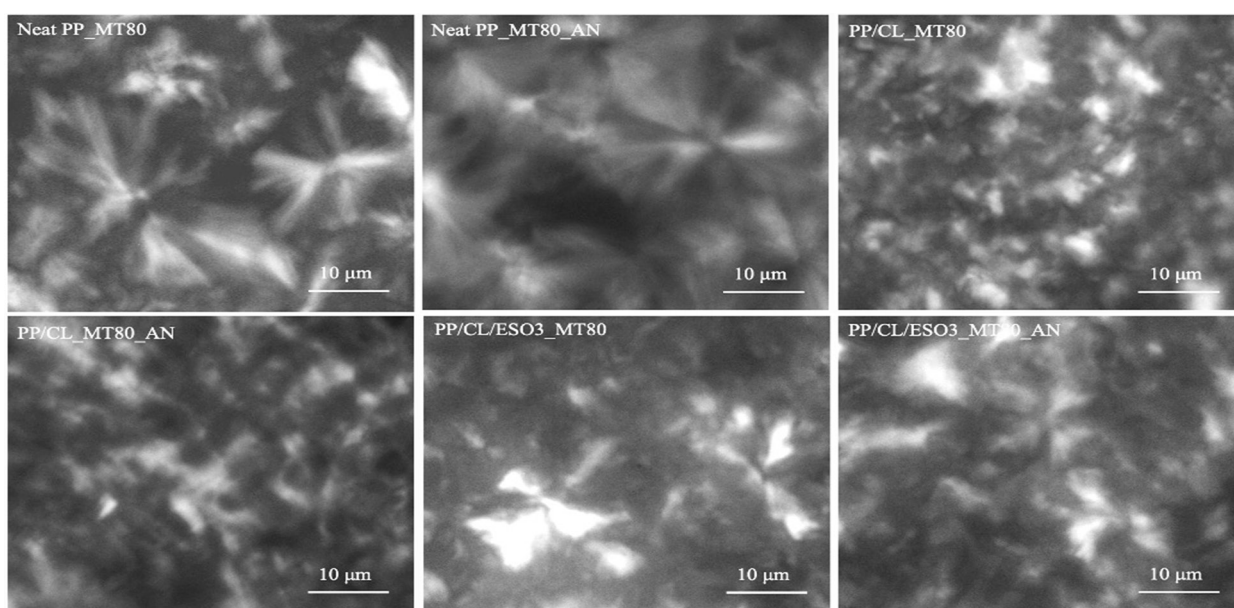

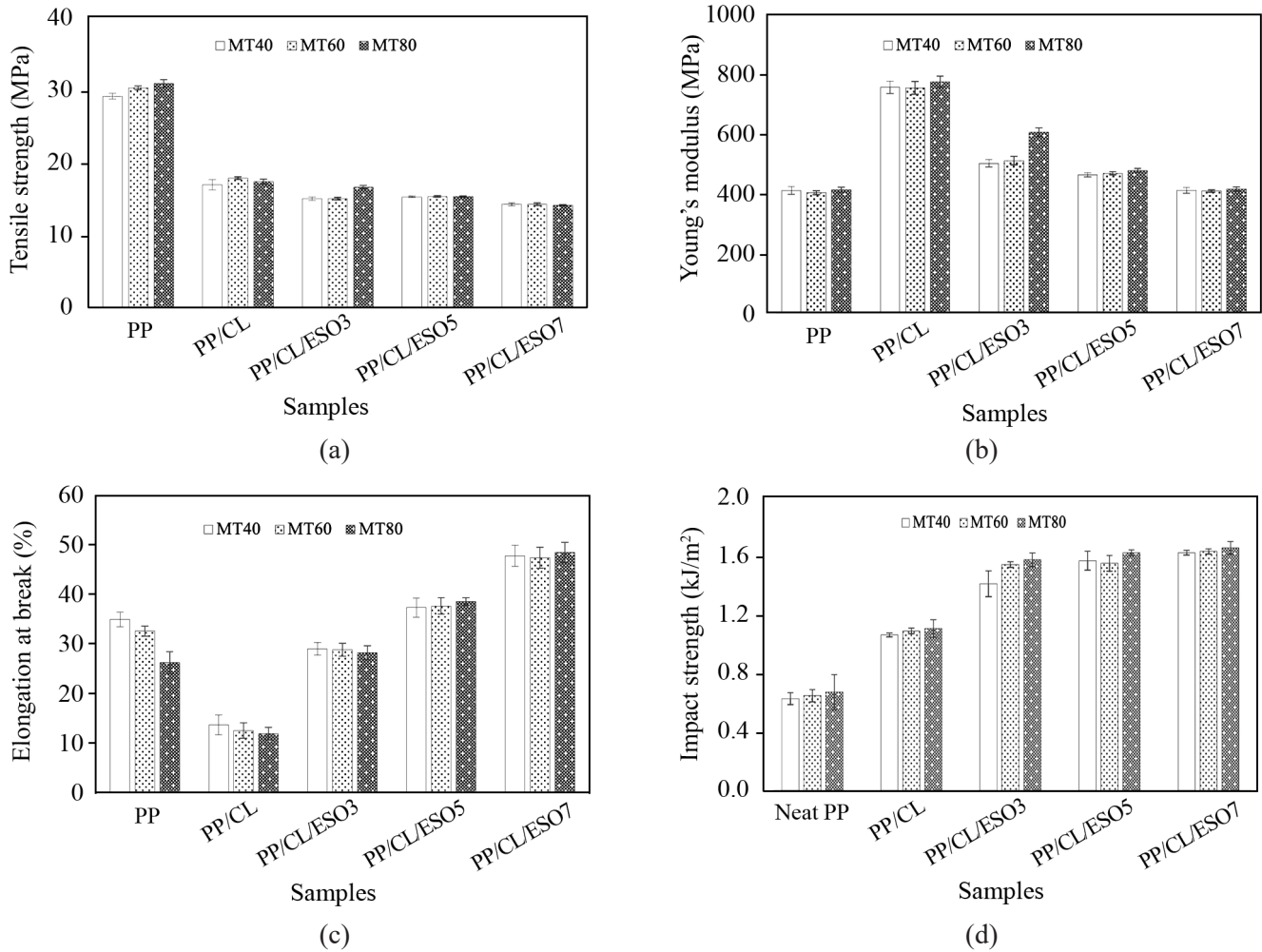**Figure 6**. POM micrographs of neat PP and its composites.

Figure 7. Effect of ESO on (a) tensile strength, (b) Young's modulus, (c) elongation-at-break and (d) impact strength of neat PP and PP/CL composites with various mold temperatures.

Young's modulus increased substantially, indicating that CL acts as a reinforcing agent. However, the elongation-at-break of PP was greatly decreased by the addition of CL. Furthermore, the increased flexibility of the PP/CL/ESO composites was accompanied by a decrease in strength and stiffness, and the tensile strength and modulus usually decrease with increasing plasticizer content [39]. The tensile strength and Young's modulus declined with the addition of ESO plasticizer. The lowest tensile and modulus values were observed at 14 MPa and 415 MPa, respectively, with 7 phr of ESO loading. On the other hand, the addition of ESO was expected to improve elongation-at-break and impact strength of the PP/CL composite as observed in Figure 7. The incorporation of ESO into PP/CL provided a great increase in elongation-at-break, which shifted to 27.2%, 38.7%, and 44.8%, for PP/CL/ESO3, PP/CL/ESO5, and PP/CL/ESO7, respectively, as compared to the PP/CL, 12.5%. These results deduced that ESO serves as a plasticizer for

the PP chains. The presence of ESO facilitates the sliding of PP molecular chains, thereby reducing the secondary bonding forces between the polymer chains, resulting in a softer, more easily deformable mass [31]. This brings about a more flexible polymer, but it causes a loss of strength and stiffness.

The effect of mold temperature on the mechanical properties of PP/CL/ESO is also revealed in Figure 7. The tensile strength, tensile modulus, elongation-at-break and impact strength of samples are shown in dependence of the mold temperature. Specifically, as the mold temperature increased, the tensile strength of neat PP increased, while the elongation-at-break decreased. These changes are consistent with morphological structures governed by crystallization during processing [17, 26]. However, the results showed that mold temperature has less profound impact on the mechanical properties of PP/CL/ESO. Nevertheless, the use of mold temperature of 80°C improved the stiffness and impact strength of PP/CL/
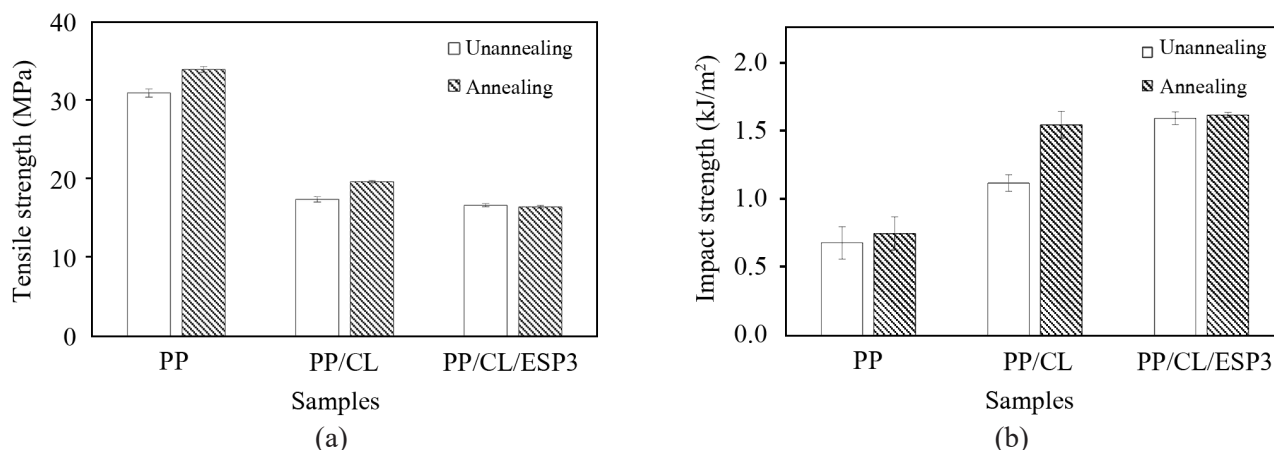
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Figure 8. Effect of annealing on (a) tensile strength, and (b) impact strength of neat PP and PP/CL composites.

ESO, especially at 3 phr of ESO concentration. At ESO content above 3 phr, the effects of mold temperature seem to be hindered by the presence of ESO.

It has been reported that the spherulite size and degree of crystallinity influenced the mechanical properties of semicrystalline polymers [17,21,40-44]. Generally, an increase in the degree of crystallinity is usually accompanied by an increased spherulite size in the absence of a foreign substance. The tensile yield tends to increase linearly with both higher crystallinity and the larger spherulite size. This is because crystalline phases are stronger and less deformable compared to amorphous phases. Consequently, the larger spherulite size and the higher degree of crystallinity, the higher tensile strength [17,25,33,43-44]. In this work, for neat PP, the spherulite size increased with rising mold temperature, while the degree of crystallinity remained unaffected by mold temperature. These results are consistent with the concept that the spherulite size plays an important role in determining tensile strength. An increase in the spherulite size results in an increase in the tensile strength. Similar results also were reported in the literature [17,25]. However, for semicrystalline polymer composites, tensile strength is influenced not only by filler/matrix interfacial adhesion and filler loading but also by key morphological structure such as degree of crystallinity, spherulite size, and spherulite morphology. The interplay between these factors is complicated and cannot always be separated.

As shown in Figure 8, annealing treatment affects the mechanical properties of all samples in different ways. Compared to the unannealed samples, the tensile strength of the annealed neat PP and PP/CL composites increases (see Figure 8 (a)). This enhancement is attributed to the increased degree of crystallinity, as discussed earlier. Annealing inducing

the improvement of the strength has been widely reported elsewhere [28-30,45]. This improvement is generally due to enhanced crystal perfection, increased lamella thickness, and a higher degree of crystallinity [28]. The impact strength of unannealed and annealed samples is also shown in Figure 8 (b). Annealing improves the impact strength for both neat PP and PP/CL, with a more pronounced increase observed for PP/CL. For neat PP, annealing provides more crystal perfection without the excessive reduction of the tie molecules number [28]. Nonetheless, for annealed PP/CL, the enhancement in impact strength is caused by the combination of annealing and the addition of CL. However, the improvement of tensile strength and impact strength of the annealed PP/CL/ESO composite cannot be observed. This finding agrees with results obtained from other literatures [10,46]. The resulting performance of the annealed PP/CL/ESO composites could be explained by two possibilities. Firstly, the adhesion between the components was damaged due to crack formation between their interphases after the annealing treatment [10]. Secondly, the annealing treatment caused the plasticizer migration out of the interlamellar amorphous region, generating voids and cracks [46]. The obtained results suggest that the annealing treatment could not help improve the mechanical properties of PP composite with the presence of ESO plasticizer.

CONCLUSION

In this study, the ESO plasticizer, mold temperature, and annealing process were found to influence the morphological and mechanical properties of PP/CL composites in different ways. It was observed that the

degree of crystallinity was significantly unchanged while the spherulite size became larger when ESO was added. Due to the plasticizing effect of ESO, elongation-at-break and impact strength improved, while the tensile strength and modulus decreased. The effect of mold temperature on the properties of injection molded PP-based composites showed an increase in both the tensile strength and Young's modulus due to the increase in the spherulite size of a PP. Furthermore, the morphological and mechanical properties of PP-based composites were shown to depend on annealing treatment. Annealing treatment led to an increase in both crystallinity and crystal perfection, which enhanced tensile strength and impact strength. However, the beneficial effects of annealing were diminished by the presence of ESO.

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CONFLICTS OF INTEREST

The authors declare that they have no conflict of interest.

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