Chapter 8

Isothermal Crystallisation Kinetics of Isora Nanofibril Reinforced Polyethylene

Summary

In this chapter, the isothermal crystallization of nanocomposites based on plasma modified polyethylene as matrix and isora nanofibrils as nanofiller have been investigated. In order to provide a theoretical basis, the isothermal crystallization kinetics of INF/PE composites has been investigated by differential scanning calorimetry (DSC) at different crystallization temperature ($T_c$). The Avrami model was applied to describe the process of isothermal crystallization. The influence of the presence of isora nanofibrils on the kinetic parameters of isothermal crystallization of the matrix polymer and the melting properties of the isothermal crystallized samples has been evaluated. According to Hoffman–Weeks theory, the values of the equilibrium melting point ($T_m^\circ$) increased with an increase in the content of INF in the composites. Results showed that INF enhanced the crystallization rate drastically, but had no much influence on the crystal structure of PE when isothermally crystallized at different temperature.

Results of this chapter have been communicated to ‘Soft Matter’ for publication.
8.1. Introduction

Nanofibril reinforced thermoplastic composites have recently gained importance in various applications as building materials and automotive components. Nano materials play a promising role in modifying the microstructure and thus the final morphology of polymeric systems. Recently polymeric composite materials have aroused much interest because these composites have unexpected properties, such as large increase in the thermal stability and mechanical strength [1]. Over the past decade there has been a growing interest in the use of lignocellulosic fibres as reinforcing elements in polymeric matrices [2-3]. Polymer nanocomposites based on nanofillers from natural materials have attracted a great deal of interest in fields ranging from the scientific community to the industry because of remarkable improvement in properties. Among various thermoplastic polymers, polyethylene is a widely used thermoplastic found in everyday life. With easy availability, low cost and good processability, polyethylene is a promising candidate as a matrix material for composites [4]. Cellulose nanofibrils are regarded as the promising reinforcement in polymer nanocomposites due to the combination of high aspect ratio, large surface area, and their ability to act as a significant reinforcement at low filler loading levels. In addition to its mechanical properties the main benefit of nanosize cellulose is its biodegradability, biocompatibility, low density and non-toxic character [5-7]. The primary
drawback of cellulose fibrils is associated with their inherent polar and hydrophilic nature and the non-polar characteristics of most of thermoplastics. It results in difficulties in compounding the filler and the matrix, and therefore in achieving acceptable dispersion levels, which yields composites with low performances [8].

Several strategies have been suggested in the literature describing the way to improve the compatibly of lignocellulosic fibres with thermoplastic polymers, eg. physical treatment such as surface oxidation activation [9] and chemical modification such as graft polymerisation [10]. The use of surface modification agents on nanofillers is required to reach a good dispersion of the filler in the polymeric matrix [11]. A well dispersed minor phase of nanomaterials can affect the crystallization characteristics of its continuous phase of polymeric matrix by acting as heterogeneous nucleating agents [12-14]. In this study we used plasma modified high density polyethylene as polymer matrix and cellulose nanofibrils are used as filler.

The crystallization behaviour of polymer is a basic problem in polymer physics. Especially the filler in a polymer will affect the crystallization behaviour of the polymer-based composites very much [15]. Kinetic parameters (rates of crystallization, molecular mobility etc.) together with thermodynamic parameters (free energy parameters) control the microstructure formation in polymers. Therefore, thermal history is one of the
most important factors for controlling the phase structure of semicrystalline polymers and its structures [16-17]. The crystallization rate of polyethylene can be enhanced in the presence of various nucleating agents [18]. Liu et al studied the isothermal crystallization kinetics of modified bamboo cellulose/poly(e-caprolactone) (MBC/PCL) composites by differential scanning calorimetry (DSC) at different crystallization temperature (Tc) and they observed that MBC accelerates the crystallization of PCL in the composites [19]. In another study microfibrillated cellulose (MFC) was used as filler to compound with PLA and the crystallization behaviour of PLA/MFC composites was investigated [20].

Results showed that MFC enhanced the crystallization rate drastically, but had no much influence on the crystal form of PLA when isothermally crystallized at different temperature. The influence of the viscose fibers and the microcrystalline cellulose on the morphological, mechanical and thermal expansion properties of polyethylene was studied by Pollanan et al. and they observed that the HDPE’s thermal dimensional stability in the flow direction was dramatically improved with cellulose fillers [21].

In the present study, the crystallization behaviour of the nanocomposites based on the plasma modified polyethylenes with isora nanofibrils under isothermal conditions has been investigated. The aim was to evaluate the influence of the presence and the concentration of the nanofibril on the kinetic parameters of
Isothermal crystallization kinetics of isora nanofibril reinforced polyethylene

Isothermal crystallization of the matrix polymer. The melting properties of the isothermal crystallized samples have also been studied.

8.2. Results and discussion

8.2.1 Isothermal crystallization behaviour

Crystallization of the polyethylenes, in the presence of INFs was investigated under isothermal conditions, as described in the experimental section. Crystallinities of the composites pointed out, how addition of filler influences the crystallization behaviour of polyethylene. The thermograms of neat PE and INF/PE composites were given in figure 8.1. Crystallization can occur at any temperature below the melting temperature $T_m$, when free energy of a polymer chain in the amorphous state and crystalline state are the same. Nucleation starts at the surface of introduced nanoparticles. The main driving force of nucleation upon cooling will be the difference in the free energy of a polymer chain in crystalline state compared to that in amorphous state.

From figure it was observed that with increasing crystallization temperature the exothermic peaks shifted to a higher value. The reason for this behaviour might be due to the increase in the nucleation density introduced by the nanoparticles in the melt of nanocomposites, as similar observations were reported with other nanocomposites [27-28]. For the same isothermal crystallization temperature, the exotherms all shift to the shorter time with the
increase of INF loadings. It indicates the crystallization rate of PE was improved by the nucleating effect of INF.

**Figure 8.1:** Isothermal thermograms of INF/PE composites (A) neat polyethylene (B) 0.5 wt% (C) 1 wt% and (D) 3 wt% isora nanofibril (INF) reinforced polyethylene composites under different crystallization temperatures.

### 8.2.2 Isothermal crystallization kinetics

The isothermal crystallization kinetics can be better visualized by evaluating the degree of crystalline conversion as a function of time at a constant
temperature. The relative crystallinity \( X_t \) at different crystallization time can be calculated by partial integration of the crystallization exotherms and are shown in figure 8.2. Based on the experimental data, the relative crystallinity \( X_t \) as a function of crystallization temperature can be calculated according to Equation (8.1).

\[
X_t = \frac{\int_{T_0}^{T_\infty} \frac{dH_c}{dT} dT}{\int_{T_0}^{T_\infty} \frac{dH_c}{dT} dT}
\]

(8.1)

Where \( T_0 \) and \( T_\infty \) represent the onset and end of crystallization temperatures and \( dH_c/dT \) is the heat flow rate. All the \( X_t \) versus time curves at various INF contents have same characteristic sigmoid shape. The first non-linear part of the S shaped curve is generally considered as the nucleation step of the crystallization process. Each curve showed a linear part considered as primary crystallization, subsequently a second non-linear part and is considered as secondary crystallization, which is caused by the spherulitic impregnation in the late stage of the crystal growth [29]. In order to fully describe the crystallization behaviour, Avrami model was employed to analyse the isothermal crystallization kinetics of neat PE and INF/PE composites.
Figure 8.2: Patterns of relative crystallinity versus time for (A) neat polyethylene (B) 0.5 wt% (C) 1 wt% and (D) 3 wt% isora nanofibril (INF) reinforced polyethylene composites under different crystallization temperatures.

8.2.3 Avrami model

Generally, the theory of Avrami [30] is used to analyse the increase of relative crystallinity with time:

\[ X_t = 1 - \exp\left[-K^{1/n}(t-t_0)^n\right] \] ................................. (8.2)
where, $X_t$ is relative crystallinity at time $t$; $t_0$ is an induction period; $K^{1/n}$ is an overall rate of crystallisation (min$^{-1}$); and $n$ is the Avrami exponent that depends on the type of nucleation and geometry of growing polymer crystals.

Taking double logarithms the equation (8.2) is transformed into

$$\ln [-\ln (1-X_t)] = \ln K^{1/n} + n \ln (t-t_0) \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (8.3)$$

Accordingly, the Avrami exponent $n$ and crystallization rate $K^{1/n}$ can be obtained from the slope and intercept respectively, from a plot of $\ln [-\ln (1-X_t)]$ versus $\ln (t-t_0)$ as shown in figure 8.3. For the isothermal crystallization, the ‘$n$’ and ‘$k$’ values can be obtained from the linear portion of the thermograms, representing 30–70% relative crystallinity [31].

The Avrami exponent $n$, the crystallization rate constant $K$, and the crystallization half-time $t_{0.5}$ at different crystallization temperatures are listed in table 8.2. The confidence intervals of overall rate constant and Avrami exponent refer to the regression analysis using student t-test with 95% of confidence level. The curves of all the samples can be divided into two sections: the primary crystallization process and the secondary one. As the fitting lines of each section are nearly parallel, the nucleation mechanism and crystal growth geometries of different crystallisation temperature are similar for all the samples [32].
The transformation follows the usual Avrami kinetics in the first stage of crystallisation. In the final stage of crystallization, where the crystallinity is approximately 80% and more, deviations from Avrami kinetics are observed due to the secondary crystallization. During secondary crystallization, impingement of the growing spherulites takes place and the Avrami model becomes invalid. This is so because the primary requirement of the Avrami model is, the spherulites must be able to grow in free space [33]. In the Avrami expression, the Avrami exponent $n$ provides qualitative information on the nature of nucleation and the growth processes. An Avrami exponent $n$ with value close to three is attributed to three-dimensional crystal growth (spherical structure) resulting from instantaneous athermal nucleation process. On the other hand, ‘$n$’ value between two and three represents non three-dimensional truncated spherical structures resulting from instantaneous nucleation, controlled by diffusion process. The non integral $n$ values indicate the presence of the combination of thermal and athermal mixed nucleation and mechanisms [34-35].

From table 8.1, it can be observed that the exponent $n$ is found to range from 1.26 to 2.38 (most of the $n$ value between 2 and 2.38). This indicates to gradual growth of two-dimensional morphology to a spherical three-dimensional morphology with a combination of thermal and athermal nucleation. These values of $n$ were in close agreement with corresponding
literature data reported for polyethylene mostly for isothermal crystallization [36-38]. The value of Avrami exponent for neat and INF reinforced PE composites are in the same range, which shows that that the addition of INF to the polyethylenes does not changes the isothermal crystallization mechanism of the corresponding matrix phase.

The values of $K$, which is related to nucleation rate and growth processes, decreased with an increase in $T_c$, which meant that the crystallization rate was decreasing. The incorporation of INF significantly increased the crystallization kinetic constant $K$, with filler content suggesting that INF can act as effective nucleating agent and accelerate the crystallization of PE in the composites.

The half crystallization time ($t_{0.5}$), defined as the time from the onset of crystallization to the time at which the relative crystallinity is 50%, are also listed in table 8.1. It can be seen that, the value of $t_{0.5}$ decreases with INF content, as the crystallization proceeds faster. Moreover, at a given crystallization time, the value of $t_{0.5}$ for INF/PE composites are lower than that for neat PE signifying that the addition of nanofibrils can accelerate the overall crystallization process. This indicates that there exist constraints on the mobility of the PE chains in the interspherulitic regions due to the presence of INF. Fillers in polymer matrix usually play dual roles, (1) acting as a nucleating agent to enhance crystallization below the percolation concentration, and (2) acting as a hindrance to retard crystallization above the
percolation concentration because of the formed network structure. Similar results have been obtained for nanocomposites based on high density polyethylene and maleic anhydride grafted high density polyethylene [39]. The good linearity of the curves (correlation coefficient $r^2 > 0.99$) demonstrates that the Avrami equation fits well with the isothermal crystallization kinetics of all samples.

Figure 8.3: Avrami plots for (A) neat polyester (B) 0.5 wt% (C) 1 wt% and (D) 3 wt% isora nanofibril (INF) reinforced polyethylene composites under different crystallization temperatures.
Table 8.1: Avrami parameters for the kinetics of isothermal crystallisation

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_c$ (ºC)</th>
<th>$t_{1/2}$ (min) exp</th>
<th>$t_{1/2}$ (min) calculated</th>
<th>slope($n$)</th>
<th>$\Delta n$</th>
<th>$K_A^{ln}$ (min)</th>
<th>$\Delta K_A^{ln}$ (min)</th>
<th>$r^2$</th>
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</table>
8.2.4 Activation energy

Hoffman formulated an Arrhenius-like relationship [40] for the temperature dependence of the growth rate of crystallites. When simplifying it in terms of reciprocal half time and arrive at:

\[
t_{0.5}^{-1} \propto (-E_A/RT_c) \tag{8.4}
\]

Where \(E_A\) is the activation energy (Jmol\(^{-1}\)), \(R\) is gas constant (JK\(^{-1}\)mol\(^{-1}\)) and \(T_c\) is the crystallization temperature. The slope of semi-logarithmic plots of \(t_{0.5}^{-1}\) versus \((1/T_c)\) yields the activation energy \((E_A)\) and the values are given in table 8.2.

The decrease in \(E_A\) reflects a reduction in interfacial free energy and therefore, the system should crystallize easier, with less difficulty. From the table 8.2, it is observed that as compared to neat PE, the composites of INF/PE had a lower \(E_A\) value.

This result suggests that the addition of INF into PE matrix can induce the heterogeneous nucleation and increase the crystallization ability of PE during the crystallization processes. The addition of nanomaterials caused a decrease in the \(E_a\) values, which made the molecular chains of polyethylene easier to crystallize and thus there is an increase in rate of crystallization [41]. Hao et al. [42] reported the same trend of activation energy values with respect to the filler concentration for PP/Si\(_3\)N\(_4\) nanocomposites.
Table 8.2: Activation energy of PE using Hoffman’s Arrhenius-like relationship

<table>
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<th>Sample</th>
<th>Activation energy (kJ mol$^{-1}$)</th>
<th>$r^2$</th>
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<td>3 wt% PE</td>
<td>-14.42</td>
<td>0.9848</td>
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8.3 Conclusions

The isothermal crystallization kinetics of neat PE and PE/INF composites were investigated. In isothermal crystallization kinetics, the Avrami model was found to be suitable to explain the crystallization kinetics of these systems. The incorporation of INF significantly increased the crystallization kinetic constant $K$, with filler content suggesting that INF can act as effective nucleating agents and accelerate the crystallization of PE in the composites. The spherulite growth showed a gradual growth of two-dimensional morphology to a spherical three-dimensional morphology with a combination of thermal and athermal nucleation.

It can be seen that, the value of $t_{0.5}$ decreases with increasing INF content, as the crystallization proceeds faster. Moreover, at a given crystallization time, the value of $t_{0.5}$ for INF/PE composites are lower than that for neat PE, signifying that the addition of nanofibrils can accelerate the overall
crystallization process. This indicates that there exist constraints on the mobility of the PE chains in the interspherulitic regions due to the presence of INF. It is also observed that as compared to neat PE, the composites of INF/PE had a lower $E_a$ value.
References


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