

Effect of biobased and biodegradable nucleating agent on the isothermal crystallization of poly(lactic acid)

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Abstract—The effect of chemically modified thermoplastic starch (CMPS) on the thermal properties and isothermal crystallization kinetics of poly(lactic acid) (PLA) was studied by differential scanning calorimetry (DSC) and compared to that of granular starch and an inorganic nucleating agent, talc. Nucleated PLA showed an additional crystallization of PLA, which affected the melting temperature. The crystallinity and crystallization rate of PLA were considerably enhanced by addition of CMPS, even at 0.1% content, and the amount of the CMPS had little effect on the thermal properties and isothermal crystallization kinetics of PLA. The effect of CMPS as a nucleating agent was comparable to that of granular starch but slightly less than that of talc. However, CMPS can offer a fully biodegradable nucleating agent with no residues remaining for the biobased and biodegradable polymers.

Key words: Poly(lactic acid), Nucleating Agent, Isothermal Crystallization, Chemically Modified Thermoplastic Starch

INTRODUCTION

Biobased and biodegradable polymers can form the basis of an environmentally preferable, sustainable alternative to current materials based exclusively on petroleum feedstocks [1,2]. These biobased materials have advantages in terms of their sustainability and lifecycle, especially as relating to carbon-based polymeric materials such as plastics, water soluble polymers. Biopolymers are generally capable of being disposed in safe and ecologically sound ways through disposal processes (waste management) such as composting, soil application, and biological wastewater treatment. Single use, short-life, disposable products can be engineered to be biobased and biodegradable.

In recent years, extensive studies have been conducted on the properties of materials related to PLA, because of its being a typical biobased and biodegradable synthetic polymer [3-15]. Moreover, PLA is a biodegradable polymer with a relatively lower cost than other biodegradable polymers, has good mechanical properties and is commercialized worldwide. However, commercialized PLA has low crystallinity and a slow rate of crystallization, which limits its use in plastic or film applications. In general, the addition of a nucleating agent to polymers with a medium crystal growth rate has been widely practiced in the fabrication of plastics, not only for improving the mechanical properties, but also for shortening the cycle period in injection molding processes [16-20]. Conventional nucleating agents, such as talc and boron nitride, are effective for many kinds of polymers including biodegradable polymers.

More recently, Inoue et al. [19,21-24] tried to apply biobased and biodegradable nucleating agents such as cyclodextrins, starch, and their inclusion complexes to biodegradable polymers. However, the preparation process of nucleating agent proved to be compar-

tively difficult to control. Sun [25] also observed the effect of starch and talc as a crystallization agent on the crystallization kinetics of PLA, because PLA plays a key role in its composites and blends. Thus, it is necessary to study various environmentally friendly nucleating agents for the biobased and biodegradable polymers such as PLA.

We investigated the effect of CMPS, which is a reactive thermoplastic, biobased and biodegradable material, as a nucleation agent on the isothermal crystallization kinetics of PLA. In addition, the effect of the CMPS concentration was observed in this study. The results were compared with those of talc, which is a typical inorganic nucleating agent for various polymers, and granular starch, which is also a biobased and biodegradable polymer but not thermoplastic material.

EXPERIMENTAL

1. Materials

Poly(lactic acid) (NatureWork[®] PLA Polymer 4032D) with a number average molecular weight of 98000, polydispersity of 2.1, spe-

Table 1. Sample codes and compositions of PLA/nucleating agent

Sample codes	Composition (wt%)			
	PLA	CMPS	Starch	Talc
PLA	100			
Starch1.0	99		1	
Talc1.0	99			1
CMPS0.1	99.0	0.1		
CMPS0.5	99.5	0.5		
CMPS1.0	99	1		
CMPS5.0	95	5		
CMPS10.0	90	10		

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cific gravity of 1.24 and a melt flow index of 4-8 g/10 min (measured at 190 °C under a load of 2.16 kg) was obtained from Cargill Dow LLC. The PLA was dried in a vacuum oven for 24 hr at 50 °C. Corn starch (11% inherent moisture) and talc were obtained from Shindongbang Inc. and Ducksan Pure Chemical Co. Ltd., Korea. The starch and talc were dried in a vacuum oven at 100 °C for 24 hr. The procedure used for the preparation of the chemically modified thermoplastic starch (CMPS) has been well described in previous studies [13,26]. The prepared CMPS was grounded into fine powder and then dried at 100 °C for 24 hr.

2. Specimen Preparation

As represented in Table 1, PLA and nucleating agents were mixed in a plastic bag before being extruded in a twin-screw co-rotating extruder (Berstoff, 90-2-Eo, Germany). The screw diameter was 25 mm with a L/D ratio of 48. The extruder was operated at 300 rpm with a constant feed rate of 5 kg/hr and barrel and die temperatures were 65-190 °C and 185 °C, respectively. The extrudates of specimens were pelletized and then dried in a vacuum oven for 24 hr at 50 °C.

3. Characterization

To observe their thermal properties, the samples were heated from room temperature to 200 °C at a heating rate of 20 °C/min and maintained at this temperature for 5 min to remove the thermal history. Subsequently, the samples were quenched to -80 °C and reheated to 200 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. Isothermal characterization was performed by using differential scanning calorimetry (DSC; Perkin-Elmer Pyris 6). To observe their isothermal crystallization characteristics, the specimens were kept at 200 °C for 5 min and then quenched to a desired crystallization temperature. The isothermal temperatures were varied from 85 to 125 °C in 5 °C intervals and the samples were held at each isothermal temperature for a enough time to allow for their complete crystallization. In addition, we observed the melting behavior of the isothermally crystallized samples by reheating them to 200 °C at a rate of 10 °C/min.

The morphology of the selected samples was investigated by studying the fractured surfaces under cryogenic conditions with a scanning electron microscope (SEM; Hitachi model s-4100; Japan). The fractured samples were coated with gold particles prior to the experiment.

Table 2. The effect of nucleating agents on the thermal properties of PLA

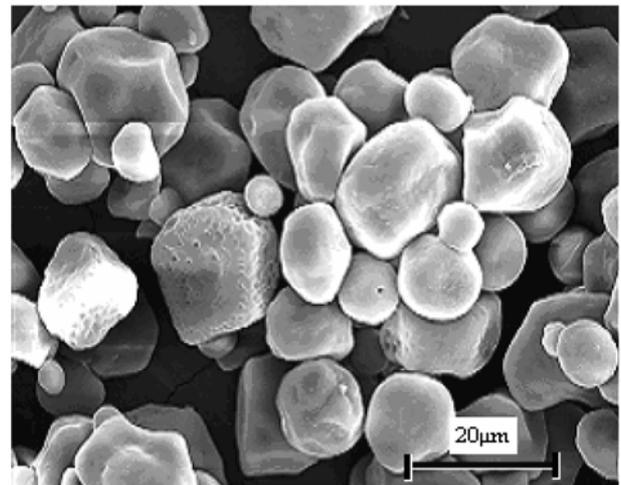
Sample codes	T_g (°C)	T_{cc}^a (°C)	ΔH_c^b (J/g)	T_m (°C)	Crystallinity (%)
PLA	64	129	-	168	2.4
Starch1.0	62	106	20.9	170	25.7
Talc1.0	63	96	22.0	170	36.0
CMPS0.1	65	111	24.2	173	28.3
CMPS0.5	64	112	23.9	172	25.9
CMPS1.0	63	113	27.7	172	30.1
CMPS5.0	64	112	22.8	172	27.4
CMPS10.0	62	108	25.4	171	30.6

^aCold crystallization temperature.

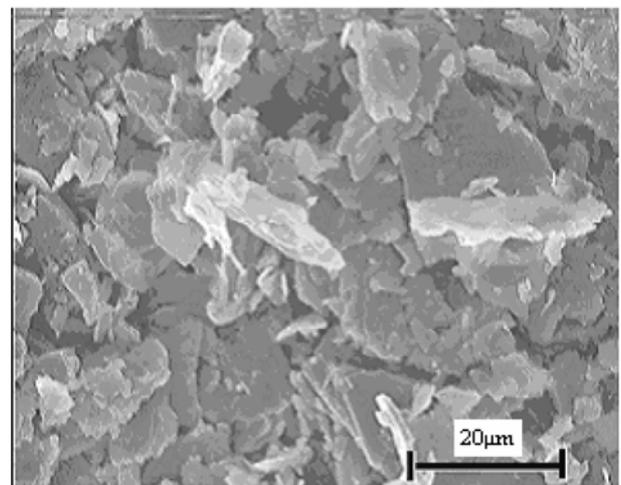
^bHeat of crystallization on second heating process.

4. Theory of Isothermal Crystallization Kinetics

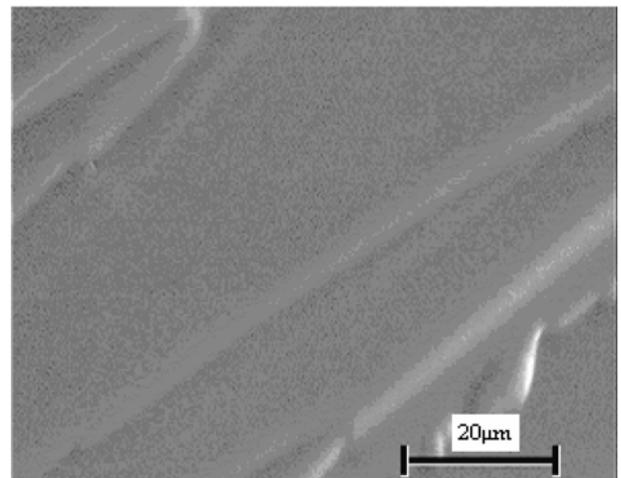
The Avrami [27] equation below is widely used to describe the isothermal crystallization process in polymers:



(a)



(b)



(c)

Fig. 1. Scanning electron micrographs of granular starch (a), talc (b), and CMPS (c).

$$\alpha(t)=[1-\exp(-Kt^n)] \quad (1)$$

where $\alpha(t)$ is the fraction of crystallized material at time t , K is the overall kinetic rate constant, which contains the nucleation and growth parameters, and n is the Avrami exponent, which depends on the mechanism of nucleation and the form of crystal growth. In general, the Avrami equation is often converted into the traditional linear form:

$$\ln[-\ln(1-\alpha(t))]=\ln K+n \ln(t) \quad (2)$$

In our study, the so-called Avrami plots $\ln[-\ln(1-\alpha(t))]$ versus $\ln(t)$ were computed to obtain the values of K and n . The half crystallization time, $t_{1/2}$, which is the time taken for 50% of the total crystallinity to be achieved, was calculated by the following equation:

$$t_{1/2}=(\ln 2/K)^{1/n} \quad (3)$$

RESULTS AND DISCUSSION

1. Thermal Properties on Second Heating

The thermal properties of samples consisting of pure PLA, talc1.0, starch1.0 and PLA/CMPS blends are listed in Table 2. All of the thermal properties were obtained from the second heating curves. We could not find the crystallization temperatures on cooling, except in the case of the PLA/talc at a cooling rate of 10 °C/min, due to the very slow crystallization rate characteristics of PLA. On the other hand, the crystallization temperature on heating, which is often re-

ferred to as the cold crystallization temperature (T_{cc}), was significantly affected by the addition of the nucleating agent and the type of nucleating agent. Usually, a lower crystallization temperature on cooling indicates slower crystallization, whereas a lower crystallization temperature on heating indicates faster crystallization. Generally, the cold crystallization temperature is important in industrial application when the processed articles are annealed for special purposes, such as to increase crystallinity and enhance the dimensional stability. In this kind of post processing, a lower T_{cc} means that a lower energy is needed to accomplish the purposes brought about by annealing. As listed in Table 2, the T_{cc} was decreased by 16, 24 and 33 °C by the addition of 1% of CMPS, granular starch and talc as a nucleating agent, respectively. Based on these results, talc and granular starch seem to be better nucleating agent than CMPS.

In this study, we attempted to interpret the variation in the decrease of T_{cc} decrease with the type of nucleating agent by conducting a morphological study. As shown in Fig. 1, talc is an irregular-shaped particle with a coarse surface, while granular starch is roughly spherical with grooves and small voids on its surface. Fig. 2 shows the fractured surfaces of the samples of talc1.0, starch1.0 and CMPS10.0. Interestingly, their morphologies are different from each other: the morphology of talc1.0 (see the circles in Fig. 2(a)) shows a typical incompatible surface between the talc and PLA, while that of starch1.0 (see the circles in Fig. 2(b)) shows a slightly improved wetting between PLA and starch. CMPS1.0 and CMPS10.0 (see the circles in Fig. 2(c) and (d)) show very good interfacial ad-

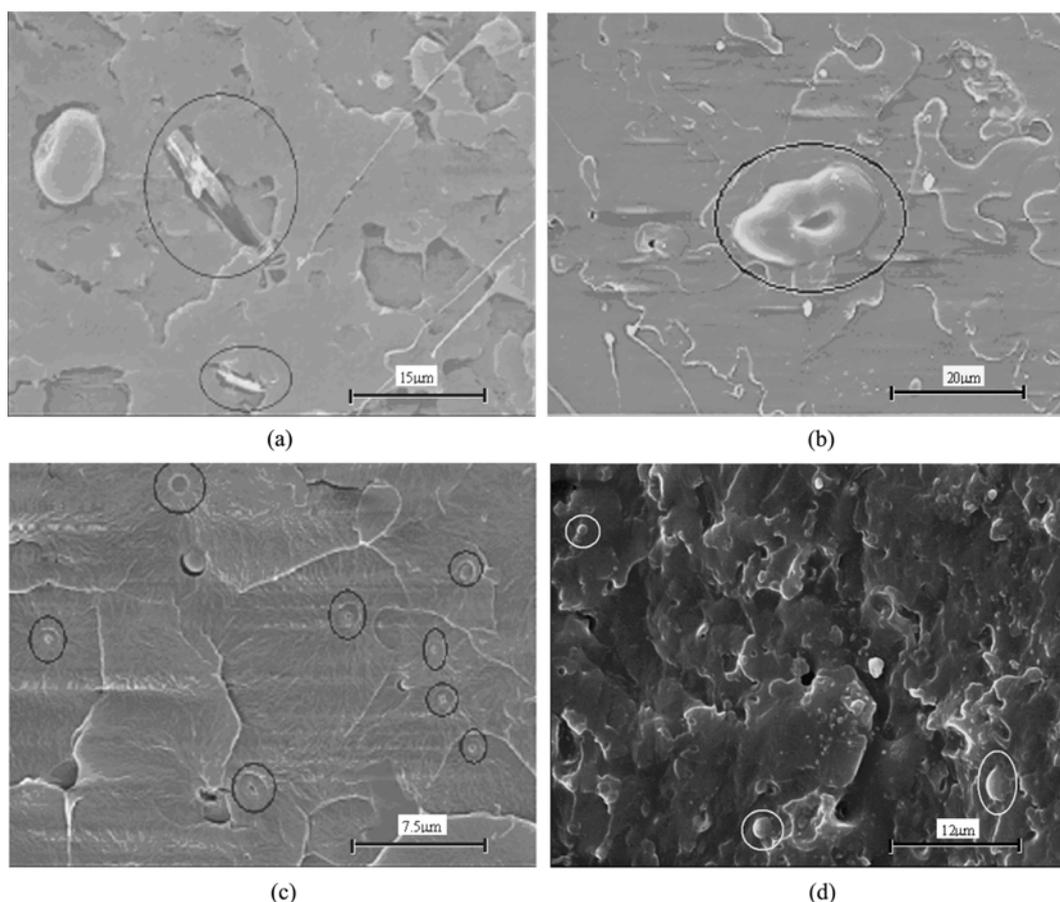


Fig. 2. Scanning electron micrographs of the fractured surfaces of talc1.0 (a), starch1.0 (b), CMPS1.0 (c), and CMPS10.0 (d).

hesion and their sizes are very small compared to those of talc and starch. These morphologies might affect the T_{cc} and overall crystallization of PLA. The largest decrease of T_{cc} observed for the talc1.0 might be due to the existence of spontaneous cold spots on the surface of the talc, resulting from the insulation of the heat transfer between PLA and talc in the heating process. As shown in Fig. 2(a), there is a big void at the interface of PLA and talc, which might prevent the transfer of heat from the matrix to the talc particles, with the result that the temperature at the surface of the particle would become lower than that of the surroundings. Thus, the supercooled spots become the center of nuclei, and then the PLA molecules around the nuclei start to form crystals at low temperature [17,18]. The wetting of the grooves of the starch granule, which act as centers of the heterogeneous nuclei and absorb the chains or segments of the polymer, was slightly improved compared to that of talc1.0, but there is still cleavage between starch and PLA, as shown in Fig. 2(b). In the case of the CMPS1.0 and CMPS10.0 (Fig. 2(c) and (d)), the CMPS particles are very small spheres with a smooth surface and are well wetted by PLA. In our previous work [13,26], PLA and CMPS formed a compatible blend through a reaction between the reactive groups. Thus, CMPS was less effective on the T_{cc} compared to the talc and starch because it had neither supercooled spots nor grooves.

The T_g of PLA was not greatly affected by the addition of the nucleating agent or the type of nucleating agent. However, the T_m

and crystallinity of PLA were increased by about 2-5 °C and 23-34% by the addition of nucleating agent, respectively. It is well known that the melting temperature is highly dependent on the crystal perfection [28]. The increase of the T_m and crystallinity of PLA indicates that the nucleating agents enhanced the crystallization rate and improved the perfection of the crystals. The difference of the effect on the T_m and crystallinity of PLA with the type of nucleating agent was little. Moreover, the value of the heat crystallization (ΔH_c) of talc1.0 is very similar to that of PLA/CMPS blends and starch1.0. In earlier studies [19,29-31], polymers with talc did not show a heat of crystallization on reheating process after quenching, indicating that most of the crystallization process was completed during the quenching procedure. But, in this study, PLA containing talc showed the heat of fusion, which might be due to the intrinsically slow crystallization rate of PLA.

It is a very interesting result that the effect of CMPS on the crystallinity of PLA was approximately similar to that of the talc and starch, despite the fact that CMPS particle had neither supercooled spots nor grooves. This result might be explained that the numbers of particles of CMPS, which can act as a nucleating agent, are larger than that of talc and granular starch at the same weight fraction, that is, a larger number of CMPS particle seemed to compensate for its weakness as a nucleating agent. As shown in Fig. 2, the morphologies of talc1.0 and starch1.0 show large particles, while CMPS blends show several small particles and the size CMPS particle increased with

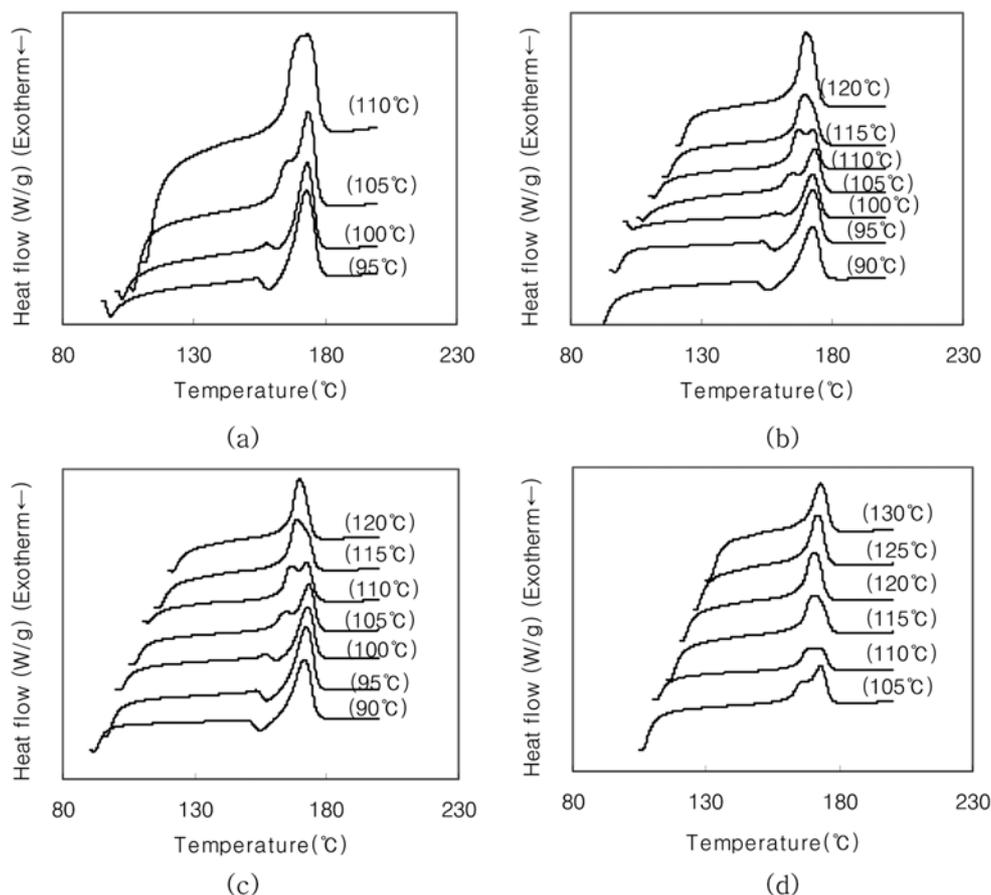


Fig. 3. DSC melting thermograms of pure PLA (a), CMPS1.0 (b), starch1.0 (c), talc1.0 (d) after isothermal crystallization at various temperatures.

increasing the amount of CMPS. However, the number of CMPS particles seemed not to be increased with increasing the content of CMPS, because the effects of its content on the thermal properties were very little. In this study, we did not compare the number of CMPS particles with the content of CMPS.

2. Melting Behavior of Isothermally Crystallized Samples

Fig. 3 represents the melting thermograms of the pure PLA, PLA/CMPS blends, talc1.0 and starch1.0 obtained by DSC after isothermal crystallization at various isothermal crystallization temperatures. For all of the samples that were isothermally crystallized at temperatures 100, 95 and 90 °C, a small crystallization exothermic peak

was observed prior to the major melting peaks, indicating that recrystallization occurs upon heating. As the crystallization temperature increased, the exothermic peak disappeared and a shoulder-melting peak before the major melting peak appeared instead. The area of this new melting peak increased and shifted to a higher temperature with increasing isothermal crystallization temperature. Finally, this new melting peak become the major melting peak, that is, the original major melting peak gradually merged into the new melting peak. This kind of phenomenon for the pure PLA, PLA/starch and PLA/talc blends has been also observed in earlier studies [2,32] and this melting behavior of PLA/CMPS blends was also not affected by

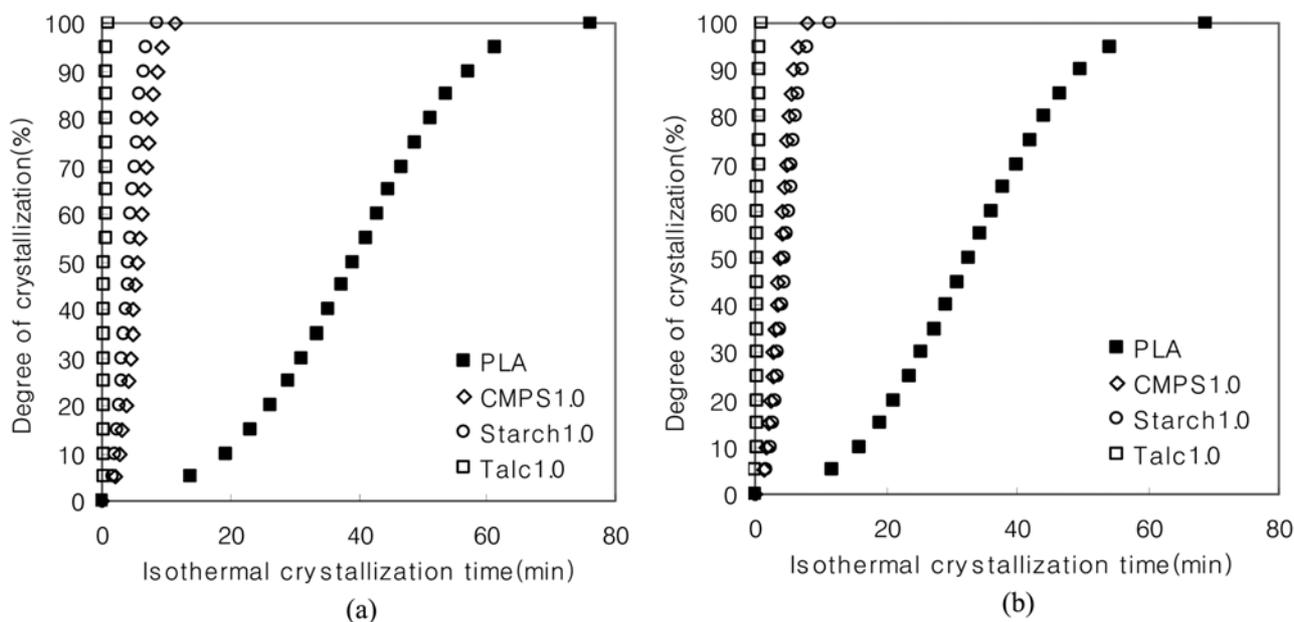


Fig. 4. Integral crystallization curves of pure PLA, CMPS1.0, starch1.0, and talc1.0 at the isothermal crystallization temperature of 110 °C (a) and 105 °C (b).

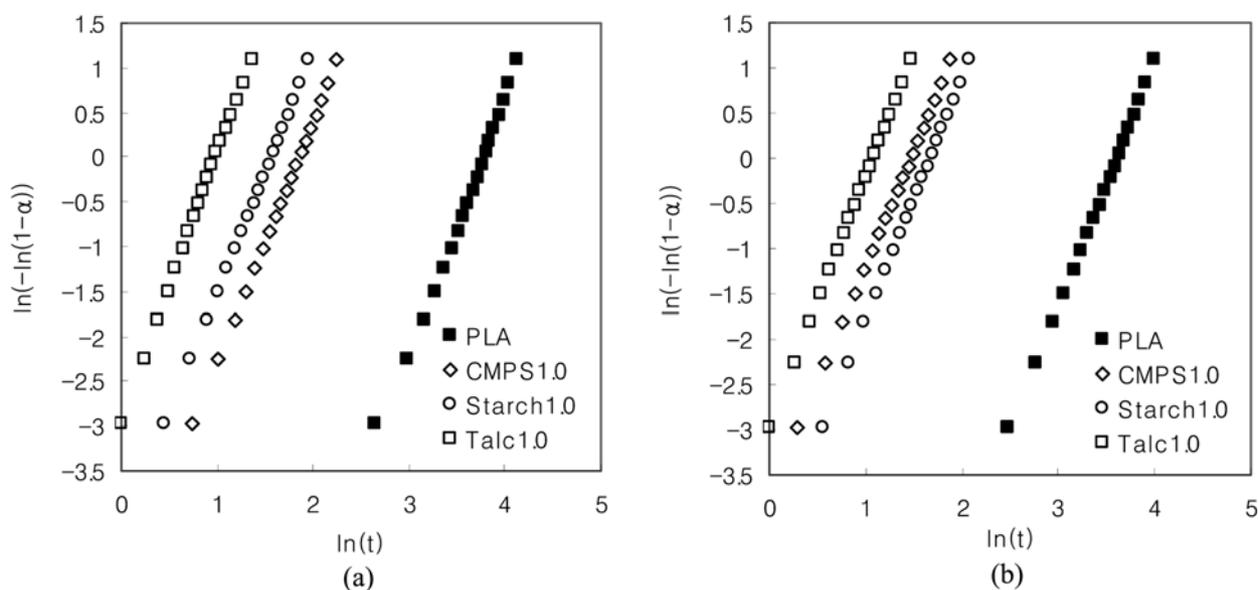


Fig. 5. Plots of $\ln[-\ln(1-\alpha(t))]$ versus $\ln(t)$ of pure PLA, CMPS1.0, starch1.0, and talc1.0 at the isothermal crystallization temperature of 110 °C (a) and 105 °C (b).

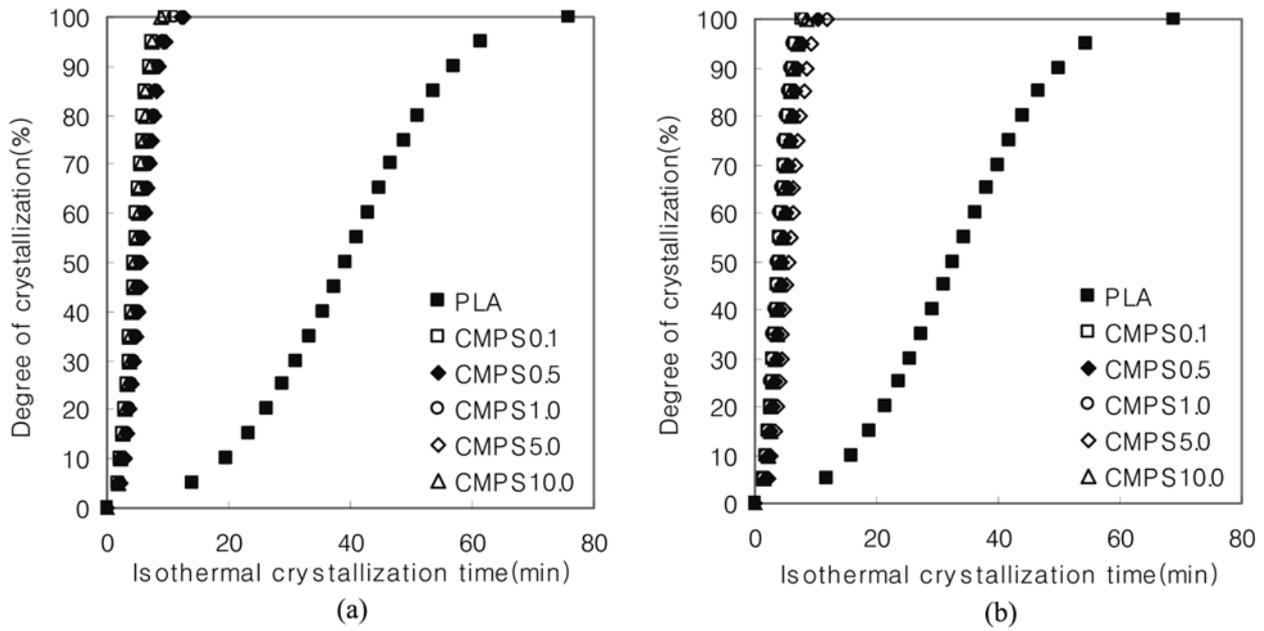


Fig. 6. Integral crystallization curves of PLA containing various amounts of CMPS at the isothermal crystallization temperature of 110 °C (a) and 105 °C (b).

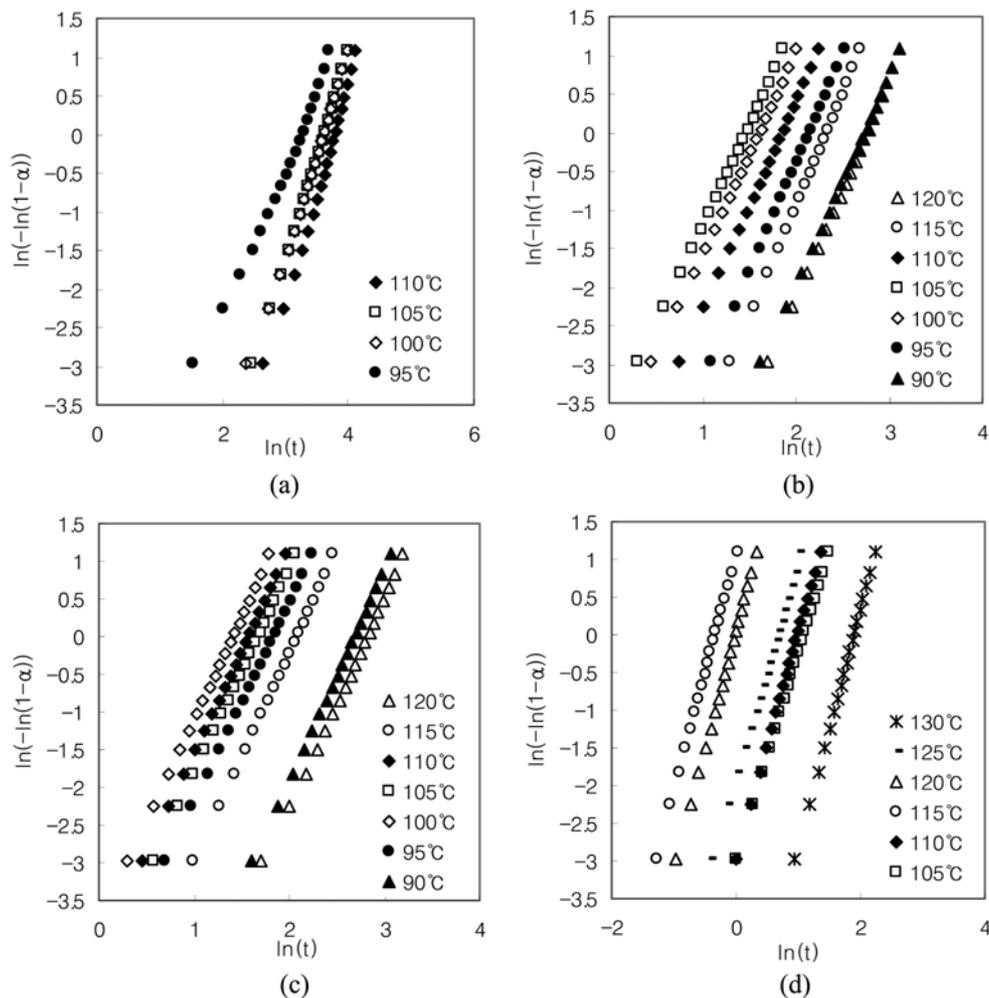


Fig. 7. Plots of $\ln[-\ln(1-\alpha)]$ versus $\ln(t)$ of pure PLA (a), CMPS1.0 (b), starch1.0 (c), and talc1.0 (d) at the various isothermal crystallization temperatures.

the amount of CMPS.

3. Isothermal Crystallization Behavior

Figs. 4 and 5 show the integral isothermal crystallization curves and the plots of $\ln[-\ln(1-\alpha(t))]$ versus $\ln(t)$ for the pure PLA, PLA/CMPS, PLA/starch, and PLA/talc samples at 110 and 105 °C. As shown in these figures, the induction time is greatly decreased by the addition of nucleating agent. Talc was the most effective of the tested nucleating agents, while CMPS and granular starch showed very similar results. The content of CMPS did not affect the integral isothermal crystallization and the plots of $\ln[-\ln(1-\alpha(t))]$ versus $\ln(t)$. As regards the effects of the amount of nucleating agent on the whole crystallization process, using an excessive amount of nucleating agent had a negative nucleation effect, due to its agglomeration [33]. Unlike the former inorganic nucleating agent filled polymer, the nucleating effect of the amount of CMPS on the integral isothermal crystallization was not decreased by increasing the CMPS content, as shown in Fig. 6, even though the PLA containing the smallest amount of CMPS (0.1%) showed a similar induction time compared to that with the highest amount of CMPS (10%). This result also might be due to about the same number of CMPS particles with its content, which can act as a nucleating agent, as discussed

above.

Figs. 7 and 8 show the plots of $\ln[-\ln(1-\alpha(t))]$ versus $\ln(t)$ for the pure PLA and PLA with talc 1%, starch 1%, CMPS 1%, and those of PLA with various contents of CMPS at different isothermal crystallization temperatures, respectively. The parameters of the Avrami equation were estimated from these plots. As shown in Figs. 7 and 8, the plots are slightly nonlinear, due to the additional crystallization [25]. The n and K values obtained from the slope and interception of the best straight lines fitting the experimental points at a low degree of transformation are listed in Table 3. The average n value in the T_c range tested was 2.4 for the pure PLA, 2.7 for the starch1.0, 3.0 for the talc1.0, and 2.6-2.7 for the PLA/CMPS blends. The average n value was slightly increased by the addition of the nucleating agent, while it was not changed by the amount of CMPS. The Avrami exponent value of 3-4 means that the spherulitic growth of PLA occurred in three directions [28,34]. There was some confusion concerning the n values of pure PLA and nucleated PLA, as described in the literature [25], because they are affected by many factors.

It is well known that the overall crystallization rate is determined by the rate of nucleation and the crystal growth process. The rate

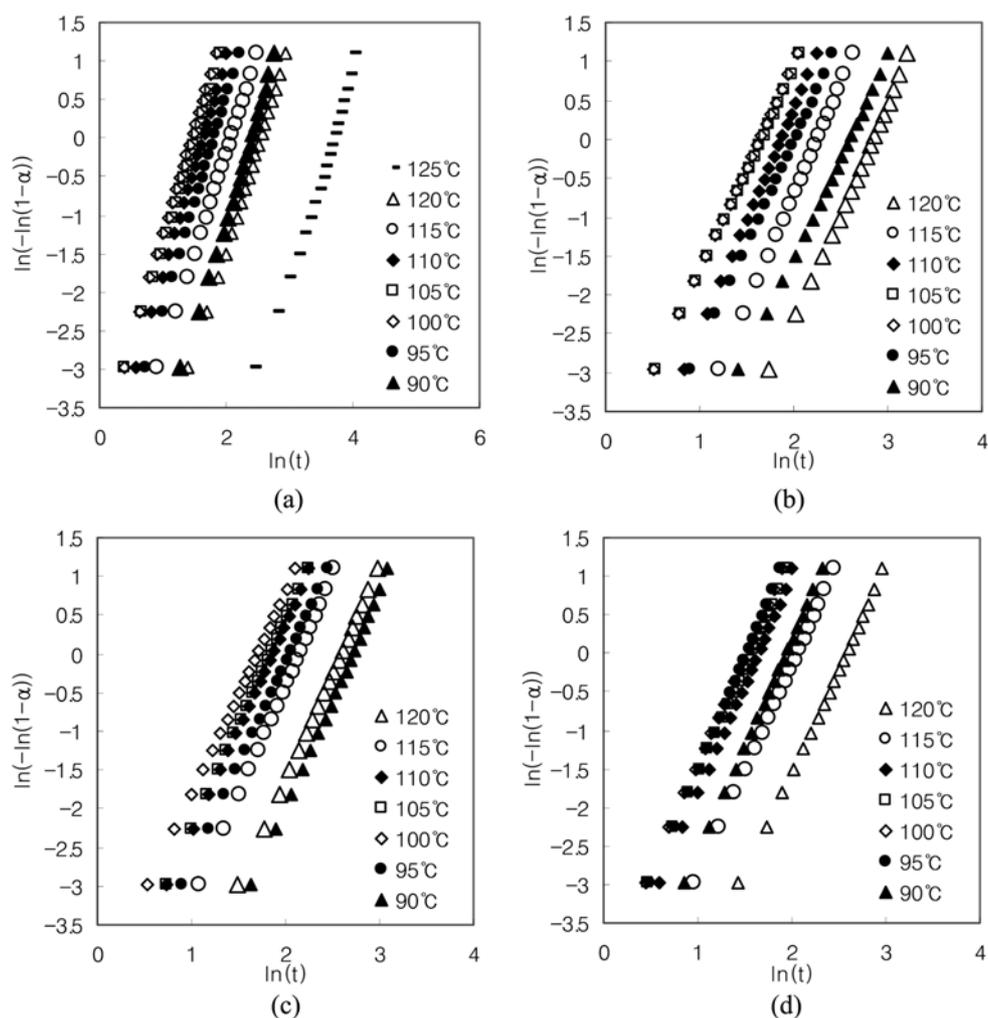
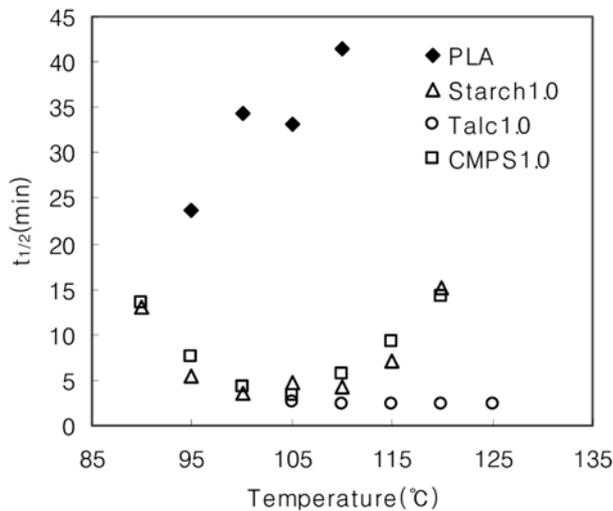
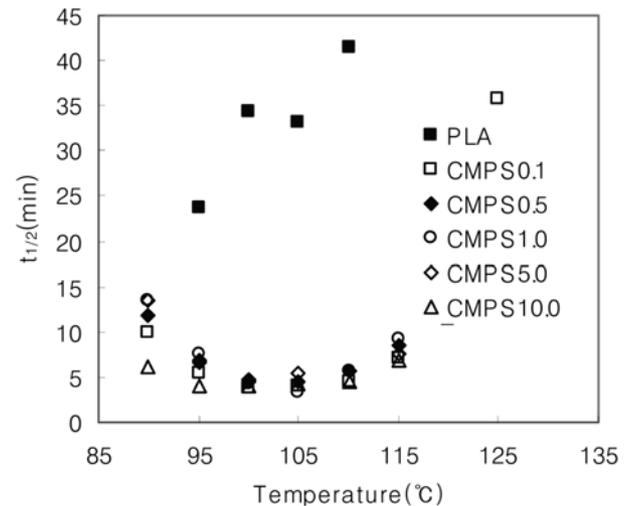


Fig. 8. Plots of $\ln[-\ln(1-\alpha(t))]$ versus $\ln(t)$ for CMPS0.1 (a), CMPS0.5 (b), CMPS5.0 (c), and CMPS10.0 (d) at the various isothermal crystallization temperatures.

Table 3. Isothermal crystallization kinetic parameters of samples

Sample codes	T_c ($^{\circ}\text{C}$)	K (min^{-n})	n	Sample codes	T_c ($^{\circ}\text{C}$)	K (min^{-n})	n
PLA	110	7.7×10^{-5}	2.5	CMPS 0.5	110	4.7×10^{-3}	2.9
	105	8.9×10^{-5}	2.6		105	1.3×10^{-2}	2.6
	100	2.2×10^{-4}	2.3		100	1.4×10^{-2}	2.6
	95	4.2×10^{-4}	2.0		95	5.0×10^{-3}	2.6
Starch 1.0	120	6.0×10^{-3}	2.6	CMPS 1.0	90	1.6×10^{-3}	2.5
	115	3.5×10^{-3}	2.7		120	5.3×10^{-4}	2.7
	110	1.5×10^{-2}	2.7		115	1.3×10^{-3}	2.9
	105	1.1×10^{-2}	2.7		110	7.0×10^{-3}	2.7
	100	2.4×10^{-2}	2.6		105	3.6×10^{-2}	2.51
	95	8.3×10^{-3}	2.6		100	1.6×10^{-2}	2.6
	90	2.1×10^{-3}	2.7		95	2.4×10^{-3}	2.8
Talc 1.0	130	2.8×10^{-3}	3.1	CMPS 5.0	90	7.1×10^{-4}	2.6
	125	0.16	2.7		120	9.3×10^{-4}	2.7
	120	1.00	3.1		115	2.5×10^{-3}	2.8
	115	2.97	3.2		110	7.5×10^{-3}	2.6
	110	4.65	3.2		105	7.5×10^{-3}	2.7
	105	6.15	2.5		100	1.3×10^{-2}	2.5
CMPS 0.1	125	2.2×10^{-4}	2.3	CMPS 10.0	95	5.0×10^{-3}	2.6
	120	1.4×10^{-3}	2.6		90	6.4×10^{-4}	2.7
	115	5.1×10^{-3}	2.5		120	1.4×10^{-3}	2.5
	110	1.1×10^{-2}	2.7		115	4.0×10^{-3}	2.7
	105	1.9×10^{-2}	2.6		110	1.0×10^{-2}	2.8
	100	1.8×10^{-2}	2.8		105	1.5×10^{-2}	2.7
	95	7.0×10^{-3}	2.7		100	1.5×10^{-2}	2.7
	90	2.1×10^{-3}	2.5		95	1.2×10^{-2}	2.9
CMPS 0.5	120	5.5×10^{-4}	2.6	90	5.2×10^{-3}	2.7	
	115	1.7×10^{-3}	2.8				

**Fig. 9. The effect of nucleating agent on the half-time crystallization ($t_{1/2}$) as a function of the isothermal temperature.****Fig. 10. The effect of CMPS content on the half-time crystallization ($t_{1/2}$) as a function of the isothermal temperature.**

of nucleation and the density of nuclei are sensitive to the crystallization temperature, while the rate of crystal growth is only dependent on temperature. Generally, the values of both K and $t_{1/2}$ are evaluated to compare the overall crystallization rate of materials. Fig. 9 shows the curves of $t_{1/2}$ versus T_c for each kind of nucleating agent,

and Fig. 10 shows the effect of the CMPS content on the curves of $t_{1/2}$ vs T_c . As shown in Fig. 9, the $t_{1/2}$ value of PLA was greatly reduced by the addition of the nucleating agents, talc, starch and CMPS, at all of the tested crystallization temperatures, indicating that all of the tested nucleating agents can increase the crystallization rate of

PLA. According to the explanation of Gao et al. [35] about the shifting of the $t_{1/2}$ of a polymer caused by the addition of nucleating agent, the nucleation rate is controlled by the free enthalpy of formation of the nuclei of critical size and free energy of activation that govern the diffusion of the polymer segments across the phase boundary. In the high temperature region, the free enthalpy is the dominant factor controlling the nucleation rate, while the free energy of activation exerts the greatest influence on the nucleation rate at low temperatures, because of the large amount supercooling. Thus, it might be that pure PLA has a high free enthalpy, resulting in a slow nucleation rate, whereas a nucleating agent reduces the free enthalpy and enhances the primary nucleation at high temperature. The values of $t_{1/2}$ of the pure PLA decreased as the T_c decreased from 120 °C to 95 °C, while that of talc1.0 was constant with T_c . For Pure PLA, at a T_c below 95 °C it was difficult to record the data, which might be due to the decreased molecular motion. For talc1.0, at a T_c below 105 °C and above 125 °C it was difficult to analyze the data because of the fast crystallization rate. Meanwhile, the plots of $t_{1/2}$ vs. T_c of the starch1.0 and PLA/CMPS blends were concave curves. This means that there is a maximum overall crystallization rate at 105 °C [8]. The minimum $t_{1/2}$ value is 24.7 min at a T_c of 95 °C for the PLA, 0.4 min at a T_c of 105 °C for the talc1.0, 3.6 min at a T_c of 100 °C for the starch1.0, and 3.2 min at a T_c of 105 °C for the CMPS1.0. The samples of PLA with different CMPS contents have minimum $t_{1/2}$ values ranging from 3.2 to 4.8 min at around 105 °C, as shown in Fig. 10. In the case of the same T_c , the $t_{1/2}$ value of PLA was significantly decreased by the addition of CMPS, while it was not affected by the content of CMPS, as shown in Fig. 11. Though it was observed that inorganic nucleating agent of talc is the most effective crystallization agent, CMPS could be as effective a nucleating agent as granular starch.

The K value is another variable that is included in the comparison of the overall crystallization rate of the polymers. As shown in Table 3, at the same T_c , talc1.0 has the largest K value, starch1.0 and PLA/CMPS blends intermediate K values, and pure PLA has the smallest K value. It was also revealed that the K values for PLA/

CMPS samples were affected very little by the amounts of CMPS. As in the case of $t_{1/2}$ value, the K values of pure PLA and talc1.0 decreased with increasing T_c . What is more, the K values of starch1.0 and PLA/CMPS blends at first increase with increasing T_c ; then, after reaching a maximum values, they decrease as the T_c is further increased. The maximum rate of overall crystallization occurs at T_c of around 105 °C.

CONCLUSION

In this work, the effect of CMPS on the thermal properties and isothermal crystallization kinetics of PLA was studied and compared to that of the inorganic nucleating agent, talc, and newly proposed nucleating agent, granular starch. The thermal properties and crystallization rate of PLA were greatly increased by addition of nucleating agent. The half-crystallization times ($t_{1/2}$) of the starch1.0 and PLA/CMPS blends showed a minimum half-crystallization time at around 105 °C. In the case of PLA with various contents of CMPS, the crystallinity, overall crystallization rate, K, and the Avrami exponent, n, were not dependent on the content of CMPS. SEM study revealed that PLA/CMPS blends had neither supercooled spots nor grooves, but it had larger numbers of particles, which can act as a nucleating agent, compared to talc and granular starch. In addition, they showed that the interfacial adhesion between CMPS and PLA was very good, which can provide no compensation of mechanical properties. Although the effect of CMPS as a nucleating agent was slightly less than that of talc, CMPS can offer a fully biodegradable nucleating agent for the biobased and biodegradable polymers such as PLA with some advantages of no residues remaining, no compensation of mechanical properties, cost effectiveness and easy preparation because of its thermo-plasticity.

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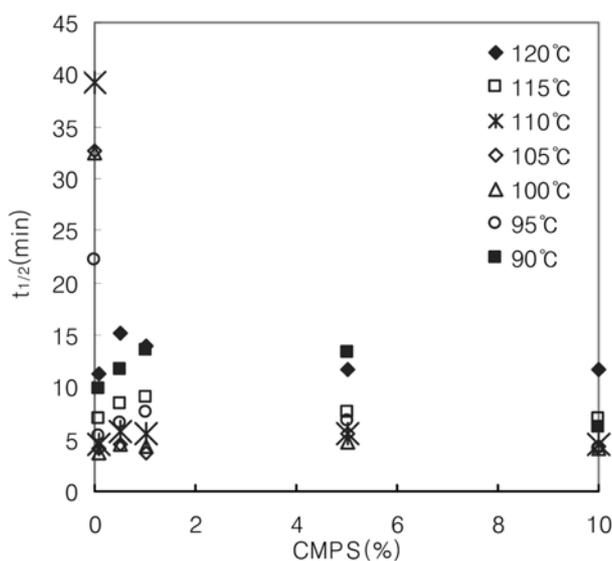


Fig. 11. The half-time crystallization ($t_{1/2}$) as a function of CMPS composition at the same isothermal temperature.

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