Effect of nano calcium carbonate and attapulgite on isothermal crystallization time of polypropylene under static and dynamic conditions

Song Yuan¹², Yi Li¹², Qiong Zhang¹², Jun Wen¹²
¹ Jiangsu Xuzhou Construction Machinery Research Institute, 221004, China
² State Key Laboratory of Intelligent Manufacturing of Advanced Construction Machinery, Xuzhou Construction Machinery Group, 221004, China
*Corresponding author’s e-mail: zhangqiong52806@163.com

Abstract. The isothermal crystallization time of polypropylene/nano calcium (PP/CaCO₃) and polypropylene/attapulgite (PP/ATP) under static and dynamic conditions were investigated by using differential scanning calorimeter and Rheological experiments. Relatively, in static conditions, the calcium carbonate was easier to accelerate the crystallization process due to its shape. In the shear field the attapulgite is more advantageous to shorten crystallization time indicating that the attapulgite dispersed in the PP matrices confined the PP chains and hindered the movement of the PP chains.

1. Introduction
Many studies have been reported on the modification of polypropylene by filling with various of nanoparticles, like montmorillonite[1], graphite[2], silica[3], calcium carbonate[4-7] and so on. Accordingly, nanoparticles should be homogeneously dispersed and exfoliated as individual platelets within the polypropylene matrices in order to achieve the good property enhancement. It is generally believed that the filling of nanoparticles is mainly due to the stress concentration of nanoparticles, which can produce microcracks when subjected to external forces, inducing the elastic deformation of the matrix, absorbing energy and achieving the toughening effect. In general, the study of nanoparticles interaction on polymer is mainly focused on the interface between matrix and nanoparticles. For polypropylene, a semi-crystalline polymer, the improvement of its toughness is also related to its relative molecular weight, inter molecular force, crystallinity and crystal form.

J Junkasem et al [8] investigated the crystallization and melting behavior, mechanical properties, and processability of CaCO₃-filled-PP with the effects of CaCO₃ of varying particle size (1.9, 2.8 and 10.5 μm) and the content(0~40 wt%) . The studies indicate that CaCO₃ acts as a good nucleating agent for s-PP. M E Errico et al[9] investigated the influence of calcium carbonate nanoparticles with different shapes (spherical and elongated) on the thermal properties and crystallization behavior of isotactic polypropylene. DSC studies show that when the amount of calcium carbonate is greater than 3%, the crystallization temperature could be higher. The addition of calcium carbonate with different length-diameter ratios will make the crystallization performance of polypropylene inconsistent. J Shen et al[10] investigated the crystal morphology and crystallization kinetics of polypropylene filled with CaCO₃ of different size and size distribution. The results showed that composites filled with CaCO₃ of effective size gradation led to a well-crystalline order and a large crystal size, while their
isothermal crystallization kinetics and crystallization rate constant \((k)\) were declined, and their Avrami exponents \((n)\) and crystallization half-life \((t_{1/2})\) were increased compared with the composites filled with single size CaCO₃.

These studies showed that nanoparticles with different sizes, shapes and contents have different effects on polypropylene thermal performance and crystalline structure. Most people tended to believe that nanoparticles mainly act as heterogeneous nucleating agents, while ignored the friction between nanoparticles and molecular chains which could limit the movement of molecular chains.

In this article, results on static and dynamic isothermal time and crystallization behaviour of isotactic polypropylene (iPP) fill with calcium carbonate (CaCO₃) nanoparticles and nano-attapulgite(ATP) are presented. In particular, the calcium carbonate is spherical and the ATP is needle.

2. Experimental

2.1. Raw materials
Isotatic polypropylene (iPP). Aggregates. Sinopec petrochemical co., LTD. Density, 0.91 g/cm³. Melt index, 1.2 g/10min. Tm, 167℃.

Nano calcium carbonate(CaCO₃). Powder. Ruicheng huana nano materials, Shanxi. Partical size, 15~40 nm. Specific surface area≥40 m²/g. Proportion, 2.5~2.6.

Nano attapulgite(ATP), powder. Jiuchuan clay technology co., LTD, Jiangsu. Average diameter of stick powder is 80nm.

Aluminate coupling agent, A3. White cream solid. Decomposition temperature > 300 ℃. Yangzhou tianyang auxiliaries co., LTD.

Isopropanol, AR, Tianjin keruisi chemical, CO., LTD.

Absolute ethyl alcohol, AR, Tianjin keruisi chemical, CO., LTD.

2.2. Experimental flow

2.2.1 The treatment on CaCO₃ and ATP
Nano calcium carbonate(CaCO₃) and nano attapulgite (ATP) was spayed by isopropanol which had dissolve aluminate coupling agent(the proportion is 1%), mixing and grinding 15~20min and make the surface of inorganic nanoparticles full of agent. Then isopropanol was removed in 100℃ for 10h. then we will get CaCO₃ and ATP deal with aluminate coupling agent.

2.2.2 Sample preparation
PP and inorganic nanometer packing according to the proportion were thrown into the torque rheometer in 190℃, 40rpm, 5Kg for 15min. The content of the attapulgite or calcium carbonate was 1%. The mixture samples were press into sheet in 1mm for the test.

3. The process of isothermal crystallization

3.1 The static process of isothermal crystallization
The isothermal crystallization kinetics was investigated using a differential scanning calorimeter (DSC). All samples were heated to 230℃ at a rate of 10℃/min and held in the molten state for 5 min to eliminate the influence of thermal history. Afterwards, the samples were cooled to crystallization temperature \((T_c)\) (134 ℃, 136 ℃, 138 ℃ and 140 ℃) at a rate of 10℃/min, respectively. Figure 1a and Figure 1b are the DSC isothermal crystallization curves of PP/CaCO₃ and PP/ATP composites. All operations were carried out under a nitrogen environment.

The typical Avrami plots obtained from different temperatures are illustrated for PP/CaCO₃ in Figure 2a and PP/ATP in Figure 2b. It is clear that the Avrami equation is quite successful for analysing the isothermal crystallization kinetics. The Avrami exponent \(n\) and the rate constant \(Z(T)\)
can be obtained from the values of the slope and intercept of these straight lines. The values of K(T), n and \( t_{1/2} \) are listed in Table 1.

It can be seen from the data that the \( t_{1/2} \) of PP/CaCO\(_3\) and PP/ATP increase with the increasing of the crystallization temperature. The value of K(T), n and \( t_{1/2} \) of PP/CaCO\(_3\) are different from PP/ATP. At the same temperature, the needle attapulgite crystallized longer than the spherical calcium carbonate. This may be due to the fact that the needle particles are difficult to rotate and disperse when the molecular chain regular arrangement, which hinders the movement of the molecular chain. When the spherical calcium carbonate particles is easy to rotate and move, which has no influence on the movement of the molecular chain.

Table 1. Isothermal crystallization kinetics parameters of PP/ CaCO\(_3\) and PP/ATP blends at various T\(_c\)

| Sample    | \( T_c \) (°C) | K (T) \( \times 10^{-4} \) | n     | \( t_{1/2} \) (min) |
|-----------|----------------|----------------------------|-------|---------------------|
| PP/CaCO\(_3\) | 134           | 4.037                      | 2.86398 | 13.38               |
|           | 136           | 4.625                      | 3.03552 | 23.78               |
|           | 138           | 7.303                      | 3.11473 | 39.6                |
|           | 140           | 1.262                      | 3.23021 | 59.91               |
| PP/ATP    | 134           | 1.811                      | 1.61246 | 11.13               |
|           | 136           | 2.562                      | 1.74712 | 20.16               |
|           | 138           | 3.998                      | 1.87899 | 33.56               |
|           | 140           | 1.437                      | 1.85581 | 53.81               |

Figure 1  Isothermal crystallization curves of PP/CaCO\(_3\)(a) and PP/ATP(b) blend at various T\(_c\)

Figure 2  Avrami plots for isothermal crystallization of PP/CaCO\(_3\)(a) and PP/ATP(b) blend at various T\(_c\)
3.2 The dynamic process of isothermal crystallization

Rheological experiments of the shear flow induced isothermal crystallization. The experiments for the isothermal crystallization of the iPP in the steady shear flow \((0.5s^{-1})\) with the rotational stress rheometer, P20ETC (REOLOGICA INSTRImnts AB), in a plate configuration (diameter 20 mm, gap 0.8mm), under \(N_2\) atmosphere. The following thermomechanical history has been investigated. The annealing treatment has been realized at 230°C for 5 min to erase any crystalline fragments that could affect the subsequent crystallization process. The cooling step from the temperature 230°C to the crystallization temperature has been performed with a rate of 10°C min\(^{-1}\). The temperature profile has been verified by a thermocouple placed inside the molten sample between the tools. The isothermal crystallization has been investigated at \(T_c\) \((134 \, ^\circC, 136 \, ^\circC, 138 \, ^\circC\) and \(140 \, ^\circC\) respectively.

![Figure 3](image)

Figure 3 PP/CaCO\(_3\) (a) and PP/ATP (b) blend shear viscosity of different temperature at the shear rate of 0.5s\(^{-1}\)

Figure 3a and Figure 3b present the comparison of the viscosity at various \(T_c\) respectively, and at the shear rate of 0.5s\(^{-1}\). At the early stage, the viscosity is constant approximately, then started to increase rapidly after a certain time. This level-upturn transition behaviour has been reported by numerous researchers and utilized to define a rate of the crystallization characteristic. Hadinata et al\([11]\) define the time at the viscosity reached twice of it’s initial value as the onset time of the crystallization process. The onset times obtained in our experiment are summarized in table 2.

| Sample    | \(T_c\) \( (^\circC)\) | \(t_{on}\) \( (\text{min})\) |
|-----------|----------------|-----------------|
| PP/CaCO\(_3\) | 134°C | 8.03             |
|           | 136°C | 11.47            |
|           | 138°C | 14.95            |
|           | 140°C | 16.10            |
| PP/ATP   | 134°C | 4.11             |
|          | 136°C | 5.15             |
|          | 138°C | 7.23             |
|          | 140°C | 11.30            |

It can be seen from table 1 and table 2 that under the action of dynamic shear the crystallization induction time is shorter than static, and ATP filled PP is greater than calcium carbonate. Both nano-calcium carbonate and nano-attapulgite can play the role of heterogeneous nucleating agents in PP static crystallization, and their contribution to crystallization induction time in shear field varies greatly because of different shapes. Calcium carbonate is an amorphous particle, which is easy to rotate and slide freely in PP matrix. When the composite is subject to external forces, it is easy to slide and it is not obvious hinder the molecular chain moving. Attapulgite is a kind of needle-shaped particles and it can penetrate in the molecular chain, and not easy to slip and spin. The attapulgite can orientate along the shear forces and limit the molecular chain segments in the molecular network and accelerated crystallization.
4. Conclusions
The isothermal crystallization processes of PP/CaCO₃ and PP/ATP are characterized both in static and dynamic. Both the DSC and rheological experiments indicate that temperature has significant effect on the crystallization time. In static isothermal crystallization, the calcium carbonate is easier to accelerate the crystallization process, and the attapulgite is more helpful in dynamic shear field.

References
[1] Ma, J.S., Zhang, S.M., Qi, Z.G., Li, G., Hu, Y.L. (2002) Crystallization Behaviors of Polypropylene/Montmorillonite Nanocomposites. Journal of Applied Polymer Science, 83: 1978–1985.
[2] Cerezo, F.T., Preston, C.M.L., Shanks, R.A. (2007) Morphology, Thermal Stability, and Mechanical Behavior of [Poly(propylene)-grafted Maleic Anhydride]-Layered Expanded Graphite Oxide Composites. Macromolecular Materials and Engineering, 292:155-168.
[3] Zoukrami, F., Haddaoui, N., Vanzeveren, C., Sclavons, M., Devaux, J. (2008) Effect of compatibilizer on the dispersion of untreated silica in a polypropylene matrix. Polymer International, 57:756-763.
[4] Mishra, S., Sonawane, S.H., Singh, R.P. (2005) Studies on characterization of nano CaCO₃ prepared by the in situ deposition technique and its application in PP-nano CaCO₃ composites. Journal of Polymer Science: Part B: Polymer Physics, 43:107-113.
[5] Zebarjad, S.M., Tahani, M., Sajjadi, S.A. (2004) Influence of filler particles on deformation and fracture mechanism of isotactic polypropylene, Journal of Materials Processing Technology, 155-156:1459-1464.
[6] Avella, M., Cosco, S., Lorenzo, M.L.D., Pace, E.D., Errico, M.E., Gentile, G. (2006) Nucleation activity of nanosized CaCO₃ on crystallization of isotactic polypropylene, in dependence on crystal modification, particle shape, and coating. European Polymer Journal, 42:1548-1557.
[7] Chen, Q. (2007) Study on iPP isothermal crystallization induced by shear flow. Acta Polymerica Sinica, 5:47-471.
[8] Supaphol, P., Harnsiri, W., Junkasem, J. (2004) Effects of calcium carbonate and its purity on crystallization and melting behavior, mechanical properties, and processability of syndiotactic polypropylene. Journal of Applied Polymer Science, 92:201-212.
[9] Avella, M., Cosco, S., Lorenzo, M.L.D., Pace, E.D., Errico, M.E. (2005) Influence of CaCO₃ nanoparticles shape on thermal and crystallization behavior of isotactic polypropylene based nanocomposites. Journal of Thermal Analysis and Calorimetry, 80:131-136.
[10] Zhang, J., Ding, Q.J. Zhou, N.L., LI, L.L., Ma, Z.M., Shen, J. (2006) Studies on crystal morphology and crystallization kinetics of polypropylene filled with CaCO₃ of different size and size distribution. Journal of Applied Polymer Science, 101:2437-2444.
[11] Hadinata, C., Gabriel, C., Rullmann, M., Laun, M. (2005) Comparison of shear-induced crystallization behavior of PB-1 samples with different molecular weight distribution. Journal of Rheology, 49:327-349.