Effect of High Energy Electron Irradiation on HDPE and LDPE Studied by Differential Scanning Calorimetry (DSC)

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Abstract

The effect of high energy electron irradiation on the thermal properties of high density polyethylene (HDPE) and low density polyethylene (LDPE) are studied using Differential Scanning Calorimetry (DSC). A systematic change in the thermal properties in respect of crystallinity and specific heat has been observed during thermal annealing for un-irradiated and irradiated samples. It is found that crystallinity and specific heat both vary with temperature. Specific heat goes on increasing upto the melting range indicating a lower crystallinity at this stage. Attempt has been made to correlate the crystallinity and specific heat of HDPE and LDPE with their structural changes occurring during heat treatment. The changes in crystallinity and specific heat, after the samples being subjected to annealing at 80°, 90° and 100°C respectively followed by the heat treatment, are found to be quite consistent. Probable explanations for the observed behaviour of both e-irradiated and un-irradiated samples are presented in this paper.

1. Introduction

High density and low density polyethylene(HDPE & LDPE)are semi-crystalline, polymers made up of crystalline and amorphous regions. One of the fundamental properties which affect the physical properties of polymer is the degree of crystalinity. Differential Scanning Calorimetry (DSC) provides a rapid method for determining crystallinity based on the heat required to melt the polymer. The crystalline phase being a quasi stable state, generally the melting temperature of a polymer lies over a wide range and the degree of crystallinity decreases continuously with temperature within the melting range. Polymers having crystal polymorphism show transformation among different crystal modifications and melt-re crystallization during melting[1]. Crystallinity and peak melting temperature of poly ethylene undergo an increase after irradiation , depending upon the dose and the molecular weight of the material (2).

2. Experimental Details

HDPE (crystallinity70%), LDPE (crystallinity 40%) samples from Buna AG Merseburg, Germany, are used for irradiation with 8MeV electron beam at a dose of 100 KGy in the as received sate. For DSC measurement the samples are cut into suitable sizes so that the weights of the samples remain in between 15 to 20 mg as specified for DSC.

DSC measurements were carried out by NETZSCH DSC200 F3 Maia instrument under N_2 atmosphere at a constant pressure of 0.3bar for preventing any sample oxidation and at a scanning rate of 10^0C/min. Annealing procedure consists of cooling the sample from 160^0c to the desired temperatures (80^0c,90^0c,100^0c respectively) and maintaining it for one hour before cooling to room temperature. Only for annealing at 100^0c, the cooling rate is 50^0c/min. Proteus Analysis software is used for finding out the specific heat and crystallinity of the samples.

3. Results and Discussions

DSC monitors heat effects associated with phase transitions and chemical reactions as a function of temperature. The same temperature program is used for plotting the curve between heat flow and temperature for the standard sample (sapphire) and the sample under investigation. The Heat flow into the sample is given by, $dH/dt = m * C_p * dT/dt$

Where dH/dt is the heatflow rate in calories/seconds, m is the mass of the sample in grams, C_p is the specific heat inCalories/gram/^{o}K , dT/dt is the rate of change of temperature in ^{o}K/second. The final equation which determines the specific heat of the sample is given by,

$$C_p/C_p' = m'y/my'$$

Where C_p' and m′ are the specific heat and mass of the standard, y and y′ are the ordinate deflections due to the sample and standard respectively in inches [5]. The variations of specific heat at different temperatures for reference as well as irradiated samples of HDPE and LDPE are shown in Figs.1and 2 below.

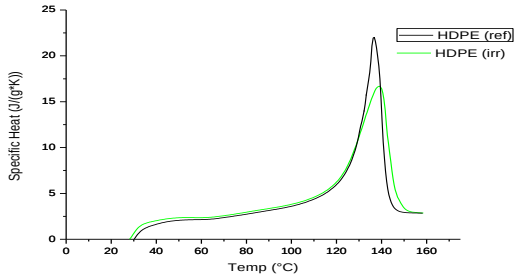

Figure 1.The variations of specific heat at different temperatures for reference and irradiate sample of HDPE

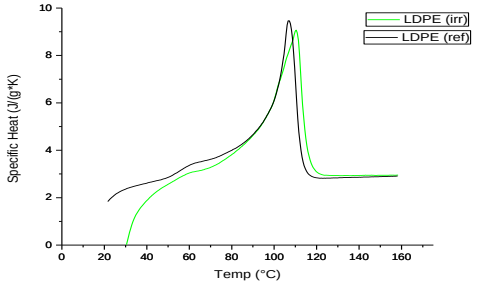

Figure 2.The variations of specific heat at different temperatures for reference and irradiate sample of LDPE

It is found that the irradiated sample has a melting peak at a higher temperature signifying a larger temperature needed to dissociate the sample completely as there is a stronger bond due to cross-linking because of irradiation(6).As the temperature increases specific heat of both reference and irradiated samples goes on increasing till the melting peak beyond which specific heat decreases.With the rise of temperature, chains of polymer samples become unfolded and stretched. So free space for molecular vibration and thus internal energy become less and heat taken from outside becomes larger. So polymer samples now have some lower crystallinity and greater specific heat within the melting range(1).Further annealing beyond melting temperature causes changes in the configuration of the polymer crystal leading to an increase in the crystallinity and decrease in specific heat.

The degree of crystallinity is defined as

$$X_c = \Delta H_f(T_m)/\ \Delta H_f^0(T_m^0),$$

Where, X_c is the weight fraction of crystallinity. $\Delta H_f(T_m)$ is the enthalpy of fusion measured at the melting point, T_m. $\Delta H_f^0(T_m^0)$ is the enthalpy of fusion of the totally crystalline polymer at the equilibrium melting point,T_m^0 [3]. Table1 presents the results of annealing at 80^0C, 90^0C and 100^0 C. Both un-annealed reference and irradiated samples have the crystallinity higher than that of annealed samples. Variations in crystallinity for different annealing temperatures are more for reference samples compared to irradiated ones. However,difference is small indicating not much change in crystallinity for low irradiation dose[4].

Table 1.Variation of crystallinity for the reference and irradiated samples

Sample	Temperature condition	Melting Area (J/g)	Crystallinity (%)
HDPE (Ref)	Unannealed	187.5	64.01
	Annealed at 80^0C	168.8	57.62
	Annealed at 90 ^{0}C	179.2	61.16
	Annealed at 100^0C	187.5	63.98
HDPE (Irradiated)	Unannealed	192.4	65.67
	Annealed at 80^0C	186.2	63.56
	Annealed at 90^0C	177.4	60.54
	Annealed at 100^0C	181.9	62.09
LDPE (Ref)	Unannealed	62.35	21.28
	Annealed at 80^0C	66.95	22.85
	Annealed at 90^0C	62.67	21.39
	Annealed at 100^0C	75.82	25.88
LDPE (Irradiated)	Unannealed	74.16	25.31
	Annealed at 80^0C	73.26	25
	Annealed at 90^0C	74.18	25.32
	Annealed at 100^0C	73.69	25.15

4. Conclusion

The temperature variation in specific heat in DSC measurement shows that after irradiation the crystallinity increases whereas the specific heat decreases till the melting peak beyond which it reverses due to configurational changes. Annealing at different temperatures results to structural changes causing variations in crystalinity depending upon morphological history of the sample

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