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Evaluation on nonisothermal crystallization kinetics of polypropylene/kaolin composites by employing Dobreva and Kissinger methods

A. Ariffin · Z. M. Ariff · S. S. Jikan

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Abstract The influences of kaolin content, processing temperature, and shear stress on crystallization of all samples were investigated by differential scanning calorimetry (DSC). The crystallization activation energy calculated using Kissinger's method displayed a decreasing trend with increasing kaolin content, processing temperature, and shear stress. A study of nucleation activity, which could indicate the influence of filler on polymer matrix, revealed that kaolin filler had a slight nucleation effect on polypropylene (PP) matrix. A thorough observation on nucleation effect also revealed that the incorporation of kaolin in tandem with increasing temperature and shear stress have contributed to successive heterogeneous nucleation in the system.

Keywords Polypropylene · Kaolin · Thermal · Isothermal · Nonisothermal · Crystallization and nucleation

Introduction

Kaolin-filled PP composite has gained much interest in the past few years because the objective of the new product is not only to reduce cost but also to improve certain properties pertaining to virgin polypropylene [1]. Kaolin is one among the best-known members of a group of clay minerals [2] while PP is a semi-crystalline thermoplastic polymer. The development of polypropylene composites has recently given rise to various activities focusing on polymer technology in its multi-faceted applications [3]. However, challenges are encountered in determining the right formulation for the filled polypropylene wherein the right prediction is required to anticipate how the filler will affect the overall characteristics and performance of the polypropylene composites [4]. In order to overcome this problem, crystallization of this polypropylene composite should be studied, since it is closely related to the situation at hand.

Extensive researches [5–8] have been published on the isothermal and nonisothermal crystallization kinetics of PP and its composites. Their studies revealed that the final properties of the filled PP composites in engineering applications are critically dependent on the extent of crystallization which in turn depends on the processing conditions. Thus, the study of nonisothermal crystallization of polymers is of great technical importance, since most practical processing techniques operate under these conditions [9].

On the development of new product, polymer processing industries strives to seek optimum processing condition. Processing of thermoplastic such as injection molding, film blowing, and fiber spinning always involves the application of shear stress; meanwhile, it is strongly believed that the shear stress profoundly affects the nucleation and crystallization behaviors [10–12]. Sun et al. [12] studied the crystallization of PP/organic montmorillonite (OMMT) composite under shear field. It was reported that the shear flow could enhance the crystallization of PP/OMMT composite even though shear strain was small. The effect of shear on crystallization became stronger with the shear strain increasing. However, the crystallization of PP/OMMT composite was not influenced by shear flow after being sheared at 2.2 s^{-1} for 10 s, and the crystallization behavior was similar with that of the unsheared sample because the filler network in PP/OMMT composite was not destroyed under small shear strain. When shear strain was large enough to destroy the filler network and align the clay layers along

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A. Ariffin (✉) · Z. M. Ariff · S. S. Jikan
School of Materials and Mineral Resources Engineering,
Engineering Campus, Universiti Sains Malaysia,
14300 Nibong Tebal, Seberang Perai Selatan, Penang, Malaysia
e-mail: azlan@eng.usm.my

the flow direction, then oriented crystals including cylindrites and strings of spherulites were formed. These aligned clay layers acted as heterogeneous nucleation agents to promote crystallization of PP [12]. The type and degree of molecular or filler orientation are largely determined by the rheological behavior of the polymer and the nature of the flow during fabrication process [13, 14].

Nevertheless, different preparation procedures would give different results for the thermal properties. The processing temperature is also an important aspect in determining the thermal behavior of polymeric material, which is altogether crucial in determining the quality of final features of the product to be produced [15]. The exact temperature to be used in polymer processing is essential because, at high temperature, polymer is bound to degrade more easily or unwanted side effects may occur. For some polymeric materials, temperatures required for processing are very crucial which leads to the necessity of knowing the exact processing temperatures [15]. A change in processing conditions such as temperature and shear stress may or may not affect the rate of crystallization. In order to optimize the industrial processing conditions, the processing temperature and shear stress influences are as crucial as the filler effect. Hence, these two processing conditions should been given thorough investigation. There has been little research related to the nonisothermal crystallization behaviors of kaolin-filled PP composites. To that effect, research regarding thermal behavior of kaolin-filled PP composite should be reviewed since it is very important in ascertaining its mechanical characteristics which are widely known as being greatly influenced by its production history [16].

In this study, we report the crystallization behavior of a commercial PP and kaolin-filled PP. The objective of this investigation is to reveal the effects of kaolin loading, processing temperature, and shear stress on commercial PP and PP/kaolin composites crystallization behavior. Differential scanning calorimetry (DSC) was used to determine the melting and crystallization behaviors of all the samples. The nucleation activity and crystallization activation energy of PP/kaolin composites were computed using Dobreva and Kissinger methods, respectively. In this article, the samples were subjected to three different processing temperatures and shear stresses followed by studies on crystallization after cessation of the above-mentioned processing conditions.

Experimental

Materials

The thermoplastic used in this study was polypropylene (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 g cm^{-3}, and melt flow index (MFI) of 25 g 10 min^{-1} was obtained when measured according to ASTM D1238-90b, at 230 °C and with 2.16 kg load. The kaolin used is refined kaolin supplied by CIBA company. The additives added were antioxidant (Irganox 1010) and ultraviolet stabilizer (Tinuvin 770 DF), both procured 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 °C with total compounding time of 25 min. These conditions have been selected 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 the fifth minute, the fillers were carefully added onto the melted PP. Each compound was milled at a 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. Sample compositions of PP composites at different kaolin loadings are presented in Table 1.

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 °C). This work involved a fixed flat-entry capillary die with diameter, 1 mm and L/D (length over diameter) ratio of 10.

Nonisothermal crystallization behaviors of kaolin-filled PP composites were studied using Perkin-Elmer DSC-7, and the weights of all samples were approximately 2 mg.

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

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

The DSC was calibrated with 10 mg of indium (T_m° = 156.4 °C, ΔH_f° = 28.5 J g^{-1}) before performing the experiment. The samples were heated from 20 to 220 °C at heating rates of 4, 6, 8, 10, and 20 °C min^{-1} under nitrogen atmosphere, and held for 5 min to remove previous thermal history. Nonisothermal crystallization kinetics were investigated by cooling these samples from 220 to 20 °C at cooling rates of 4, 6, 8, 10, and 20 °C min^{-1}.

Results and discussion

Influence of filler content

Apparently, at low cooling rate where the recrystallization is too slow, the supercooling is reduced due to the formation of stable nuclei which crystallize at high temperature. Nevertheless, the nuclei which form at high cooling rate are unstable, and thus, they crystallize at low temperature, which occurs at sufficiently high supercooling. As supported by the experimental results (Fig. 1), the supercooling greatly affects the crystallization and melting behavior of the samples.

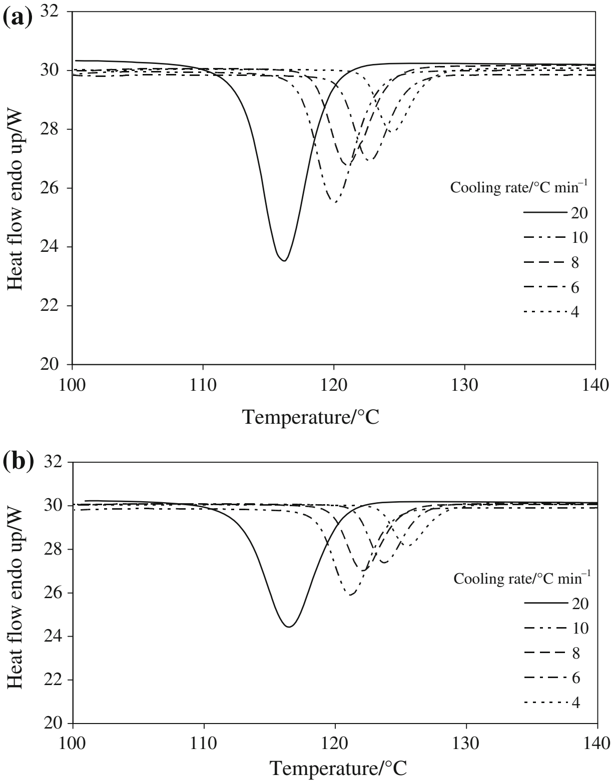

Fig. 1 DSC thermograms of samples **a** unfilled PP and **b** kaolin-filled PP 10 wt% during nonisothermal crystallization at different cooling rates

Nucleation activity

In order to better understand the evolution of nonisothermal crystallization process, the nucleation activities and crystallization activation energy of samples of the unfilled PP and PP/kaolin composites with different filler contents were analyzed. The unfilled PP and PP/kaolin composites were processed at a processing temperature of 200 °C and a shear stress of 9.8 kPa. Among the methods developed to describe these activities are equations proposed by Dobreva and Kissinger. These methods have been proven to be most successful [17–19].

The nucleating activity of the samples was determined using Dobreva's method as described by Kim et al. [20]. This method suggests a simple method for calculating the nucleation activity of foreign substrates in polymer melt, where the cooling rate and the degree of supercooling are taken into consideration. For homogeneous nucleation from a melt near the melting temperature, the following equation was used:

$$\log r = A - \frac{B}{2.3\Delta T_{\mathrm{p}}^{2}} \qquad (1)$$

However, the following equation was applied to the heterogeneous system in which the foreign particles assist in crystallization:

$$\log r = A - \frac{B^{*}}{2.3\Delta T_{\mathrm{p}}^{2}} \qquad (2)$$

$$\phi = \frac{B*}{B} \qquad (3)$$

where r is the cooling rate, A is a constant, and ΔT_p is the degree of supercooling, i.e., $\Delta T_p = T_m - T_p$, and T_p is the temperature corresponding to the peak temperature of the DSC crystallization curves, while T_m is the peak of melting temperature. B is a parameter that can be calculated from the following equation:

$$B = \frac{\omega\sigma^{3}V_{\mathrm{m}}^{2}}{3nkT_{\mathrm{m}}\Delta S_{\mathrm{m}}^{2}n} \qquad (4)$$

where ω is a geometrical factor, σ is the specific energy, V_m is the molar volume of the crystallizing substance, n is the Avrami exponent, ΔS_m is the entropy of melting, and k is the Boltzmann constant. Therefore, the nucleation activity, ϕ, was simply calculated by the ratio of the slopes, log r versus $1/\Delta T^2$ plot, with and without the nucleation agent, by using Eqs. 1 and 2. Plots of log r versus $1/\Delta T^2$ for the unfilled PP and kaolin-filled PP composites are shown in Fig. 2. Nucleation activity, ϕ, is a factor by which the work of three-dimensional nucleation decreases with the addition of a foreign substrate. The nucleation activity, ϕ, is defined as the ratio of B^* to B and is determined from the slopes of linear plots of log r versus $1/\Delta T^2$ (Fig. 2). It has

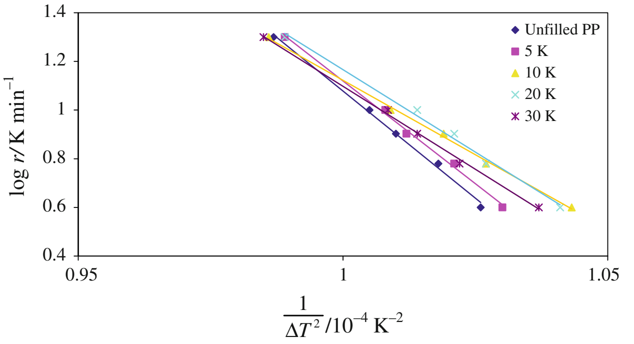

Fig. 2 Plots of log r versus $\frac{1}{\Delta T^2}$ for unfilled PP and kaolin-filled PP composites

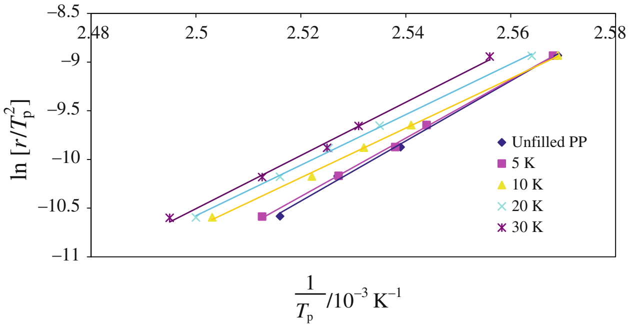

Fig. 3 Kissinger plot for evaluating nonisothermal crystallization activation energies of unfilled PP and kaolin-filled PP composites

been stated that for active surfaces, ϕ tends to approach zero whereas, if it approaches one, the surface is considered as an inert surface for nucleation [20]. The nucleation activities for 5, 10, 20, and 30 K samples were found to be 0.96, 0.69, 0.76, and 0.77 respectively. These values suggest that kaolin fillers performed effectively as nucleation agents in the PP matrix thus leading to an active surface for crystallization. The incorporation of more than 10 wt% kaolin fillers leads to reduction of nucleation activities. This fact is due to the overloaded fillers in the system, thus, restricted the alignments of polymer molecules.

Crystallization activation energy

As described earlier, the crystallization peak temperature is dependent on cooling rate. For nonisothermal crystallization processes, the Kissinger method is one of the most popular approaches for evaluating effective activation energy. Considering the influence of cooling rates on the nonisothermal crystallization process, Kissinger proposed that the activation energy could be determined by calculating the variation of the crystallization peak with cooling rate [21]:

$$\frac{\mathrm{d}[\ln(r/T_\mathrm{p}^2)]}{\mathrm{d}(1/T_\mathrm{p})} = \frac{-\Delta E}{R} \tag{5}$$

where R is the gas constant, and T_p is the crystallization peak temperature. From a plot of ln $[r/T_\mathrm{p}^2]$ versus $1/T_\mathrm{p}$, and fitting to a straight line, the crystallization activation energy, ΔE can be easily calculated from the slope.

As shown in Fig. 3, the crystallization activation energies of PP and kaolin-filled PP composites during nonisothermal crystallization were determined to be 256.2, 248.8, 211.7, 215.8, and 227.2 kJ mol^{-1}. It can be seen that the crystallization activation energy of the composites illustrated reduction as the kaolin content increased up to the 10 wt%. The introduction of 20 wt% and beyond illustrated an increment in crystallization activation energy. However, the ΔE values of 20 and 30 K are much lower compared to that of unfilled PP. These results indicate that the addition of kaolin filler into PP causes more heterogeneous nucleation.

Influence of processing temperature

Nucleation activity

We note from Fig. 4 that increasing extrusion temperature results in a change of X_c of 10 K from 29.8 to 32.3%, which clearly shows the effect of processing temperature toward the nucleation efficiency in the system. In addition, increasing processing temperature of the same filler concentration further raised the crystallization temperature. From the slopes of linear plots of log r versus $1/\Delta T^2$ (Fig. 5), the slopes of PP at three different extrusion temperatures of 180, 200, and 220 °C are observed to be 18.387, 17.632, and 17.103, respectively, whereas the slopes of 10 K composite at three different extrusion temperatures of 180, 200, and 220 °C are 15.561, 13.649, and 12.255, respectively. Therefore, the nucleation activity values of PP/kaolin composite at extrusion temperatures of 180, 200, and 220 °C were calculated to be 0.85, 0.77, and 0.72 respectively. It is apparent that the nucleation activity

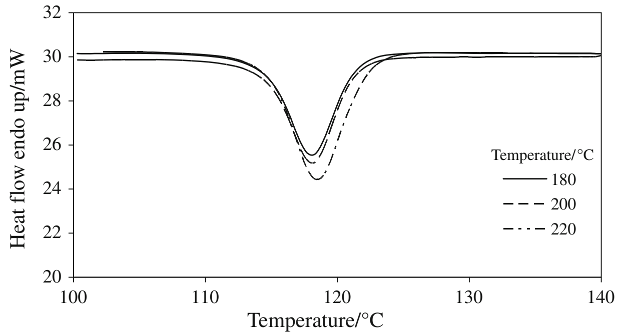

Fig. 4 DSC thermograms of kaolin-filled PP (30 wt%) during nonisothermal crystallization at different extrusion temperatures

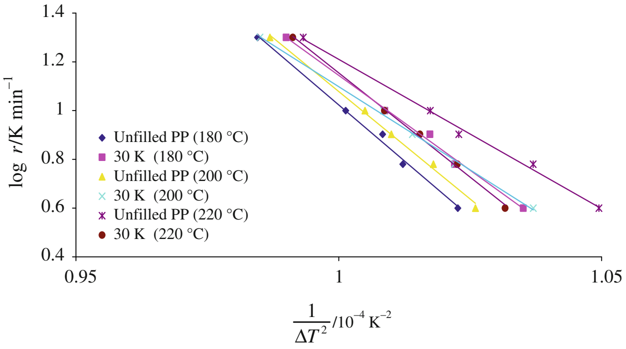

Fig. 5 Plots of log r versus $\frac{1}{\Delta T^2}$ for unfilled PP and 30 K at various extrusion temperatures (180, 200 and 220 °C)

at extrusion temperature of 200 °C is better than that of 180 °C, and the crystallization rate of 10 K extruded at 220 °C is more evidently accelerated. As discussed earlier, a decrease in crystallization temperature at low extrusion temperature (180 °C) is believed to be due to the influence of extrusion temperature on the molecular chain activities. A fine judgment that can be made on this scenario is that the crystallization temperature in the present system is slowed down by lower chain mobility as a result of small amount of kinetic energy being possessed by the PP molecules. In addition, many researches [22–24] have proven that when such unstable nuclei are formed at low temperature, then they will crystallize at low temperature, whereas the nuclei that are grown at high extrusion temperature are more stable, and therefore crystallize at higher crystallization temperature.

Crystallization activation energy

The influence of processing temperature on crystallization activation energy for 10 K can be determined from Fig. 4 and the results are shown in Fig. 6. As discussed earlier, the onset temperature of crystallization, as well as crystallization peak, is affected by the presence of high extrusion temperature. It is strongly believed that there are also differences in the crystallization activation energy of 10 K extruded at three different temperatures as the nucleation rates were dissimilar at all conditions. In order to validate this report, the crystallization activation energies of 10 K at various temperatures during nonisothermal crystallization were calculated and determined to be 231.8, 229.1, and 213.8 kJ mol^{-1}. It is apparent that the value of ΔE decreases with increasing extrusion temperature, suggesting that the extrusion temperature can greatly affects the overall crystallization process.

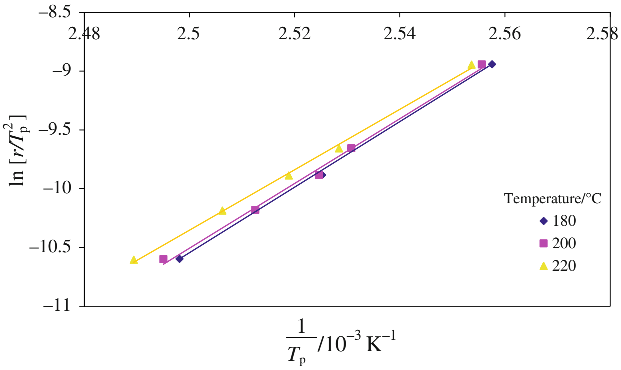

Fig. 6 Kissinger plot for evaluating nonisothermal crystallization activation energies of 30 K at various extrusion temperatures

Influence of shear stress

Nucleation activity

The nucleation activity of 10 K sample at three different shear stresses with respect to the crystallization of PP was determined using the method suggested by Dobreva. The plots of log r versus $1/\Delta T^2$ for PP/kaolin composite are shown in Fig. 7.

The slopes of unfilled PP at three different shear stresses (9.8, 19.6, and 34.3 kPa) are 18.255, 17.632, and 17.073, respectively. Whilst the slopes of PP/kaolin composites at the three different shear stresses of 9.8, 19.6, and 34.3 kPa are 15.183, 12.252, and 11.226, respectively. Therefore, the nucleation activity values of PP/kaolin composite at shear stresses of 9.8, 19.6, and 34.3 kPa were calculated to be 0.83, 0.69, and 0.66 respectively. This result shows that high shear stress is an effective parameter to stimulate nucleation activities in the PP matrix, which is consistent with the crystallization activation energy based on the Kissinger method as discussed in the next section.

Crystallization activation energy

According to Eq. 5, at a given crystallization temperature, a plot of ln $[r/T_p^2]$ versus $1/T_p$ should yield a linear

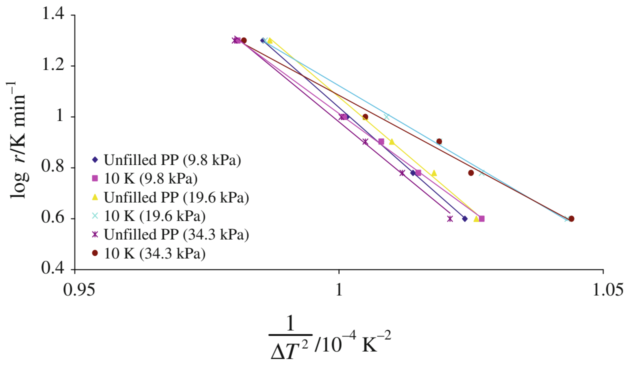

Fig. 7 Plots of log r versus $\frac{1}{\Delta T^2}$ for unfilled PP and 10 K at various shear stresses (9.8, 19.6, and 34.3 kPa)

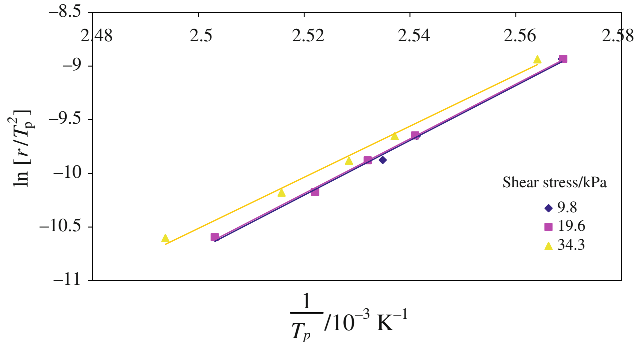

Fig. 8 Kissinger plot for evaluating nonisothermal crystallization activation energies of 10 K at various shear stresses

relationship to the activation energy values obtained. The constant and activation energies can be determined from the intercept and the slope of the line, respectively. Plots of ln $[r/T_{\mathrm{p}}^2]$ versus $1/T_{\mathrm{p}}$ at various shear stresses for 10 K are shown in Fig. 8. It can be seen that the plots constructed according to the Kissinger equation show good linearity, confirming the validity of the experimental data. The crystallization activation energies of kaolin-filled PP composites at various shear stresses during nonisothermal crystallization were determined to be 212.2, 211.7, and 198.1 kJ mol^{-1}. The activation energy values of PP/kaolin composite (10 K) decrease with an increase in shear stress, implying that the high shear stress subjected to PP matrix can accelerate the overall crystallization process.

During the shear process of base matrix, it was a competition between shear alignment and molecular orientation of PP. In the composite system, the high shear stress subjected to the system facilitates in the alignment of PP molecules and orientation of fillers. At the highest shear stress which is 34.3 kPa, the activation energy needed by the system to initiate the crystallization process is lower compared with the samples processed at the shear stress of 9.8 kPa. For the crystallization to occur, the entangled molecular chains of PP and kaolin filler networks must align in a correct orientation so as to possess a certain minimum amount of energy. This scenario shows that the high shear stress has supplied sufficient energy to PP molecules and kaolin fillers to enable their alignment according to the flow direction and to overcome the repulsion activities of PP molecules. In other words, at this stage, there was relaxation of polymer chains and kaolin particles during the process [25], thereby leading to the reduction of crystallization activation energy.

Conclusions

The crystallization behavior of PP and its composites are very relevant to the potential use of these materials in many demanding engineering applications. The study of nonisothermal crystallization behavior is important because most of the current processing techniques of polymeric materials follow the nonisothermal crystallization process. Hence, the study of crystallization kinetics is necessary for optimizing industrial process conditions and establishing excellent end-product in manufacturing kaolin-filled PP composites. The degree of crystallization of kaolin-filled PP composites was increased with the increase in kaolin loading, processing temperature and shear stress at a given cooling rate during the nonisothermal crystallization process. The crystallization activation energies calculated from Kissinger's method was slightly reduced as the kaolin content, processing temperature, and shear stress increased because the molecular chains of PP have a greater tendency to crystallize when kaolin particles, sufficient processing temperature, and shear stress were applied to the PP system. In order to attain a high performance end-product, the homogenous dispersion of filler in the polymer matrix is very crucial. The homogenous dispersion of inorganic fillers can be achieved by sufficient processing temperature and shear stress applied to the system. The nucleation activities analysis which can verify the contribution of fillers into polymer matrix revealed that kaolin particles, adequate processing temperature, and shear stress can affect the nucleation rates of PP matrix. From the results of overall crystallization behavior, it can be concluded that the addition of kaolin particles, adequate processing temperature, and shear stress can greatly accelerate the crystallization of PP.

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