Non-isothermal crystallization kinetics of high density polyethylene/graphene nanocomposites prepared by in-situ polymerization

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A B S T R A C T

High density polyethylene/graphene nanocomposites were synthesized via in-situ polymerization technique using metallocene catalyst and methylaluminoxane (MAO) as co-catalyst. The non-isothermal crystallization of the nanocomposites was studied using differential scanning calorimetry (DSC). Modified Avrami, Ozawa and the model proposed by Mo et al. were applied in the analysis. The activation energy (ΔE) was calculated using the iso-conversional method proposed by Vyazovkin. The effect of degree of transformation and temperature on ΔE was analyzed. It was found that graphene nucleates the crystallization of HDPE by lowering ΔE as well as increasing the crystallization onset temperature (T_{on}). However, at later stages of crystallization, excess amount of graphene hinder the crystal growth rate thereby retarding overall rate of crystallization, observed from increase of $t_{1/2}$ and degree of super cooling.

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1. Introduction

Polyethylene (PE) is one of the most widely used commercial polymers due to its good mechanical properties, chemical resistance and ease of processing. Incorporation of micro and nanofillers into polyethylene is an active area of research on account of improving specific properties. A nanofiller is defined as the material which have at least one dimension in the range of nanometers [1,2]. The incorporation of nanofiller affects the structural as well as physical properties of polymers and suitable application of the products could be designed based on the results.

Mechanical and physical properties of many polymeric materials are decided by crystal structure and morphology, which is influenced by the crystallization behavior of polymers [3]. Polyethylene being a semi crystalline polymer solidifies easily when undergoing crystallization. Therefore crystallization is the most important phase transition during PE fabrication process. Kinetics of crystallization and resulting degree of crystallinity are

very important parameters for processing and fabrication of PE products [4].

Several studies have been carried out to understand the isothermal and non-isothermal crystallization behavior of PE and various PE nanocomposites. Study of non-isothermal crystallization kinetics has practical significance because most of the industrial process depends on the non-isothermal crystallization characteristics [3].

Many models such as Jeizorny model [5] Ozawa and Mo-model [6,7] were used to describe non-isothermal crystallization kinetics of PE including all derivatives of PE like high density PE (HDPE), low density PE (LDPE) and ultra-high molecular weight PE (UHMWPE) and their nanocomposites. For example, fillers like nano-SiO$_2$, nano barium sulfate (BaSO$_4$), polyhedral oligomeric silesquioxanes (POSS) and alumina particles (Al$_2$O$_3$) have shown nucleation effect in the non-isothermal crystallization of HDPE [2,8–10]. SiO$_2$, BaSO$_4$, POSS and Al$_2$O$_3$ nano-fillers altered the crystal growth of HDPE as evident from the change in the Avrami index of the nanocomposites. The Avrami index for HDPE/BaSO$_4$ and HDPE/Al$_2$O$_3$ nanocomposites was lower than the neat HDPE, which was attributed to the occurrence of heterogeneous nucleation. Similarly, HDPE/nano-SiO$_2$ showed a faster overall crystallization rate observed from decrease in $t_{1/2}$ of crystallization as well as the enthalpy of crystallization. Most studies on the non-isothermal

crystallization of HDPE have concluded that Mo-method can suitably describe the crystallization behavior of HDPE and its nanocomposites [8,9,11,12]. However, Patel [4] showed that differential Nakamura model can effectively predict the non-isothermal crystallization behavior of HDPE resins. Polyolefins specifically HDPE nanocomposites based on carbon nanofillers like exfoliated graphite and carbon nanotubes have also been studied. For instance it is found that a small amount of exfoliated graphite can drastically alter the crystallization behavior of polypropylene (PP), observed from shift in the crystallization onset temperature and Avrami index. The morphological observation showed that exfoliated graphite modified the spherulitic superstructure of pure PP [13]. The converse was observed in the studies of HDPE/multi-walled carbon nanotubes (MWCNT) nanocomposites by Kim et al. [14]. This study found that MWCNTs enhance the nucleation process in the early stages of crystallization observed from lowering of the effective activation energy. However, at later stages, the crystallization process is retarded and the half-crystallization time is increased with the MWCNT concentration. The effect of different nanofillers on the crystallization onset temperature, peak temperature and activation energy is summarized in Table 1.

Like other carbon based nanofillers, graphene has also attracted enormous scientific interest, because of its outstanding physical properties like ultra-high mechanical strength, thermal and electrical conductivity and chemical functionalization capability [19]. Graphene is 2D carbon nanofiller, with single atom thick planar sheet of sp^2 hybridized carbon atoms. These carbon atoms are packed in honey comb like crystal lattice. Graphene is considered as to be, "the thinnest material in universe" [20].

Studies have found that graphene can increase the mechanical and thermal properties of PE [21,22], so it's necessary to study the insights of the crystallization behavior of HDPE/graphene nanocomposites. This paper describes the non-isothermal crystallization kinetics of HDPE/graphene nanocomposites prepared by in-situ polymerization of ethylene using zirconocene catalyst and MAO co-catalyst.

2. Theoretical background

Isothermal crystallization of polymer can be described by well-known Avrami equation [23].

$$X_t = 1 - e^{-kt^n} \tag{1}$$

Avrami equation depends on time and the volume fraction of transformed material (X_t), by taking into account the nucleation rate and increase in volume of lamellar crystals as the main processes of the crystallization, n is the Avrami exponent and is a function of nucleation process and k corresponds to growth function that depends on crystal growth and nucleation. Since Avrami equation deals with isothermal process, it is inadequate to be applied to practical processes which are mostly non-isothermal.

Owing to the inadequacy of Avrami equation, modifications have been made to compensate for the non-isothermal conditions. Ozawa method is one among them as shown in Eq. (2),

$$X_t = 1 - \frac{\exp(-K(T))}{\beta^m} \tag{2}$$

in which the crystallization is described in terms of cooling function ($K(T)$), cooling rate (β), and the Ozawa exponent m, which is assumed to be independent of temperature [6]. However, Ozawa method is not good enough for polymers which exhibit secondary crystallization such as PE. Similarly other models based on modification of Avrami method can be found in literature like methods by Mo et al. [7] and Kim et al. [14]. Both of these models are based on combination of Avrami model and Ozawa model.

2.1. Activation energy and frequency factor

The general solid state reaction law is given as [24]

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{3}$$

where α is the extent of conversion, k is the rate constant per unit time and $f(\alpha)$ is the reaction model in differential form. Eq. (3) in integral form can be written as

$$g(\alpha) = kt \tag{4}$$

where, $g(\alpha)$ is the integral of $(d\alpha)/(f(\alpha))$.

For the non-isothermal case the equation can be written as

$$\frac{d\alpha}{dT} = \frac{k}{\beta}f(\alpha) \tag{5}$$

The rate constant k can be written inform of Arrhenius equation

$$k = k_0 \exp(-E_A/RT) \tag{6}$$

whereas, k_0 is a frequency factor, time^{-1}; E_A is the activation energy, J mol^{-1}; T is the absolute temperature, K; R is the universal

Table 1
Effect of different nanofillers on crystallization of HDPE.

Authors	Materials studied	T_{on} (°C)[a]	T_p (°C)[a]	$-E_A$ (kJ/mol)
X. Shi et al. [15]	HDPE	121.1	116.4	284.2[b]
	2 wt.% graphite/HDPE	122.0	116.6	286.0[b]
	2 wt.% SWCNTs[d]/HDPE	121.0	116.5	289.8[b]
	2 wt.% MWCNTs[d]/HDPE	120.5	116.0	290.9[b]
P. Zou et al. [16]	HDPE	118.6	116.2	ND
	20 wt.% MRSF[d]/HDPE	119.6	115.0	ND
R. Ou et al. [12]	HDPE	118.5	116.6	200.0[c]
	KFW[d]/HDPE	121.1	118.5	300.0[c]
Q. Jiasheng, H. Pingsheng [9]	HDPE	116.8	119.4	166.3[b]
	5 wt.% nano SiO$_2$/HDPE	117.7	119.5	266.0[b]
M. Joshi, B.S.Butola [2]	HDPE	118.5	116.0	445.1[b]
	10 wt.% POSS[d]/HDPE	121.7	117.6	445.3[b]

[a] At 10 °C/min.
[b] Determined by Kissinger method [17].
[c] Determined by Friedman method at 50% relative crystallinity [18].
[d] SWCNTs: single walled carbon nanotubes, MWCNTs: mutiwalled carbon nanotubes, MRSF: modified rape straw flour, KWF: kevlar fiber wood, POSS: polyhedral oligomeric silesquioxanes.