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Isotactic Polybutene-1의 결정화 거동을 개선하기 위한 생분해성 미세결정 셀룰로오스의 적용

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Application of Biodegradable Microcrystalline Cellulose to Improve the Crystallization Behavior of Isotactic Polybutene-1

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Abstract: The microcrystalline cellulose (MCC) was used for inducing crystallization of the isotactic polybutene-1 (iPB) and the maleic anhydride grafted polybutene-1 (MAPB) was used as a compatibilizer. The crystallization behavior of the composite demonstrated that the addition of MCC could significantly accelerate the crystallization rate of iPB and the addition of MAPB could improve the compatibility between MCC and iPB. Moreover, the properties of the composites with MAPB were better than those without MAPB. The crystal transformation had been completed after storage for 5 days and the form I was formed after storage for 3 days which was faster than pure iPB. The non-isothermal crystallization kinetics data of the composites indicated that the modified Avrami equation could describe the non-isothermal crystallization process of the iPB/MCC composite and the $t_{1/2}$ of the composites was shortened for 24.32% and 40.27% which indicated that MCC could promote the crystallization of iPB.

Keywords: isotactic polybutene-1, microcrystalline cellulose, crystallization behavior.

Introduction

Isotactic polybutylene-1 (iPB) is a kind of polymers with molecular chain regularity greater than 90%. It has excellent comprehensive properties, especially suitable for hot water pipes in drinking, hot water heating and other fields.[1,2] Compared with the current mainstream random copolymer polypropylene (PP-R) pipe, iPB has advantages of long-term use, strong circumferential stress-bearing capacity, excellent creep resistance, low energy consumption and no scaling.[3,4] However, iPB is a polycrystalline polymer which has four kinds of crystal form I, I', II, III.[5-7] The crystal form II is formed first after hot working forming, which has the characteristics of thermodynamically unstable, good toughness, poor rigidity, and unstable mechanical properties. The irreversible damage will occur if it is subjected to external force such as extrusion or impact at the initial stage of forming, which brings great difficulties to the processing and use of the materials.[8,9] After 7 days at room temperature, the most stable and valuable crystal form I of iPB will form, which has the characteristics of poor toughness, good rigidity, and stable mechanical properties.[10] Besides, the 7 days of crystal transformation period causes that the industry can only wait for the crystal transformation to be completely reused, but there is no guarantee that there will be no damage during this period. This will inevitably lead to the problems of low production efficiency and low resource utilization.

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In past years, many researches have been conducted to accelerate the crystal transformation rate of iPB. The researches on the crystallization behavior of iPB mainly focused on the influence of processing conditions and blending modification on the crystal transformation of iPB. As early as 2002, Zhang *et al.*[11] were used the solution casting method to prepare iPB ultrasonic film which was heat-treated in 160 ℃ under nitrogen atmosphere for 15 min and then quenched to different crystallization temperatures. The morphology and crystal structure of the film were studied by transmission electron microscopy (TEM). The results demonstrated that increasing the crystallization temperature was beneficial to the formation of crystal form I. The single oriented crystal of iPB crystal form I could be directly observed in the ultrathin film after quenching to 125 ℃ for 15 min and then cooling at room temperature. Xu *et al.*[12] were used high pressure CO_2 to induce crystallization of iPB films. The results showed that the pressure CO_2 could shorten the crystal transformation period of iPB, and with the CO_2 pressure increasing, the crystal transformation became faster, which was attributed to that the pressure CO_2 could induce the stretching orientation of crystals. Su *et al.*[13] were found that quenching could greatly increase the crystal form transformation rate of iPB film through two different methods of direct quenching and first crystallization and then quenching to different temperatures. The results indicated that the crystallization temperature and internal stress played an important role in the crystal transformation rate of iPB. Zhang *et al*.[14] used halloysite nanotubes (HNT) and attapulgite (PGS) as nano fillers to modify iPB and studied their crystallization behavior after quenching. The results displayed that the matching effect between PGS and crystal form I of iPB could promote the transformation of iPB more effectively. Due to the improved compatibility of the modified HNT, the crystal transformation of iPB was greatly enhanced. This phenomenon also proved that the interfacial compatibility of iPB blends composites had an important influence on the crystal transformation rate of iPB.

At present, lots of researches have been accumulated to solve the problem of the slow crystal transformation rate of iPB, but the study of blending modification with cellulose is rare. As we know, microcrystalline cellulose (MCC) has advantages of low cost, low density, biodegradability, and renewability.[15] The most important thing is that MCC is nontoxic and harmless, which is extremely suitable for the modification of drinking water pipe. But the interfacial compatibility between polarity MCC and non-polarity iPB is poor. In our previous researches, the carboxyl group is grafted into the iPB to prepared maleic anhydride grafted polybutene-1 (MAPB) as a compatibilizer, which is used to improve the interfacial compatibility of iPB/MCC composites and study the mechanical properties of the composites. The results show that MCC can improve the mechanical properties of iPB.[16]

In this study, the MAPB was used as a compatibilizer and the iPB/MCC composites were prepared by solution blending method. The micromorphology of the composites was characterized by scanning electron microscopy (SEM). The non-isothermal crystallization and melting behavior of the composites were investigated by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). Moreover, the non-isothermal crystallization kinetics of the composites were also discussed.

Experimental

Feedstock Sources. iPB (P5050) with melt flow index (MFI) of 200 g/10 min was purchased from Mitsui Chemical Inc. MCC was purchased from Aladdin Industrial Corporation (Shanghai, China). MAPB with grafting rate (ratio of the molar mass of carboxyl group to that of MAPB) of 0.42% was self-made in the laboratory.[16] Xylene and methanol were purchased from Tianjin Damao Chemical Reagent Factory (Tianjin, China).

Preparation of the iPB/MCC Composites. The iPB (5.0 g), MCC (0, 0.25, 0.25 g) and MAPB (0, 0, 0.1 g) were added into the flask with 100 mL xylene, which was named iPB, iPB/MCC5 and M-iPB/MCC5, respectively. The reaction temperature of the system was raised to 130 ℃ and it was stirred for 6 h. The liquid in the system was poured out of the excessive methanol and precipitated into white solid. The iPB/MCC composites were obtained by suction filtration and drying.

Non-isothermal Crystallization and Melting Behavior Characterization of the iPB/MCC Composites. The non-isothermal crystallization behavior of the sample was performed by differential scanning calorimetry (DSC, DSC1, Mettler Toledo Instrument Inc., Zurich, Switzerland). The program were set as follows: (1) The samples were heated from 30 to 180 ℃ with a heating rate of 10 ℃/min and maintained for 3 min; (2) The samples were cooled from 180 to 30 ℃ with a cooling rate of 5, 10, 20 ℃/min, respectively.

The samples after non-isothermal crystallization with a cooling rate of 5 ℃/min were storage at 30 ℃ for 1, 3, 5, 7 days, respectively. The melting behavior of the samples which storage for different days was performed by DSC with a heating rate of 10 °C/min from 30 °C to 180 °C.

Polarized Optical Microscopy (POM) Characterization of the iPB/MCC Composites. The POM characterization was performed by POM (BX51, Olympus Corporation, Tokyo, Japan) with a temperature-controlling stage (LTS 420, Linkam Scientific Instruments, Tadworth, UK). The samples were heated from 30 to 180 °C with a heating rate of 10 °C/min and maintained for 3 min, then cooled from 180 to 30 °C with a cooling rate of 5 °C/min. The crystal growth of the samples was observed at 95, 80, and 70 °C, respectively.

Scanning Electron Microscopy (SEM) of the iPB/MCC Composites. The interfacial compatibility between iPB and MCC was observed by SEM (7200F, JEOL Ltd., Tokyo, Japan) at an accelerating voltage of 10 kV.

Results and Discussion

Non Isothermal Crystallization Behavior of the iPB/MCC Composites. Non-isothermal crystallization curves of the iPB/MCC composites at different cooling rate are shown in Figure 1 and the corresponding parameters are depicted in Table 1. It can be seen from the Figure 1 that the width of non-isothermal crystallization peak becomes narrower with the addition of MCC and MAPB, and the M-iPB/MCC5 has the narrowest width, which is shown that the addition of MCC can greatly accelerate the crystallization rate of iPB and the addition of MAPB has a very beneficial effect on the interface compatibility between iPB and MCC, resulting in shorting the crystallization time of the composite at the same cooling rate. In addition, the non-isothermal crystallization peak of the same sample moves towards the low temperature direction with the increase of the cooling rate. This phenomenon proves that the increase of the cooling rate leads to a decrease of the crystallization ability at high temperatures, which is not conducive to the crystallization of the composites.

Table 1 shows the non-isothermal crystallization peak parameters of the iPB/MCC composites more clearly. The crystallization start temperature ($T_{\rm on}$) and crystallization peak temperature ($T_{\rm p}$) of the samples are increased with the addition of MCC and MAPB. Compared with pure iPB, the $T_{\rm on}$ of the samples is increased by 1.24 °C (iPB/MCC5) and 4.18 °C (M-iPB/MCC5), the $T_{\rm p}$ of the samples is increased by 3.87 °C (iPB/MCC5) and 8.67 °C (M-iPB/MCC5) when the cooling rate is 5 °C/min. The $T_{\rm on}$ of the samples is increased by 1.90 °C (iPB/MCC5) and 4.61 °C (M-iPB/MCC5), the $T_{\rm p}$ of the samples is increased by 4.83 °C (iPB/MCC5) and 8.72 °C (M-iPB/MCC5) when the cooling rate is 10 °C/min. The $T_{\rm on}$ of the samples is increased by 3.16 °C (iPB/MCC5) and 4.76 °C (M-iPB/MCC5), the $T_{\rm p}$ of the samples is increased by 4.33 °C

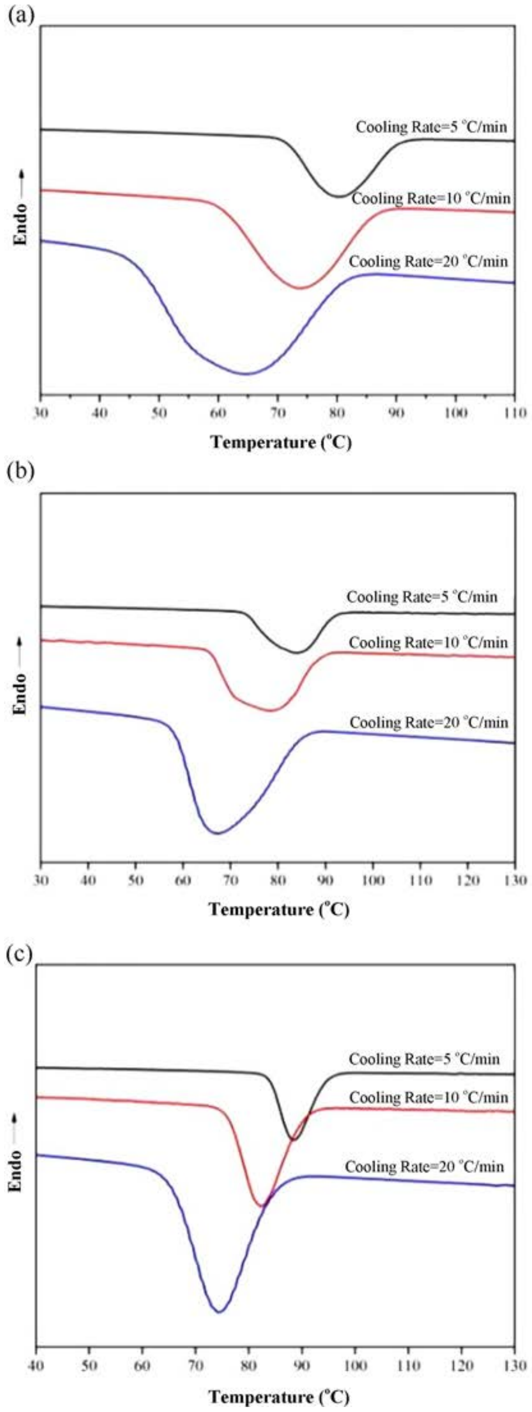

Figure 1. Non-isothermal crystallization curves of the iPB/MCC composites at different cooling rate: (a) iPB; (b) iPB/MCC5; (c) M-iPB/MCC5.

Table 1. Non-Isothermal Crystallization Peak Parameters of the iPB/MCC Composites at Different Cooling Rate

Sample	Cooling rate (°C/min)	T_{on} (°C)	T_p (°C)
iPB	5	94.07	80.11
	10	90.56	73.82
	20	86.41	64.76
iPB/MCC5	5	95.31	83.98
	10	92.46	78.65
	20	89.57	69.09
M-iPB/MCC5	5	98.25	88.78
	10	95.17	82.54
	20	91.17	74.42

(iPB/MCC5) and 9.66 ºC (M-iPB/MCC5) when the cooling rate is 20 ºC/min. The data in Table 1 indicates that the addition of MCC can significantly increase the crystallization temperature of the composites. Therefore, the composites can crystallize at a higher temperature. Moreover, the crystallization temperature growth rate of the M-iPB/MCC5 is much higher than that of iPB/MCC5, which indicates that the MAPB can greatly improve the interface compatibility between MCC and iPB. In fact, MAPB was synthesized by grafting maleic anhydride onto iPB molecular chain. In iPB/ MCC composite system, iPB molecular chain on MAPB could be completely compatible with iPB, while maleic anhydride could be esterified with hydroxyl groups on MCC molecular chain, so that iPB and MCC could obtain better compatibility.

POM of the iPB/MCC Composites. To observe the crystal growth at different temperatures, POM photos of the iPB/MCC composites at different crystallization temperature are shown in Figure 2. The spherulite size and quantity of the same sample increase with the decrease of temperature during the cooling process. Moreover, the spherulite size and quantity of M-iPB/MCC5 increase fastest which is shown that M-iPB/MCC5 has the strongest crystallization ability among all samples. At the same time, the order of spherulite size and quantity from large to small is M-iPB/MCC5, iPB/MCC5, iPB at the same crystallization temperature, which indicates that the addition of MCC can promote the growth of iPB spherulites and accelerate crystallization rate of iPB.[17] The reason for this result is that MCC has heterogeneous nucleation in iPB matrix, and the spherulites of iPB will stop growing when they touch MCC during the growth process, so the spherulites of iPB can be refined and the crystallization process can be completed in a short time. Moreover, this simulative effect is more evident after the addition of MAPB, which indicates that MAPB can

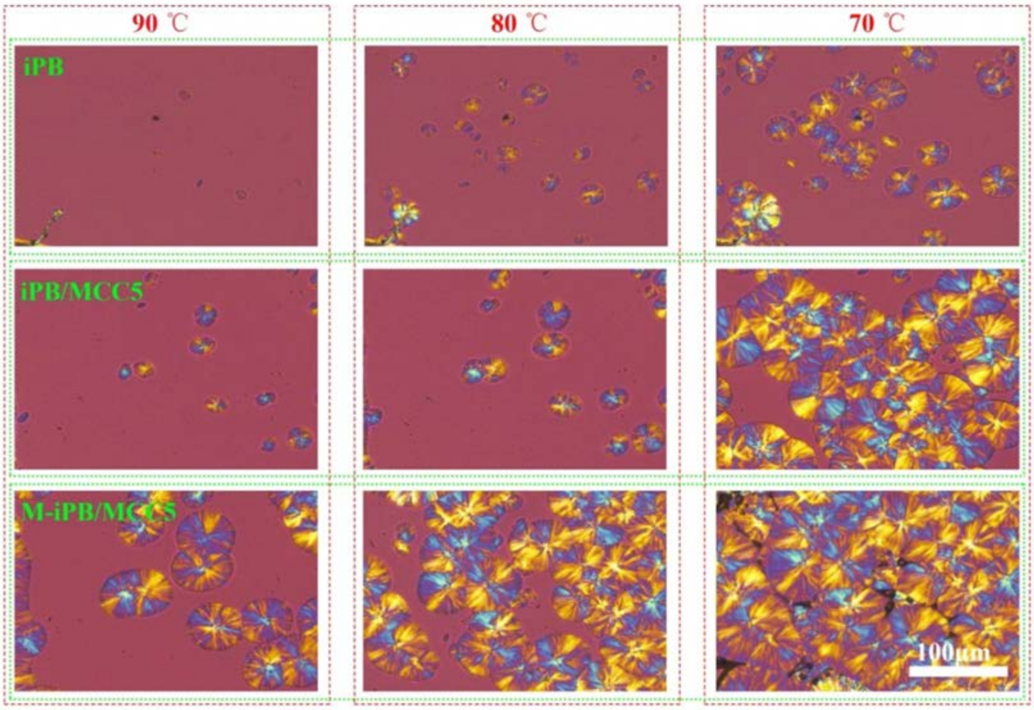

Figure 2. POM photos of the iPB/MCC composites at different crystallization temperature (cooling rate=5 ºC).

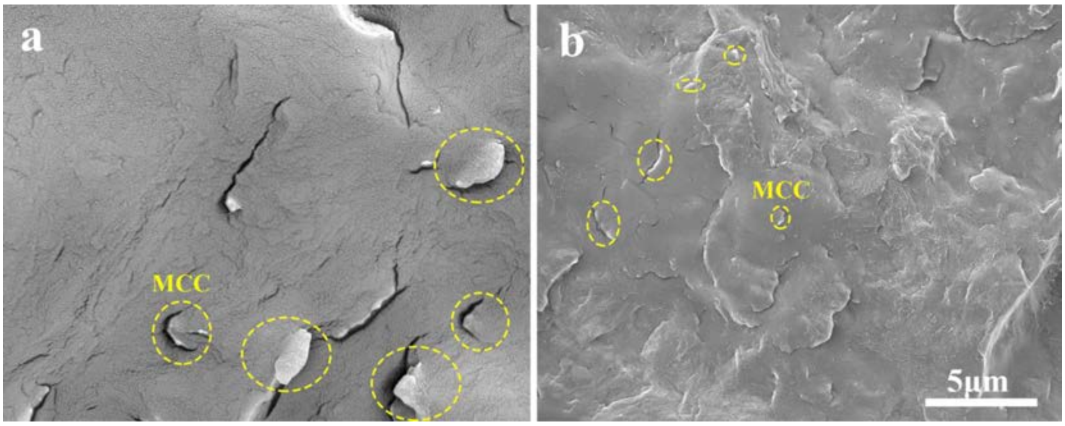

Figure 3. SEM photographs of the iPB/MCC composites: (a) iPB/MCC5; (b) M-iPB/MCC5.

improve the interface compatibility of the composites so that the crystallization property of the composite is more excellent. In addition, M-iPB/MCC5 has the largest spherulite size and quantity when the crystallization temperature increases. This result proves that the M-iPB/MCC5 still has very strong crystallization ability at high temperature. The POM photos directly reflect the influence of MCC and MAPB addition on the spherulites size and quantity of iPB, and the results are com-

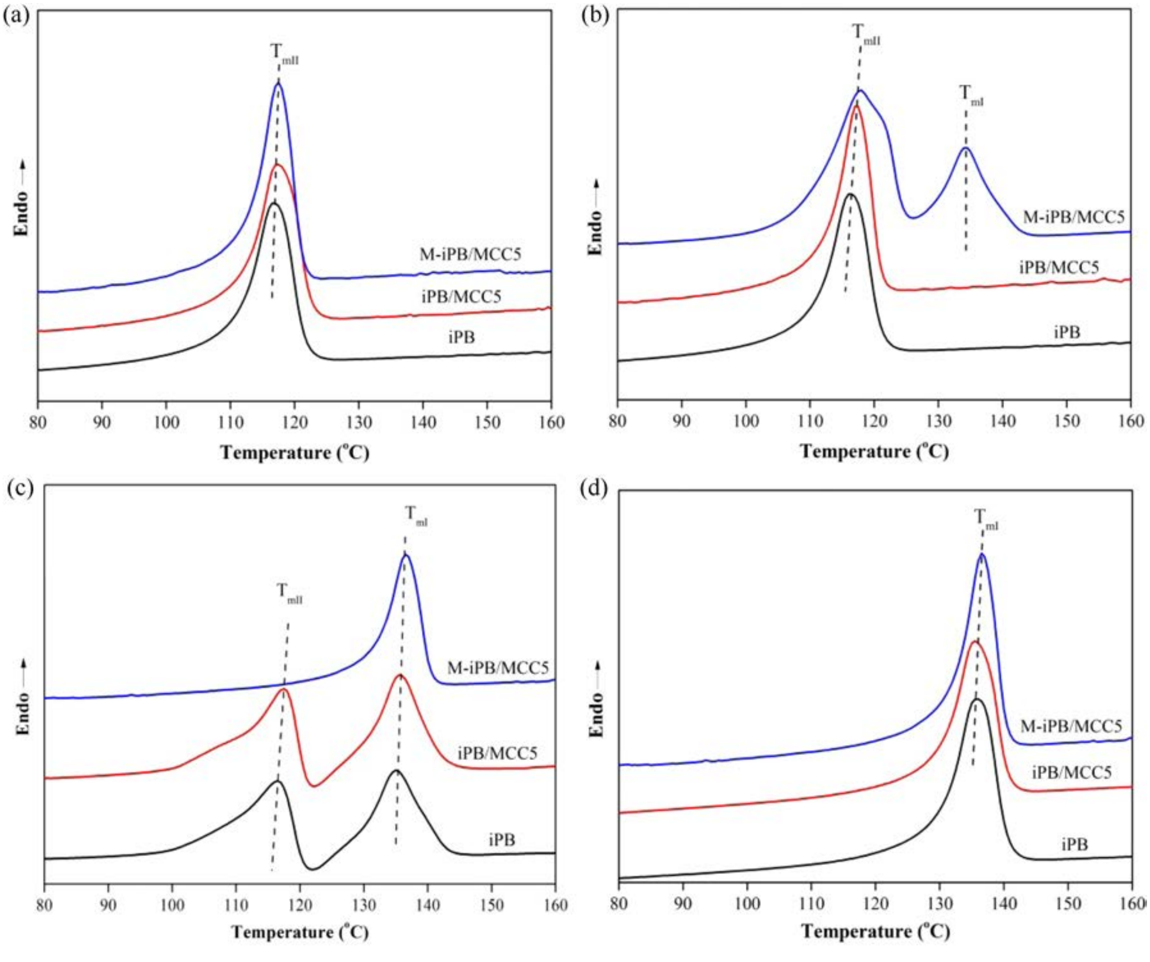

Figure 4. Melting curves of the iPB/MCC composites with different storage days: (a) after 1 day; (b) after 3 days; (c) after 5 days; (d) after 7 day.

pletely cultural with DSC data. In conclusion, we can confirm the beneficial effect of MCC on the crystallization performance of iPB, and the improvement of interface compatibility has an important contribution to accelerating the crystallization rate of iPB.

SEM of the iPB/MCC Composites. Figure 3 exhibits the SEM photographs of the iPB/MCC composites. The surface of iPB/MCC5 is rough and has many micro-cracks in Figure 3(a). Contrary to iPB/MCC5, the surface of M-iPB/MCC5 is smoother and the micro-cracks are disappeared in Figure 3(b). Meanwhile, the size and dispersion of MCC between Figure 3(a) and 3(b) have obvious differences. In Figure 3(a), the size of MCC is bigger, and there are some big gaps between MCC and iPB. This phenomenon proves that the serious agglomeration of MCC in iPB matrix results in a poor dispersion, which leads to poor interface compatibility between MCC and iPB. With the addition of MAPB, the size of MCC is decreased greatly and there is no crack between MCC and iPB. It is indicated that MAPB can improve the compatibility of MCC and iPB, which endows the composites more excellent properties.

Melting Behavior of the iPB/MCC Composites. The crystallization of form I cannot be observed directly after eliminating the thermal history. Therefore, the primary melting curves of iPB/MCC samples are used to observe the crystal forms with different storage days through the different melting temperature (T_m) of crystal forms II and I. The melting curves of the iPB/MCC composites with different storage days are shown in Figure 4 and the corresponding parameters are depicted in Table 2.

All of the samples are shown a single endothermic peak when the sample is stored for 1 day and 7 days which are corresponding to the melting peaks of form II and form I, respectively.[14] The peak temperature (T_{mII}) is about 116 ℃ and the T_{mI} is about 135 ℃, which is consistent with the melting temperature of iPB crystal form II and form I reported in the literature.[9] Compared to iPB, the T_{mII} and T_{mI} of iPB/MCC5 and M-iPB/MCC5 are increased by 0.4, 0.65 ℃ and 1.07, 1.13 ℃, respectively. This phenomenon proves that the stable crystal form I of iPB cannot directly induce by MCC. Moreover, the addition of MCC can promote the T_m of the sample increase, and the increase is more obvious for the sample with MAPB. The results always show that the MAPB promotes the interface compatibility between MCC and iPB, and improves the properties of the composite.

Surprisingly, some important changes appear in the melting curves of the composites with storage for 3 days and 5 days. After storage for 3 days, the endothermic peaks of the form I and form II are observed in the melting curves of M-iPB/MCC5, meanwhile iPB and iPB/MCC5 still have only the endothermic peak of form II. After storage for 5 days, the M-iPB/MCC5 is shown a single endothermic peak of form I which means that the crystal transformation has been completed. Besides, the iPB and iPB/MCC5 are shown two endothermic peaks of the form I and form II. In addition, the increase of T_{mII} or T_{mI} is shown the same rules with the samples storage for 1 day and 7 days. The results indicate that the addition of MCC is beneficial to accelerating the crystal transformation of iPB, but this acceleration is closely related to the interface compatibility between MCC and iPB. The composites with MAPB have completely transformed into the form I in the 5 days of storage which has great significance for shortening the storage time of iPB and speeding up the product circulation in the iPB industry.

Table 2. Melting Curves Peak Parameters of the iPB/MCC Composites with Different Storage Days

Sample	Storage days	T_{mI} (°C)	T_{mII} (°C)
iPB	1	-	116.33
iPB/MCC5		-	116.73
M-iPB/MCC5		-	117.60
iPB	3	-	116.61
iPB/MCC5		-	117.17
M-iPB/MCC5		134.32	117.60
iPB	5	135.01	116.33
iPB/MCC5		135.58	117.32
M-iPB/MCC5		136.92	-
iPB	7	135.14	-
iPB/MCC5		135.79	-
M-iPB/MCC5		136.92	-

Non-isothermal Crystallization Kinetics of the iPB/MCC Composites. As previously described, iPB is a kind of polymorphism polymers. The unstable form II is generated first after hot working forming. It takes a long time for 7 days to transform into stable crystal form I at room temperature. Therefore, the crystallization rate of iPB includes two processes of melt to form II and form II to form I. No matter which process is accelerated, the total crystallization rate can be accelerated. The melting curves of the composites indicate that the addition of MCC is beneficial to accelerating the crystal form II to form I of iPB. However, only the crystallization of form II can be observed directly during the non-isothermal crystallization process of iPB, so the non-isothermal crystallization kinetics of the form II of the iPB/MCC composites are calculated in this research.

As we know, the classical Avrami equation (eq. (1)) is commonly used to study the isothermal crystallization kinetics of polymers.[18,19] However, polymer crystallization is always a non-isothermal process in production and processing application. Therefore, the Avrami analysis method modified directly extends the Avrami equation to the analysis of non-isothermal crystallization kinetics. The essence of this process is to treat the crystallization process as isotherm, and then to correct the kinetic parameter k. The non-isothermal crystallization mechanism of polymers is determined according to the kinetic constant k_c and Avrami index n obtained under non-isothermal crystallization conditions.[20]

$$\log[-\ln(1-X(t))] = n\log t + \log k \tag{1}$$

Where the $X(t)$ is the relative degree of crystallinity, n is the Avrami index, t is the crystallization time, k is the kinetic parameter.

The relative degree of crystallinity $X(T)$ can be calculated according to the non-crystallization curves of the iPB/MCC composites at different cooling rate by eq. (2).

$$X(T) = \int_{T_0}^{T}\left(\frac{dH}{dT}\right) / \int_{T_0}^{T_\infty}\left(\frac{dH}{dT}\right) dT \tag{2}$$

Where T_0 and T_∞ is the starting and ending temperature of the crystallization, dH/dT is corresponded to the crystallization heat flow rate at different temperature (T).

Because crystallization is a non-isothermal process, the relationship between crystallinity $X(T)$ and crystallization time (t) can be converted according to eq. (3). The result is shown in Figure 5.

$$t = (T_0 - T)/\phi \tag{3}$$

Where T_0 is the starting temperature of crystallization, the T is the crystallization temperature at time t and the φ is the cooling rate.

The log [-ln(1–$X(t)$)] is plotted with log$t$ *via* Avrami equation. The Avrami index n can be obtained from the slope and log k can be obtained from the intercept. Then the cooling rate ϕ is corrected for the obtained k_c according to eq. (4).

$$\log k_c = (\log k)/\phi \tag{4}$$

Non-isothermal crystallization kinetics curves and kinetic parameters of the iPB/MCC composites are obtained after data processing of Figure 5 according to eq. (1) and (4), which are shown in Figure 6 and Table 3, respectively.

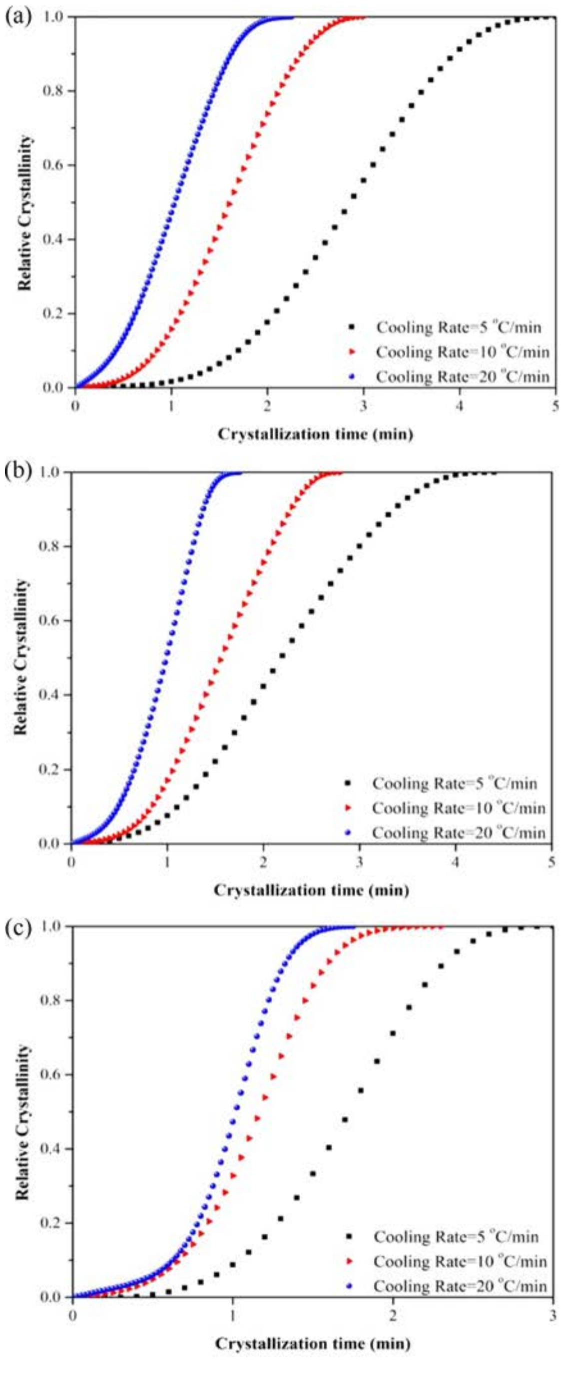

Figure 5. Relative crystallization *versus* crystallization time of the iPB/MCC composites: (a) iPB; (b) iPB/MCC5; (c) M-PB/MCC5.

In Figure 6, the modified Avrami equation can describe the non-isothermal crystallization process of the iPB/MCC composites. The value of Avrami index n of iPB and M-iPB/

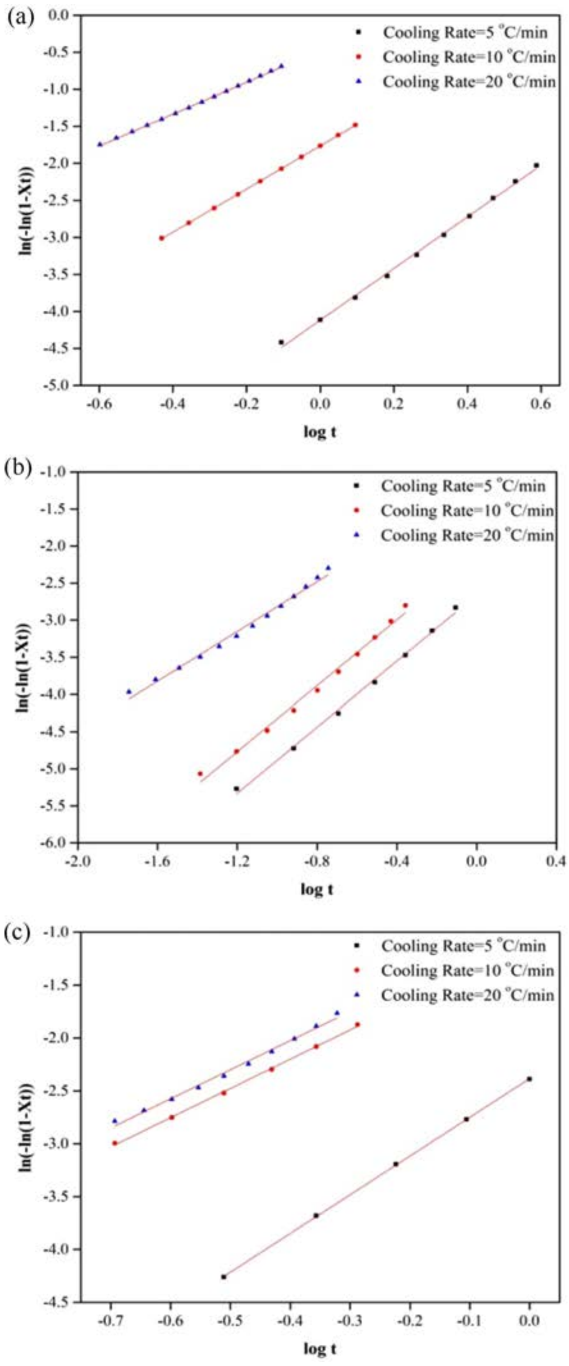

Figure 6. Non-isothermal crystallization kinetics curves of the iPB/MCC composites: (a) iPB; (b) iPB/MCC5; (c) M-iPB/MCC5.

MCC5 is about 3, iPB/MCC5 is about 2, which indicates that the crystal growth mode of iPB and iPB/MCC5 is two-dimensional growth and M-iPB/MCC5 is three-dimensional growth.[21] In addition, the non-isothermal crystallization process of iPB is mainly homogeneous nucleation, while the other samples have homogeneous nucleation and heterogeneous nucleation due to the addition of MCC. The phenomenon proves that MCC can change the crystal growth mode of iPB on the premise of good compatibility.

Table 3. Non-Isothermal Crystallization Kinetic Parameters of iPB/MCC Composites

Sample		n	k_c	$t_{1/2}$ (min)
iPB	5	3.5	0.15	2.88
	10	2.9	0.67	1.61
	20	2.7	0.85	1.04
iPB/MCC5	5	2.2	0.29	2.18
	10	2.1	0.72	1.56
	20	1.7	0.88	0.99
M-iPB/MCC5	5	3.7	0.33	1.72
	10	2.8	0.78	1.18
	20	2.7	0.90	1.01

The k_c of iPB, iPB/MCC5 and M-iPB/MCC5 increases and the half crystallization time $t_{1/2}$ is shortened with the increase of the cooling rate. It shows that the crystallization rate of the composites is directly proportional to the cooling rate which is due to the slow transformation from molten state to crystallization when the cooling rate is lower, and the effect of the cooling rate on crystallization is weak. With the increase of the cooling rate, the crystallization is greatly affected by the cooling rate. It is proved that the cooling rate has a significant effect on the crystallization of the system. At the same cooling rate, the k_c values of iPB/MCC5 and M-iPB/MCC5 are significantly higher than that of iPB and the $t_{1/2}$ of iPB/MCC5 and M-iPB/MCC5 at cooling rate of 5 ºC/min is shortened for 24.32% (0.7 min) and 40.27% (1.16 min) which indicates that MCC can promote the crystallization of iPB.

Conclusions

In this study, the MAPB was used as a compatibilizer and the iPB/MCC composites were prepared by solution blending method. The DSC and POM date of the composites were shown that the addition of MCC could significantly increase the crystallization temperature, promote the growth spherulites and accelerate the crystallization rate of iPB. Moreover, the properties of the composites with MAPB were better than those without MAPB. The SEM photograph of the composites was shown that the size of MCC was decreased greatly and there was no crack between MCC and iPB with the addition of MAPB, which indicated that MAPB could improve the compatibility of MCC and iPB. The melting curves of the composites with different storage days were shown that the form I observed in the melting curves of M-iPB/MCC5 after storage for 3 days and the crystal transformation of M-iPB/MCC5 had been completed after storage for 5 days. The results indicated that the addition of MCC was beneficial to accelerating the crystal transformation of iPB, but this acceleration was closely related to the interface compatibility between MCC and iPB. The non-isothermal crystallization kinetics date of the composites were indicated that the modified Avrami equation could describe the non-isothermal crystallization process of the iPB/MCC composites and the $t_{1/2}$ of iPB/MCC5 and M-iPB/MCC5 at cooling rate of 5 ºC/min was shortened for 24.32% (0.7 min) and 40.27% (1.16 min) which indicated that the MCC could promote the crystallization of iPB.

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