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Effect of Carbon Nanotubes on Thermal Properties and Crystallization Kinetics of High Density Polyethylene

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1- Introduction

High Density Polyethylene is a semi-crystalline polymer known as the primer choice among thermoplastics for most engineering applications but its application has been limited compared to the potential as its thermal stability and melting point are not suitable enough for some industrial applications.

To enhance its thermal properties different organic and inorganic fillers have been used. Among them, carbon nanotubes (CNTs) have been particularly interested because of their special properties.

The study of crystallization behavior of HDPE has significant importance as the macroscopic properties of semi-crystalline polymers mainly depend on their crystallization behavior and the addition of fillers significantly affects it. Since the practical processes such as industrial applications proceed under dynamic or non-isothermal conditions, therefore many researches have focused on the non-isothermal crystallization of polymers.

Addition of fillers significantly affects the crystallization behavior of polymers. The most common effect of carbon nanotubes is their role as nucleating agents. There are also reports of changing in Avrami index and crystallinity index.

Although numerous studies have addressed the kinetic behavior of polymer thermal degradation, but the number of researches about crystallization kinetic is limited. Among the most applicable methods, Avrami, Kissinger and Flynn-Wall-Ozawa are used in this study.

2- Experimental

High density polyethylene (HDPE) provided by INEOS company, England, was used in this study. 95% pure multi walled carbon nanotubes (MWCNT) with external diameter ranging from 20 to 60 nm and 5-15 µm length were obtained from Nanolin, China.

To enhance the thermal stability and processability of HDPE, 0.2 wt% calcium-stearate and 15 wt% antioxidants were added to HDPE powder. Weight percentage of CNTs in nanocomposites was 1, 2.5 and 5. HDPE and the mixture of the nanocomposite powder were dried in vacuum oven at 80℃ for 4 hours prior to the extrusion process. Then, the materials were mixed for 1 min, after the torque being constant, in extrusion machine operating at 190℃ and a rotor speed of 90 rpm. Finally, the molten mixture was squeezed into the mold with pressure of 700 bar and held there for 30 s. Temperature of the injection molding and mold were 190℃ and 30℃, respectively. The samples are labeled as HDPE, PCNT1%, PCNT2.5% and PCNT5%.

Non-isothermal crystallization kinetics of HDPE and its nanocomposites were investigated by differential scanning calorimetry (Shimadzu DSC 60. All the samples were heated to 180℃ at the rate of 10℃/min and held there for 5 min to eliminate previous thermal history. After complete melting, the samples were cooled down to room temperature. Then all the samples reheated to 180℃ at 10℃/min heating rate. Different cooling rates of 10, 20 and 30℃/min were selected for each sample.

Scanning electron microscopy (SEM) (VP1450) was used to observe the microstructure of HDPE and PCNT1% samples. At first, samples were dissolved in toluene and then held at 80℃ until the complete evaporation of solvent. Prepared thin films were separately etched for 48 h in H2SO4/ H3PO4/ KMnO4 solution with 68/30/2 weight percent.

3- Results and Discussion

Onset and peak temperature, solidification enthalpy, crystallinity index for HDPE and its nanocomposites at different cooling rates are calculated and summarized in Table 1. At the same cooling rate, T_p and T_o were enhanced in presence of carbon nanotubes, which indicates that the CNTs affected the crystallization kinetics. Increasing trend of onset temperature by increase in CNT content of HDPE shows that the carbon nanotubes acted as nucleation sites. The increase in solidification enthalpy by increase of CNTs weight percentage can be attributed to higher specific heat capacity of CNTs compared to HDPE. Similar to variation of enthalpy values, relative

Table 1 Onset and peak temperature, solidification enthalpy, crystallinity index for HDPE and its nanocomposites at different cooling rates

sample	Cooling rate	T_{onset}	T_{peak}	ΔH	X
HDPE	10	118.24	115.37	109.76	37.45
	20	117.37	113.91	125.83	42.93
	30	118.6	111.13	167.01	56.98
PCNT 1%	10	119.71	116.27	137.66	47.44
	20	118.09	114.4	160.70	55.38
	30	117.73	113.26	154.82	53.35
PCNT 2.5%	10	120.54	116.66	150.58	52.69
	20	118.18	114.91	144.63	50.61
	30	118.32	113.01	166.95	58.42
PCNT 5%	10	121.19	118.45	170.47	61.22
	20	119.78	115.82	164.73	59.16
	30	118.6	114.28	160.67	57.70

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crystallinity also increased by addition of carbon nanotubes in polymer matrix.

Table 2 shows average values of n and k extracted by Avrami method. Constant k values exhibited an incremental trend with increase in CNTs weight percent. Furthermore, Avrami index is changed as the weight percent of carbon nanotubes increases, which indicates changing in nucleation and growth mechanism of spherolites.

Table 2 n and k values for HDPE and its nanocomposites at different cooling rate

Sample	Cooling rate	n	k
HDPE	10	3.2	1.32×10^{-5}
	20	3.4	2.699×10^{-5}
	30	3.5	3.754×10^{-5}
PCNT 1%	10	2.5	8.6×10^{-5}
	20	2.5	6.8918×10^{-4}
	30	2.8	4.4386×10^{-4}
PCNT 2.5%	10	2.8	9.166×10^{-6}
	20	2.3	1.2465×10^{-4}
	30	3	8.087×10^{-4}
PCNT 5%	10	2.7	5.067×10^{-5}
	20	2.8	1.271×10^{-4}
	30	2.6	7.031×10^{-4}

The microstructure of HDPE and PCNT1% nanocomposite are demonstrated in Fig. 1. The ordered spherolitic structure can be observed in HDPE verifying the Avrami method results. According to Fig. 1b, the microstructure is not spherolitic anymore. In only a few sites spherolites are just formed but smaller than the pure HDPE. It is due to the confinement imposed by CNTs during the crystallization of polymer. Nucleating effect of carbon nanotubes can be also observed.

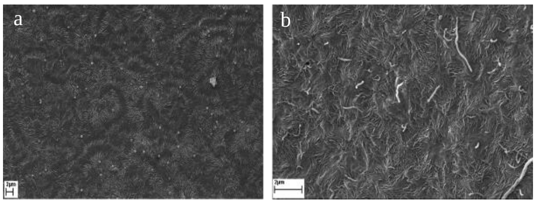

Fig. 1 Microstructure of a) HDPE – 5000x and b) PCNT1% - 20000x

Activation energy of crystallization process for HDPE, PCNT 1%, PCNT 2.5% and PCNT 5%, using Kissinger model, are 160, 463,385 and 339 kJ.mol^{-1}, respectively. Results present that as the weight percentage of carbon nanotubes is increased, a reduction occurred in activation energy. Moreover, E_a of all nanocomposite samples are higher than HDPE showing that despite nucleating effect of carbon nanotubes, polymeric chains movement and ordering were not as easy as pure polyethylene.

Kissinger method gives an average value of activation energy for the whole crystallization process. Ozawa-Flynn-Wall (OFW) method estimates the activation energy in progressive conversion value (α). In Fig. 2 E_a is plotted against α. As can be observed, the activation energy declined with increase of the crystallization index. Nucleation and growth both took place in crystallization process with different activation energies. At early stages of crystallization, the process was mainly controlled by nucleation which had higher values of E_a. As the crystallization proceeded, the significant role of growth caused the reduction of activation energy. According to Fig. 2, the presence of carbon nanotube increased activation energy of nanocomposites compared with neat HDPE at first stage of nucleation and growth of spherolites.

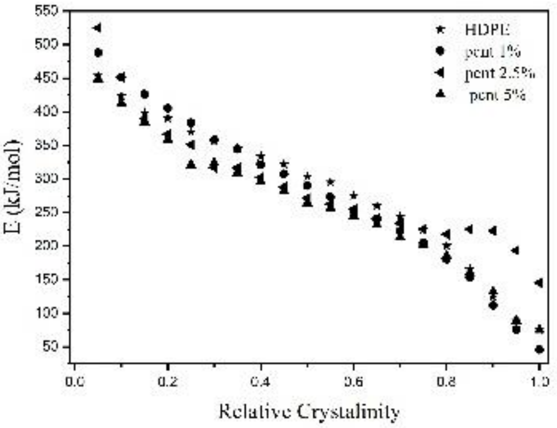

Fig. 2 Activation energy versus conversion fraction obtained by OFW method for different samples

4- Conclusions

In this study, HDPE and its nanocomposites with 1, 2.5 and 5 weight percent of carbon nanotube were prepared using mini-extrusion machine. Thermal properties and crystallization kinetics of samples were studied by DSC methods at different cooling rates. Results shows that solidification and enthalpy increases in presence of CNTs. Carbon nanotubes acts as nucleation sites. Moreover, relative crystallinity in nanocomposites is higher than pure polyethylene. Furthermore, Avrami index (n) decreases from 3 to around 2 in nanocomposites. Activation energy of all nanocomposite samples, calculated by Kissinger method, are higher than HDPE. OFW method results shows decrease of activation energy as the crystallization conversion fraction increases.