Effect of Iron Loading on Quiescent Crystallization of Syndiotactic Polypropylene/Iron Composites

Naveed Ahmad
Department of Chemical and Materials Engineering, College of Engineering, Northern Border University (NBU), Arar, Saudi Arabia
naveed.ahmad@nbu.edu.sa (corresponding author)

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ABSTRACT

The present study investigates the crystallization kinetics of the syndiotactic polypropylene/iron (sPP/Fe) composites using the rheological and Differential Scanning Calorimetry (DSC) techniques to evaluate the impact of varying iron content. Rheology, which is particularly sensitive under slow crystallization kinetics, was employed to complement the widely used DSC method. The current study aimed to integrate the aforementioned approaches to provide a comprehensive understanding of how the iron content influences the crystallization behavior of the sPP composites. Non-isothermal and isothermal crystallization experiments revealed that the increasing iron content significantly enhanced the crystallization and melting temperatures, indicating improved thermal stability and crystallinity. The rheological measurements, carried out using an Atomic Rheometric Expansion System (ARES), demonstrated higher sensitivity than the DSC at low iron concentrations, providing a more precise detection of crystallization kinetics. The results showed excellent agreement between the two techniques, confirming the robustness of rheology as a complementary method. This study underscores the importance of the iron content in tailoring the thermal and mechanical properties of sPP composites and highlights the value of integrating rheological methods with traditional thermal analysis for polymer characterization.

Keywords-Atomic Rheumatic Expansion System (ARES); Differential Scanning Calorimetry (DSC); polymer composites; quiescent crystallization kinetics

I. INTRODUCTION

Polymer crystallization is the process through which molecular chains align, forming lamella -a well-organized and ordered region [1]. Partial alignment of these molecular chains leads to the formation of larger spheroidal structures known as spherulites. These spherulites consist of folded chains arranged into lamellae. According to the thermodynamic principles, a crystal exists in a lower energy state than a liquid below the melting point. At the melting point, both phases are in equilibrium, where the Gibbs free energy (ΔG) equals zero [2]. DSC is a widely utilized technique, which examines the thermal transitions of polymers, such as melting, glass transition, and crystallinity [3]. DSC measures the heat flow absorbed or released by a polymer as a function of temperature. During cooling, as polymers form ordered crystalline structures, they release heat, making crystallization an exothermic process. This is reflected in DSC as a dip in the heat flux curve, representing a decrease in the heat flow. The temperature at the dip's minimum is referred to as the crystallization temperature (T_C), and the dip area corresponds to the latent heat of crystallization. While DSC provides valuable thermal data, its sensitivity may be insufficient for slow crystallization rates near the thermodynamic limit. Rheological techniques offer greater precision and sensitivity in such cases by monitoring the changes in viscoelastic moduli over time. These changes, which indicate the transition from liquid to solid, occur due to microstructural transformations in the polymer. This capability makes rheological techniques distinct from conventional methods, like DSC, particularly when studying slow crystallization kinetics [2-6].

Polymer crystallization plays a crucial role in determining the final properties of polymer products. Key influencing factors include the molecular weight (M_w), polydispersity index, tacticity, and the presence of fillers, like clay and iron [7–17]. Recent research has extensively explored these factors, yielding valuable insights into the crystallization behavior of polymers under various conditions. A study on isotactic poly(1-butene) (iPB-1), synthesized using metallocene catalysts, examined its polymorphic behavior and crystallization from the melt [8]. By employing C_2- and C_1-symmetric metallocene catalysts, researchers controlled the molecular mass and detected concentration revealing that highly isotactic materials crystallize into the metastable Form II when rr-stereodefects are below 2 mol%. In sPP, the relationship between syndiotacticity and crystallization has been analyzed using X-ray diffraction and FT-IR spectroscopy. Studies show that short permeance times at 0 °C promote faster crystallization into the helical form at room temperature, while longer times stabilize the trans-planar mesomorphic form [9]. Research into the effect of the M_w on crystallization kinetics highlights its critical role under both quiescent and shear-induced conditions [10, 11]. Fiber pull-out tests on isotactic polypropylene demonstrated that increasing the M_w at a constant shear rate exponentially enhances crystallization kinetics. Similarly, rheological tests confirmed that a higher M_w and broader Molecular Weight Distribution (MWD) lead to faster crystallization rates under flow conditions. Interestingly, the dependence of crystallization kinetics on the Mw diminishes under quiescent conditions because only short polymer segments (~100 monomers) contribute to crystalline growth, making the Mw less significant, which is relative to the overall degree of polymerization [12–14]. However, the Mw becomes a key factor under shear, controlling the growth rate of crystalline structures [15]. A critical Mw has been identified below which the polymer becomes insensitive to the shear flow. The role of the shear and step shear flow in crystallization has also been extensively studied [16, 17]. Experiments on poly(1-butene) and polypropylene revealed that a critical shear rate at constant strain or a critical shear strain at constant shear rate significantly enhances overall crystallization kinetics. The Mw effects were evident in step shear flow-induced crystallization but absent under quiescent conditions.

In a previous study, the combined effects of the shear flow and polymer M_w on crystallization were analyzed through the introduction of the dimensionless Weissenberg number (W_i) [17]. This parameter, defined as the product of the material's intrinsic relaxation time and the deformation rate of the flow process, was used to study how shear flow influences the crystallization kinetics of polybutene with varying M_w. It was observed that shear flow significantly accelerates crystallization kinetics, as indicated by the faster dynamics of light intensity in turbidity measurements. By examining dimensionless crystallization times, which compare crystallization times under shear with those under static conditions, researchers found that kinetic deviations from the quiescent state occur at lower shear rates as the M_w increases. When the dimensionless crystallization times for different M_w were plotted against Wi, they converged onto a single master curve. The role of the shear flow was further investigated utilizing polarized optical microscopy, DSC, rheological techniques, and X-ray diffraction techniques [18]. It was concluded that the long-chain branched polypropylene exhibited faster crystallization rates compared to the linear polypropylene. Additionally, during the induction period at low shear rates, the long-chain branched polypropylene was more sensitive to the shear flow, emphasizing the importance of the chain relaxation time in nucleation under shear conditions.

The crystallization behavior was also compared under shear and extensional flow for high M_w isotactic poly-1-butene [19]. Employing an extensional viscosity fixture on a rotational rheometer, it was found that the extensional flow induced more pronounced crystallization than the shear flow. Beyond a critical extension rate, the onset of the crystallization time significantly reduced as the extension rate increased. Further exploration with a filament stretching rheometer revealed that the extensional flow effectively facilitated the crystallization process in isotactic poly-1-butene [20, 21]. The degree of crystallinity increased from 45% to 62% with extension rates rising from 0.01 s^{-1} to 50 s^{-1}, as measured by the DSC and small angle X-ray scattering. Notably, flow-induced crystallization did not occur below a certain extension rate, and a reduction was observed beyond a higher critical threshold.

Recent research has also explored the impact of additives on the thermal and rheological properties of polymer composites. Studies on syndiotactic polypropylene/starch composites showed that increasing the starch content enhances the mechanical response and thermal stability of the composites [22]. Similarly, investigations into the syndiotactic polypropylene/iron composites demonstrated that a higher iron content improves the melt rheological response [23].

In the present work, the quiescent crystallization behavior of the sPP/iron composites was examined by integrating DSC and rheological techniques, aiming at elucidating the relationship between the crystallization response and iron dosage in sPP/iron composites.

II. METHODOLOGY

A. *Materials*

Crystallization investigations were conducted on sPP/Fe composites, which were synthesized in the laboratory [24]. The iron content in the composites was varied from 3% to 12%, with increments of 3%. The sPP with a syndiotacticity degree of 60%, was supplied by Sigma Aldrich. As shown in Table I, the samples varied based on the iron content.

TABLE I. MATERIALS AND THEIR PROPERTIES

Samples	% of Fe
sPP-1	12
sPP-2	9
sPP-3	6
sPP-4	3

B. *Experimental Procedure*

Crystallization studies were carried out using both rheological and DCS techniques. Both methods are employed for the thermal characterization of materials. While DSC is useful for thermal characterization, rheology is more sensitive to low crystallization kinetics. This is because rheological characterization is based on the material's mechanical response (elastic modulus) at low temperatures during which the response is sharper, making rheology more accurate in this range, where DSC may not perform as well. Both DSC and rheology equipment are equipped with an intercooler system that allows operation at temperatures as low as -60° Rheological measurements were conducted using an ARES [25]. Two types of experiments, isothermal and non-isothermal, were performed on samples in the form of 8 mm discs, with a constant strain of 5%. The stepwise procedure for all the experiments is outlined below.

1) *Non-Isothermical Crystallization Experiments (ARES)*

- **Annealing:** Samples were annealed at 200 °C to make the crystal-free.

- **Linearity Check:** The linearity of all samples was checked in the strain range of 1-10%. A strain of 6% was selected.
- **Cooling:** After annealing and linearity check, the samples were cooled from 200 ^{o}C to 50 ^{o}C at a rate of 200 ^{o}C/min using a temperature ramp test.

2) *Isothermal Crystallization Experiments (ARES)*

- **Annealing:** Samples were annealed at 200 ^{o}C to eliminate any initial crystalline structures.
- **Linearity Check:** Linearity was again confirmed in the strain range of 1-10%, with 6% having been selected.
- **Temperature Ramp:** The sample was cooled from 200 °C to a temperature near the melting point of the polymer composites to study crystallization kinetics at that range.

3) *Non-Isothermical Crystallization Experiments (DCS)*

- **Annealing:** A 3 mg sample was heated to 200 °C for five minutes to make it crystal-free.
- **Cooling:** The sample was cooled to -30 °C at a rate of -10 °C/min.
- **Data Collection:** Crystallization temperature, melting temperature, and glass transition temperature were recorded using the TA 60 software.

4) *Isothermal Crystallization Experiments (DCS)*

- **Annealing:** The sample was annealed at 200 °C to ensure a crystal-free starting point.
- **Cooling:** After annealing, the sample was cooled to -30 °C at a rate of -20 °C/min.
- **Crystallization Monitoring:** Crystallization was monitored between the crystallization and melting point temperatures.

III. RESULTS AND DISCUSSION

The non-isothermal and isothermal crystallization behaviors of the sPP/Fe composites were analyzed using both rheological and DSC techniques. The crystallization temperatures, melting point temperatures, and thermodynamic crystallization temperatures were determined from these experiments. A comparison of the peak temperatures obtained from the two methods revealed a good agreement. Furthermore, the activation energy of crystallization was calculated and examined as a function of the iron content in the sPP/Fe composites.

A. *Effect of Iron Contents on Crystallization Temperature*

The experimental results were used to determine the crystallization temperatures using DSC and rheological techniques. Regarding the DSC non-isothermal crystallization test, the crystallization temperature was calculated from the peak of the heat flow curve. Using the rheological technique, the crystallization temperature was determined from the plot of the complex modulus versus the temperature. To enhance the sensitivity of the rheological data, the first derivative of the complex modulus with respect to the temperature was calculated and plotted against the latter. This derivative plot closely resembled the DSC thermogram, enabling a direct comparison between the two methods.

The crystallization temperatures obtained by both methods were plotted as a function of iron content, as shown in Figure.1. The results indicate that increasing iron content leads to an increase in the crystallization temperature. This suggests that the addition of iron enhances the crystallinity of the polymer chains, likely due to its influence on the molecular architecture and chain dynamics. These findings are further supported by time sweep tests performed using the ARES rheometer. During these tests, an increase in the elastic modulus was observed, indicating an improvement in the mechanical response of the polymer composites, which is consistent with higher crystallinity. A comparison of the crystallization temperatures calculated using DSC and rheological methods is also displayed in Figure 1. The results demonstrate an excellent agreement between the two techniques. The crystallization temperature data for all samples, determined using both methods, are summarized in Table II.

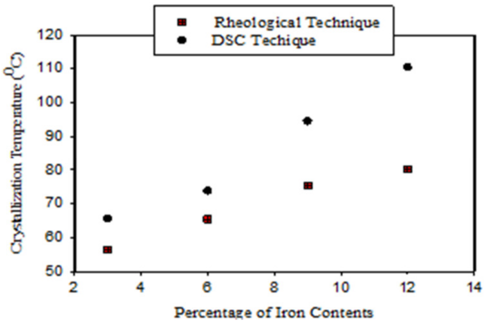

Fig. 1. Crystallization temperature as a function of Fe content of sPP/Fe composites.

TABLE II. CRYSTALLIZATION TEMPERATURES OF SYNDIOTACTIC POLYPROPYLENES/IRON.

Samples	% of Fe	Crystallization Temperature (^{o}C) (ARES)	Crystallization Temperature (^{o}C) (DCS)
sPP-1	12	80.20	110.40
sPP-2	9	75.30	94.50
sPP-3	6	65.40	73.80
sPP-4	3	56.50	65.60

B. *Effect of Iron Content on Thermodynamics Cystallization Temperature*

The thermodynamic crystallization temperature was determined from isothermal crystallization tests using both ARES and DSC techniques.

1) *Rheological Measurements*

For the rheological technique, isothermal crystallization tests were performed by cooling the sample from 200 ^{o}C to temperatures close to the melting points of the composites. During the temperature ramp test (data not shown here),the behavior of both moduli could be classified into three distinct stages:

- Initial Plateau Stage: Both moduli remain constant, indicating no crystallization. The time spent in this phase is referred to as the induction time.
- Upturn Phase: A sharp increase in the moduli is observed, signifying the onset of crystallization.
- Crossover Point: The storage modulus surpasses the loss modulus, marking the progression of the crystalline structure formation.

For the sPP/Fe samples with a higher iron content, the induction time was found to be shorter, indicating faster crystallization rates. This behavior suggests that higher iron content enhances the nucleation process, likely due to the impact of the iron on the molecular architecture.

2) *DSC*

Isothermal crystallization tests were also performed using the DSC. The thermodynamic crystallization temperature was determined from the peak of the heat flow curve during the isothermal testing. The thermodynamic crystallization temperatures calculated using both techniques were compared, and an excellent agreement was observed, as depicted in Figure 2. The results indicate a clear trend: as the iron content increases, the thermodynamic crystallization temperature also increases. This enhancement can be attributed to the strengthening effect of the filler, which improves the thermal stability and mechanical strength of the composites. Consequently, both melting points and crystallization temperatures rise with an increasing iron content. Table III presents the thermodynamic crystallization temperature data for all samples, as determined by both methods.

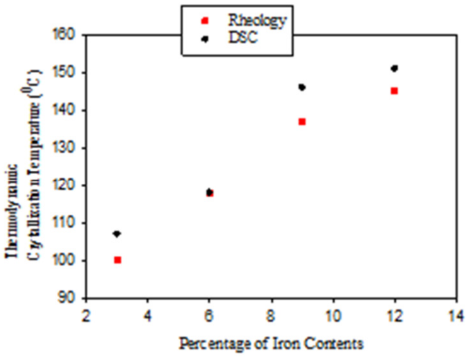

Fig. 2. Thermodynamic crystallization temperature as a function of Fe content of sPP/Fe composites.

TABLE III. THERMODYNAMIC CRYSTALLIZATION TEMPERATURES OF SYNDIOTACTIC POLYPROPYLENE/IRON USING ARES AND DSC

Samples	**% of Fe**	**Thermodynamics Crystallization Temperature (°C) (ARES)**	**Thermodynamic Crystallization Temperature (°C) (DSC)**
sPP-1	12	145	151
sPP-2	9	137	146
sPP-3	6	118	118
sPP-4	3	100	107

C. *Effect of Iron Content on Activation Energy*

The activation energy for crystallization was determined by applying the Arrhenius equation to the experimental data. The slope of the Arrhenius fit to the plot of log(t) versus 1/T (where t is the crystallization time and T is the crystallization temperature) was used to calculate the activation energy.

The relationship between the activation energy and iron contents is illustrated in Figure 3. The results exhibit a clear trend: the activation energy increases with the increase in the iron content. This indicates that the addition of iron strengthens the polymer composites, potentially making the crystallization process more energy-dependent due to the enhanced interaction between the polymer chains and the filler material.

Table VI provides the activation energy data for all the samples, as determined using both the DSC and ARES techniques.

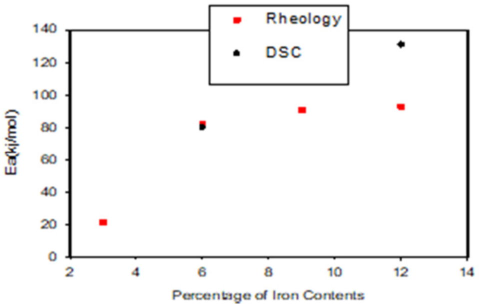

Fig. 3. Activation energy of Spp/Fe composites as a function of Fe content.

TABLE IV. ACTIVATION ENERGY OF SYNDIOTACTIC POLYPROPYLENE/IRON USING ARES AND DSC

Samples	**% of Fe**	**Activation Energy (ARES) (kJ/mol)**	**Activation Energy (DSC) (kJ/mol)**
sPP-1	12	92.70	131
sPP-2	9	90.60	
sPP-3	6	82.	80
sPP-4	3	21.50	

IV. CONCLUSIONS

The crystallization measurements of the sPP/Fe composites at varying levels of iron content reveal that iron significantly influences both the crystallization temperature and activation energy. The results indicate that activation energy increases with a higher iron content, highlighting the role of iron in enhancing the thermal stability and structural dynamics of the polymer chains.

In non-isothermal crystallization, the crystallization temperature (peak temperature) was found to be sensitive to the iron content in the polymer. This sensitivity underscores the effect of iron on the crystallinity and molecular architecture of the composites. A potential explanation for the discrepancies observed between the thermodynamic crystallization temperatures and peak crystallization temperatures obtained from the Differential Scanning Calorimetry (DSC) and rheological techniques lies in the differing sensitivity levels of the two methods. The rheological technique was shown to be more sensitive and accurate for the samples witha low iron content, particularly at lower crystallization kinetics, where DSC measurements might lack precision.

These findings suggest that rheological characterization offers a more reliable approach for detecting subtle variations in the crystallization behavior, especially under conditions where low crystallization rates prevail.

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