

# Influence of filler content and processing parameter on the crystallization behaviour of PP/kaolin composites

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**Abstract** Kaolin-filled polypropylene (PP) composites with various kaolin content, processing temperature and shear histories were compounded using a heated two roll-mill. Prior to thermal analysis, the samples were subjected to extrusion process via capillary rheometer. The influences of kaolin content, processing temperature and shear stress on crystallization of all samples, including isothermal and nonisothermal crystallization behaviour were investigated by differential scanning calorimetry (DSC). The results showed that the increasing kaolin content, processing temperature and shear stress have shifted the crystallization exothermic peak to higher temperature and reduced the overall crystallization time.

**Keywords** Polypropylene · Kaolin · Thermal · Isothermal · Nonisothermal · Crystallization · Nucleation

## Introduction

Polypropylene (PP) is one of the most widely used thermoplastic in many demanding applications. It has many advantages as a base matrix for thermoplastics composites owing to its relatively low cost and high chemical resistance coupled with ease of fabrication. Fabrication and design of variety new products with improved mechanical properties need detailed understanding of the crystallization behaviour

of those polymeric products. Extensive researches [1–3] have been published on the isothermal and nonisothermal crystallization kinetics of PP and its composites with different fillers. For example, Luyt et al. [4] observed a decrease in the crystallization temperature after the introduction of wollastonite filler. The crystallization in the present system is diminished as a result of lower chain mobility. The storage moduli and tensile measurement showed that the composites have higher stiffness than pure PP over the whole range of test temperature. It has been mentioned in many studies [5, 6] that the reason for this behaviour is the strong influence of fillers on the polymer chain dynamics. Jain et al. [7] successfully using a combined Avrami–Ozawa approach to describe the non-isothermal crystallization kinetics of PP/silica nanocomposites. They discovered that silica acted as heterogeneous nucleating agent. The silica fillers accelerate the nucleation activity, resulting in more perfect crystals and increase the crystallinity of the system. The increase in crystallinity results in higher yield stress and the decrease in entanglement eventually results in lower strain modulus. In the study of crystallization behaviour of PP/maleic anhydride-grafted polypropylene (PP-g-MAH)/organic-montmorillonite (Org-MMT) nanocomposite, Xu et al. [8] has employed the Avrami analysis modified by Jeziorny, Ozawa method and a method developed by Liu to describe the nonisothermal crystallization process of the samples. The values of half-time,  $Z_c$ , kinetic parameter,  $F(T)$  and function of cooling rate,  $K(T)$  showed that the crystallization rate of composites was faster than that of PP at a given cooling rate. Whereas nonisothermal kinetic crystallization corresponded to tridimensional growth with heterogeneous nucleation. This clearly indicated that Org-MMT and PP-g-MAH have heterogeneous nucleation effect on pure PP, which results in a decrease of crystallite size. George et al. [9] proved that

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isothermal crystallization rates and the nucleation activity of PP-fumed silica nanocomposites increased with increasing filler content up to 7.5 wt%.

Other researchers have investigated how the addition of various clay fillers would affect the crystallization behaviour, including the crystal forms variation and heterogeneous nucleation ability of fillers in most polymeric material [10, 11]. For a filled polymer material, monitoring the change of its crystallization rate brought about by filler such as kaolin is particularly important. The addition of filler which is expected to act as nucleation agent in the filled PP would increase the crystallization rate. The scientific and technological interest for tailoring and modifying the PP properties has been driving a very vivid research on the base matrix and plate-like kaolin fillers. This scenario significantly altering the properties of PP using only small incorporation levels of filler. The melting and crystallization behavior of the system are greatly influenced by the relative amount and the dispersion level of fillers [12, 13]. Although the crystallization behaviour of PP/kaolin composites has been widely reported, nonetheless, there were infrequently explorations on the crystallization from melt under the influence of processing temperature and shear stress in PP/kaolin composite [14]. Normally, ample processing temperature and shear stress are needed in processing polymeric material due to the two main effects. First, it could contribute to the realignment of the polymer network anisotropically trailing the flow direction on the respective molten matrix and fillers. The second effect was to orientate the fillers parallel to the flow path [14]. In this study, the vital effects of processing parameter such as processing temperature and shear stress on the crystallization kinetics of PP/kaolin composites were investigated. In addition, the crystallization and melting temperatures, enthalpies of crystallization and fusion and degree of crystallization of the system were also evaluated in the presence and absence of filler incorporation.

## Experimental

### Materials

The thermoplastic used in this study was PP copolymer resin grade Pro-Fax SM-240 supplied by Titan PP Polymers (M) Sdn. Bhd. The SM-240 was received in pellet form with a density of  $0.894 \text{ g cm}^{-3}$  and melt flow index (MFI) of  $25 \text{ g } 10 \text{ min}^{-1}$  was obtained when measured according to ASTM D1238, at  $230 \text{ }^\circ\text{C}$  and with 2.16 kg load [15]. The kaolin used is refined kaolin supplied by CIBA company. The additives added were antioxidant (Irganox 1010) and ultra-violet stabilizer (Tinuvin 770 DF), both were from CIBA company.

### Sample preparation

A heated two roll-mill was used in compounding the samples. All composites were prepared by melt compounding; this procedure involved melting of pure PP matrix on the heated rolls. The temperature of the rolls was set at  $185 \text{ }^\circ\text{C}$  with total compounding time of 25 min. These conditions have been selected in order to homogenize fillers in the PP matrix. The total mixtures of sample which is 200 grammes were loaded on the heated two roll-mill. First, the pure PP matrix was filled onto the rolls. At fifth minute, the fillers were carefully added onto the melted PP. Each compound was milled at constant rotational speed. After 25 min, the rolls were stopped and the compound was quickly removed from the heated rolls. Finally, the molten compound was sheeted through a laboratory scale two-roll mill at 2.0 mm nip setting and then cut into small particles for extrusion process.

### Testing

The composites were extruded using Shimadzu capillary rheometer model CRT-500 (at three different shear stresses of 9.8, 19.6 and 34.3 kPa and at temperatures of 180, 200 and  $220 \text{ }^\circ\text{C}$ ). This work involved a fixed flat-entry capillary die with diameter = 1 mm and  $L D^{-1}$  (length over diameter) ratio of 10.

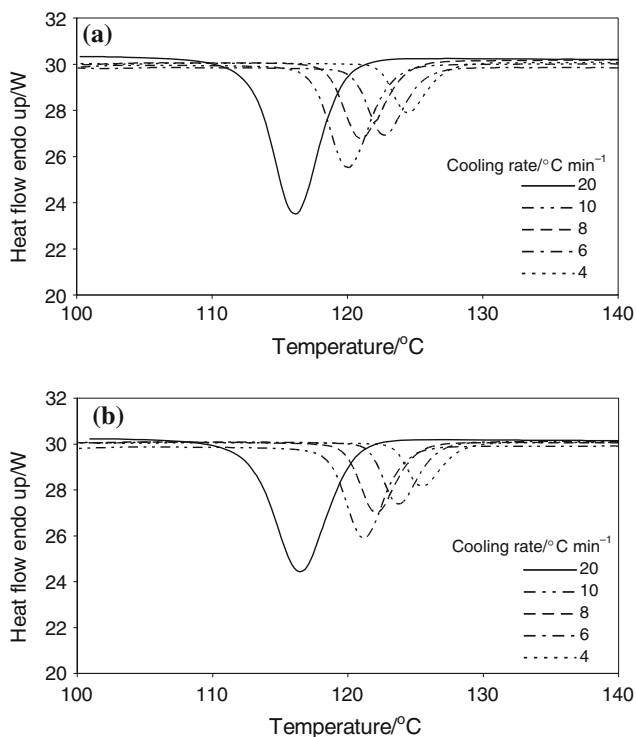
Nonisothermal crystallization behaviors of kaolin-filled PP composites were studied using Perkin–Elmer DSC-7 and the mass of all samples were approximately 2 mg. The DSC was calibrated with 10 mg of indium ( $T_m = 156.4 \text{ }^\circ\text{C}$ ,  $\Delta H_f = 28.5 \text{ J g}^{-1}$ ) prior to performing the experiment. The samples were heated from 20 to  $220 \text{ }^\circ\text{C}$  at a heating rate of 4, 6, 8, 10 and  $20 \text{ }^\circ\text{C min}^{-1}$  under a nitrogen atmosphere, and held for 5 min to remove previous thermal history. Nonisothermal crystallization kinetics were investigated by cooling these samples from  $220\text{--}20 \text{ }^\circ\text{C}$  at constant cooling rates of 4, 6, 8, 10 and  $20 \text{ }^\circ\text{C min}^{-1}$ .

## Results and discussion

### Influence of filler content

DSC analysis provides quantitative evaluation of the crystallization behaviour of unfilled PP and its composites. The crystallization behaviour of all samples was studied at cooling rates between 4 and  $20 \text{ }^\circ\text{C min}^{-1}$ . The nonisothermal crystallization curves of unfilled PP and kaolin-filled PP are shown in Fig. 1.

Normally, molecular chains of PP can crystallize by themselves (self-nucleation effect) or crystallize with the presence of inorganic filler such as kaolin leading to



**Fig. 1** DSC crystallization curves of samples (a) unfilled PP and (b) kaolin-filled PP 10 wt% during non-isothermal crystallization at different cooling rates

heterogeneous nucleation effect in filled PP system. When kaolin fillers are well dispersed in the PP matrix, the heterogeneous nucleation effect dominates the crystallization process and one broad crystallization peak can be observed resulting from the co-existence of self-nucleation and heterogeneous nucleation effects. The melting peak becomes broad when PP is filled with 10 wt% of kaolin indicating that, in comparison to PP, there were more crystallites with lower perfection formed in PP/kaolin composites. It is believed that this may result from some impediment in the melting process of filled PP because of combination of small particle size and uniform distribution of kaolin in PP matrix. At this phase, the growth of crystallites was delayed due to restricted alignment of PP molecules network by kaolin fillers. It leads to low mobility of polymer segments in the regions of lamellae surfaces during polymer melting process. Consequently, these analyses showed that the incorporation of kaolin fillers enhanced the PP nucleation mechanism but also hindered the crystallite growth which corresponds to the broader melting peak of PP/kaolin composites in DSC curves.

It is shown that the crystallization peak temperature ( $T_p$ ) of kaolin-filled PP is higher than those of unfilled PP. The  $T_p$  of both samples were shifted to lower temperatures with increasing cooling rates. The faster the cooling rate, the lower the temperature range at which the crystallization

occurs. At slower cooling rate, the sample passes through the recrystallization process gradually. There is adequate time for the melted sample to reorganize and generate formation of nuclei leading to emergence of crystallization at higher temperature [16]. Nevertheless, at higher cooling rates, the sample passes through the recrystallization state so swiftly that there is insufficient time for the polymer network to reorganize thus leading to reduction in the amount of perfect nuclei. The reorganization process is largely inhibited and subsequently contributes to the decrease in the peak temperature of exotherm. For example, the crystallization temperature of PP increased approximately 2 °C in the presence of 30 wt% of kaolin particles (at cooling rate of 20 °C min<sup>-1</sup>) and the crystallization temperature of all samples increasing when the cooling rates were increased.

From these curves (Fig. 1), some useful parameters for the nonisothermal crystallization analysis, such as the onset temperature of crystallization ( $T_{m\ onset}$ ), the crystallization temperatures, e.g. the exothermic peak maxima ( $T_p$ ) and the end temperature of crystallization ( $T_c$ ) can be obtained. The crystallization temperature ( $T_p$ ) and the degree of crystallization ( $X_c$ ) for unfilled PP and 10 K are listed in Tables 1 and 2. The enthalpy of crystallization ( $\Delta H_c$ ) can also be calculated from the enthalpy of crystallization normalized to the PP content by assuming that the thermodynamic contributions of filler phase in this system is negligible. The degree of crystallization of unfilled PP was

**Table 1** Sample compositions according to weight percentage (wt%) of PP composites at different kaolin loading

Sample	PP/wt%	Kaolin/wt%
Unfilled PP	100	–
5 K	95	5
10 K	90	10
20 K	80	20
30 K	70	30

**Table 2** DSC Data for PP and kaolin-filled PP composites at a cooling rate of 20 °C min<sup>-1</sup> (processed at processing temperature = 200 °C and shear stress = 9.8 kPa)

Sample	$T_{m\ onset}/^{\circ}\text{C}$	$T_m/^{\circ}\text{C}$	$T_s/^{\circ}\text{C}$	$T_p/^{\circ}\text{C}$	$T_c/^{\circ}\text{C}$	$\Delta H_c/J\ g^{-1}$	$X_c/\%$
PP	152.2	162.0	119.7	116.2	112.76	62.72	30.0
5 K	153.1	162.8	119.4	116.3	112.47	63.14	31.8
10 K	152.9	162.7	120.5	116.3	113.57	60.57	32.2
20 K	154	162	120.9	117	113.9	51.83	31.0
30 K	153.9	164	121.48	118.3	114.36	44.62	30.5

$T_m$  the peak of melting temperature,  $T_{m\ onset}$  the onset of melting temperature

calculated using Eq. 2a whereas Eq. 2b was applied to the composite system. The degree of crystallization of all samples are listed in Table 2.

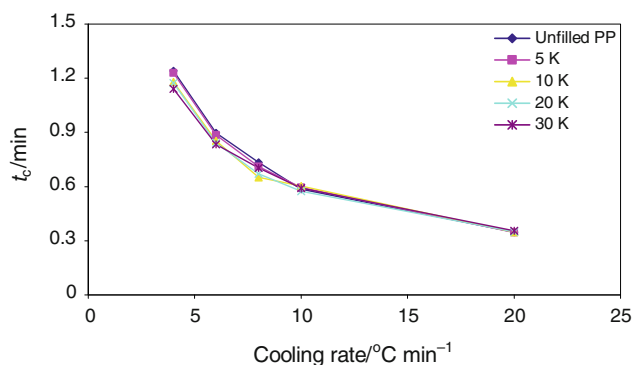
$$X_c = \frac{\Delta H_c}{\Delta H_f} \times 100 \quad (2a)$$

$$X_c = \frac{\Delta H_c}{\Delta H_f(1 - W_f)} \times 100 \quad (2b)$$

where  $\Delta H_c$  is the heat of fusion,  $\Delta H_f$  is the heat of fusion for 100% crystalline and  $W_f$  is the mass fraction. The value of  $\Delta H_f$  used for pure crystalline PP was assumed to be  $209.0 \text{ J g}^{-1}$  [17]. As listed in Table 2, the degree of crystallization ( $X_c$ ) of the composites was increased by the kaolin content up to 10 wt%. Nonetheless,  $X_c$  of the composites tend to decrease when the kaolin loading exceeds 10 wt%. At a given cooling rate,  $T_p$  of kaolin-filled PP composites was higher than that of unfilled PP. This clearly implies that the incorporation of kaolin results in the heterogeneous nucleation to the PP matrix. At an early stage of crystallization, the molecular chains of PP might be in contact with the filler surface and limit the movement of polymer chains. The movement of polymer chains which is in a form of distorted network can be quickly relaxed and reestablished. This scenario helped to increase the structural stability of polymer matrix [4] giving an increase in the crystallization peak temperature.

As shown in Fig. 2, the overall crystallization time ( $t_c$ ) reduces with increasing kaolin loading at low cooling rates ( $<8 \text{ }^\circ\text{C min}^{-1}$ ), but higher cooling rates showing overlapping of  $t_c$  values. This scenario signifies that the  $t_c$  values are becoming independent towards higher cooling rates ( $>8 \text{ }^\circ\text{C min}^{-1}$ ). In nonisothermal crystallization, the temperature can be related to overall crystallization time ( $t_c$ ) scale by using the following equation

$$t_c = \frac{(T_s - T_e)}{r} \quad (1)$$



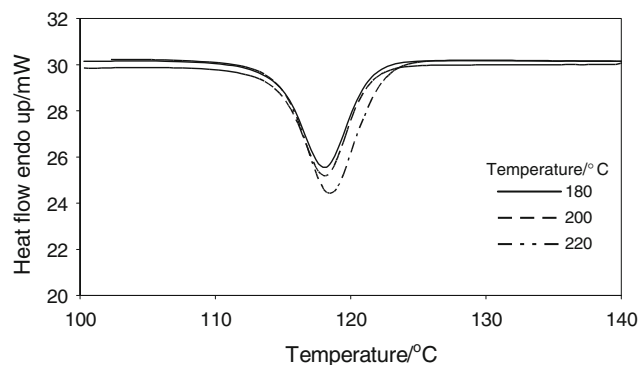
**Fig. 2** Overall crystallization time versus cooling rate at different kaolin loading

where  $r$  is the cooling rate,  $T_s$  is the initial crystallization temperature and  $T_e$  is the final crystallization temperature. The observed increase of  $T_p$  and decrease of  $t_c$  with increasing kaolin content are typical characteristics of nucleation-controlled polymer crystallization [1]. The results show that the higher the cooling rate, the shorter the time needed for completing crystallization. A reduction in crystallization time due to the incorporation of fillers is widely reported by several researchers [7, 18].

### Influence of processing temperature

Figure 3 shows the DSC crystallization curves of nonisothermal crystallization for 30 K at a cooling rate of  $20 \text{ }^\circ\text{C min}^{-1}$ . Prior to thermal analysis, the samples were extruded at shear stress of 19.6 kPa and at various extrusion temperatures. The  $T_p$ ,  $T_{m \text{ onset}}$ , and other crystallization parameters for the samples are listed in Table 3. The observed onset temperature and crystallization peak temperature decreases slightly with increasing processing temperature with processing temperature of  $220 \text{ }^\circ\text{C}$  illustrates the obvious difference. In addition, samples which were processed at extrusion temperature of  $220 \text{ }^\circ\text{C}$  displayed the highest  $X_c$ . This earlier crystallization phenomenon on the influence of processing temperature can be interpreted as the result of an increase in nucleation activities. Processing at high extrusion temperature induces the molecular chains mobility of PP, and reduces the free energy barrier for crystallites formation which is able to accelerate the rate of crystallization.

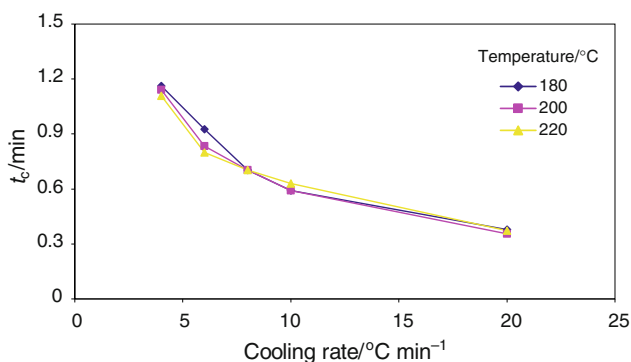
To further confirm that faster crystallization was accelerated by extrusion temperature, samples at three different extrusion temperatures were comparatively investigated. The crystallization time values for the same sample (30 K) discussed in the above paragraph can be obtained from Fig. 4. There was visible different between the crystallization time



**Fig. 3** DSC curves of kaolin-filled PP (30 wt%) during nonisothermal crystallization at different extrusion temperature

**Table 3** DSC Data for 30 K samples which were extruded at various processing temperature (at a cooling rate of 20 °C min<sup>-1</sup>)

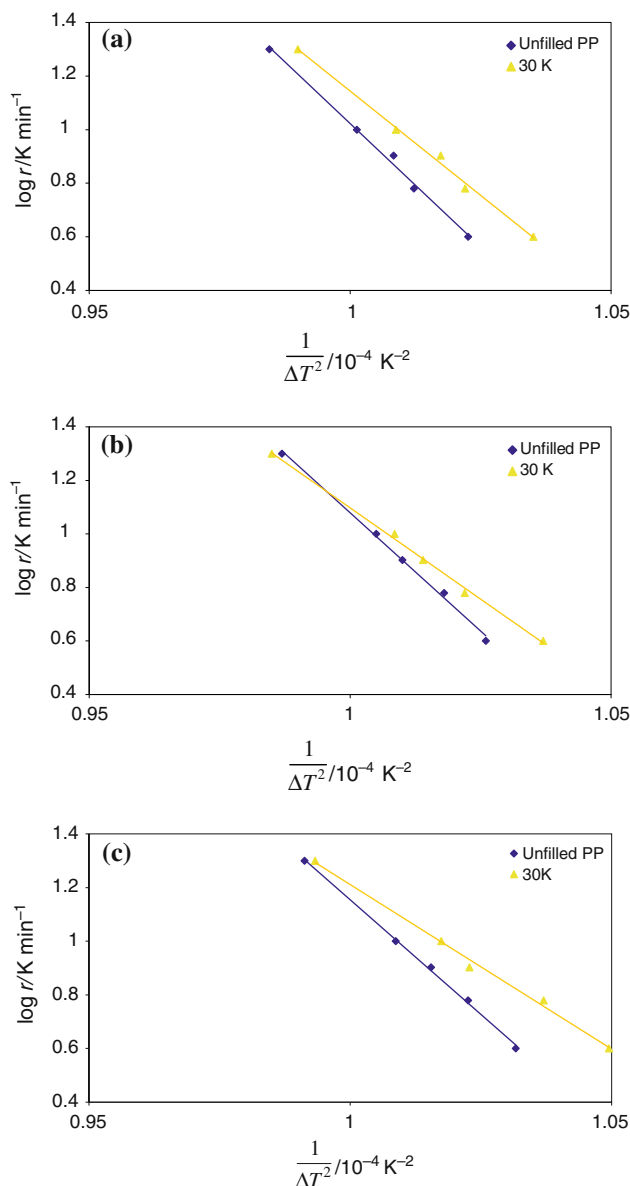
Processing temperature/°C	$T_{m\ onset}/^{\circ}\text{C}$	$T_m/^{\circ}\text{C}$	$T_g/^{\circ}\text{C}$	$T_p/^{\circ}\text{C}$	$T_c/^{\circ}\text{C}$	$\Delta H_c/\text{J g}^{-1}$	$X_c/\%$
180	154.1	162.1	122.4	118	114.83	43.6	29.8
200	153.9	162.4	122.38	118.3	114.36	44.62	30.5
220	153.4	163.4	121.6	118.6	114.15	47.99	32.8

**Fig. 4** Overall crystallization time versus cooling rate at different extrusion temperature

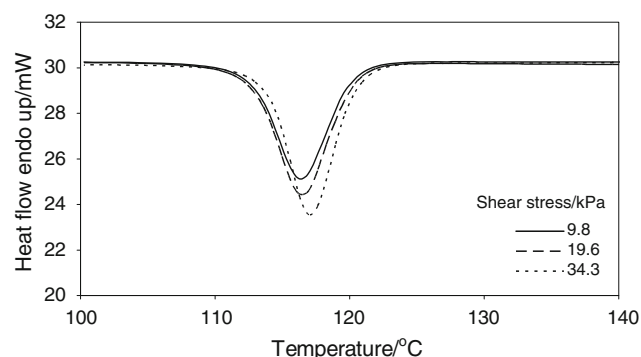
of 10 K extruded at processing temperatures of 180, 200 and 220 °C. Even though only small differences could be seen, the crystallization time is decreasing with increasing extrusion temperature. At faster cooling rates, the process of recrystallization is hindered, resulting in decreasing of  $t_c$ . Whereas, at slower cooling rates, it is suggested that PP crystals melt and recrystallize into more perfect crystals. This effect is typically associated with melting followed by recrystallization into more stable crystals and recrystallized samples at higher temperature [19, 20] and therefore, increasing the  $t_c$  value at slow cooling rate. It can be seen from Fig. 4 that 30 K composite showed dependency of  $t_c$  on extrusion temperature. Apparently, at a given cooling rate, 30 K sample which is extruded at highest temperature took shorter time to complete the crystallization. These results signify that increasing the processing temperature could initiate the self- (refer to Fig. 5) and heterogeneous nucleation activities to facilitate the overall crystallization process. However, the crystallization time shows similar results as obtained in the influence of filler content that at cooling rate of 8 °C min<sup>-1</sup> and beyond demonstrates that the  $t_c$  values are becoming self-governing from cooling rates.

#### Influence of shear stress

In order to understand the initial melting behavior and crystallization response of PP/kaolin composite samples at various shear stresses, DSC analysis of extruded sample (10 K) were conducted at a cooling rate of 20 °C min<sup>-1</sup> and the relative first scans are shown in Fig. 6. The

**Fig. 5** Plots of  $\log r$  versus  $\frac{1}{\Delta T^2}$  for unfilled PP and 30 K at various extrusion temperatures **a** 180 °C, **b** 200 °C, and **c** 220 °C

increase in shear stresses has shifted steadily the exotherm towards higher temperature region. Thus, increasing the crystallization of PP macromolecule segments at higher shear stress. According to the DSC curves shown in Fig. 6,  $T_p$ ,  $\Delta H_c$  and  $X_c$  at a cooling rate of 20 °C min<sup>-1</sup> for 10 K



**Fig. 6** DSC curves of kaolin-filled PP (10 wt%) during non-isothermal crystallization at different shear stresses

**Table 4** DSC Data for 10 K samples which were extruded at various shear stresses (at a cooling rate of  $20\text{ }^{\circ}\text{C min}^{-1}$ )

Shear stress/kPa	$T_{m\text{ onset}}/^{\circ}\text{C}$	$T_m/^{\circ}\text{C}$	$T_g/^{\circ}\text{C}$	$T_p/^{\circ}\text{C}$	$T_c/^{\circ}\text{C}$	$\Delta H_c/\text{J g}^{-1}$	$X_c/\%$
9.8	152.5	162	120.6	116	113.57	56.99	30.3
19.6	152.9	162.7	120.5	116.3	109.44	60.57	32.2
34.3	152.6	163.2	121.7	117.8	114.56	66.96	35.6

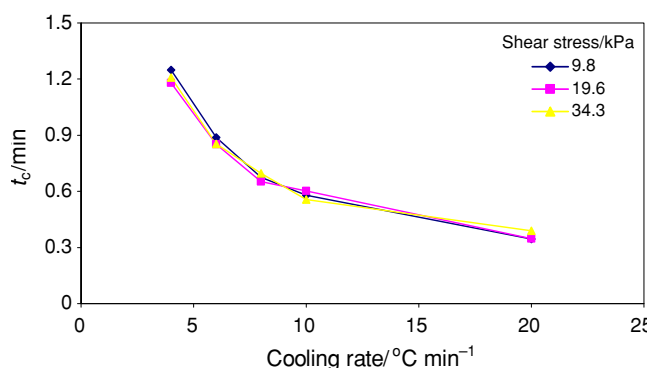
composite can be obtained and these values are listed in Table 4.  $\Delta H_c$  estimated by integration of the area under the exothermic region of the DSC thermogram increases with the increasing shear stresses (see Table 4), indicating an increase in the degree of crystallinity of samples.

From Table 4, it can be seen that the  $X_c$  values of all unfilled PP and PP/kaolin composites were increased with increasing shear stress. This phenomenon could be explained by the effective heterogeneous nucleation effect of kaolin particles on PP macromolecule chains for sample processed at highest shear stress. As shown by the result for samples extruded at highest shear stress of 34.3 kPa giving the highest  $X_c$  value.

This could be easily explained by focusing on the effect of shear stress. If the applied shear stress is sufficiently large, the crystallization rate of samples will be significantly accelerated as proven in these experimental results, which is of great importance to production. When the shear stress is applied to the system, the entangled polymer chain network and the filler network were both stretched and oriented along the flow direction. The oriented and realigned PP molecular chain networks and redispersed kaolin particles which acted as heterogeneous nucleation agents induced the formation of oriented crystals [11]. This scenario greatly influenced the crystal morphology of PP and enhanced number of crystals in the PP matrix. Consequently, the evidence of shear stress on crystallization began to be tangible.

The influence of shear stress on  $T_p$  was also evaluated and shown in Table 4. In brief, by controlling the processing parameter, samples with different thermal behaviour could be obtained. It is clear that shear stress has strong influences on thermal behaviour of PP/kaolin composites. Different shear stress histories have changed and moved  $T_p$  to higher temperatures.

Figure 7 shows the crystallization time dependence of the cooling rate for 10 K after the samples were extruded at three different shear stresses. It can be seen that the  $t_c$  values of the sample extruded at highest shear stress (for cooling rates  $<8\text{ }^{\circ}\text{C min}^{-1}$ ) are lower than those extruded at lower shear stresses. This suggests that high shear stress does contribute to the raise in crystallization rate. From the above description, it was clear that shear effect on crystallization time of PP was also tangible in 10 K. During the extrusion process, when the low shear stress (9.8 kPa) was exerted, the crystallizable entity was increased with the increase of kaolin content. As it is well known that there is the effect of heterogeneous nucleation with the addition of clay fillers in polymer composites [11, 21]. However, when the shear stress was large enough to overcome the chaotic situation of entanglement and realignment of PP molecules. At this point of time, the sufficient shear stress also destroyed some of the filler network and dispersed the kaolin books (layer) into individual plate-like filler. In this case, more surface area of kaolin fillers were exposed to PP chains and available as heterogeneous nucleation sites for polymers. Simultaneously, the high shear stress could also enhance the nucleation of PP due to the shear-induced chain alignment. Thus, the number of oriented crystals in 10 K was increased greatly, but the size of crystal was decreased which leads to a decrease in the crystallization time. As discussed earlier, the same scenario occurring in the influence of shear stress illustrating that the  $t_c$  values for cooling rates at  $8\text{ }^{\circ}\text{C min}^{-1}$  and above are less dependent from cooling rates.



**Fig. 7** Overall crystallization time versus cooling rate of 10 K at different shear stresses

## Conclusions

All of the investigated samples were prepared at a wide range of processing temperature and shear stress. The crystallization peak of filled PP was shifted to higher temperature if compared to that of unfilled PP, clearly showing the nucleation efficiency of kaolin fillers. The wider melting peak of the composite compared to that of unfilled PP shows the effect of fillers. The incorporation of kaolin particles leads to the formation of small crystallites with lower perfection in PP matrix. In this study, dependence of processing temperature and shear stress condition on crystallization kinetics of all samples were also demonstrated. The results showed that both processing temperature and shear stress have influence on crystallization behaviour. The overall crystallization time which indicates the time for the sample to crystallize during non-isothermal crystallization process was reduced by raising the processing temperature and shear stress and addition of kaolin content (for cooling rates  $<8\text{ }^{\circ}\text{C min}^{-1}$ ). Nonetheless, results attained in the influences of filler content, processing temperature and shear stress showed that the  $t_c$  values (at cooling rate of  $8\text{ }^{\circ}\text{C min}^{-1}$  and beyond) are becoming self-governing from cooling rates.

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