Thermal Analysis in High Energy Electron Irradiated Polystyrene Studied by Differential Scanning Calorimetry

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Abstract

The variation in the microstructure in terms of the thermal properties, such as specific heat(Cp), glass transition temperature(Tg) of 8 MeV electron irradiated Polystyrene (PS) at different doses have been measured using Differential Scanning Calorimetry (DSC). The variation in size of free volume influences very little on the value of Tg, it increases as the free volume size increases. The variation of specific heat (Cp) as a function of temperature both above and below the glass transition temperature (Tg) are observed. It is also found that the specific heat and the rate of heat absorption decrease with the increase of electron irradiation dose. As the irradiation dose increases, the scission process becomes dominant and causes decrease of molecular weight and increase the amount of free volume in the sample. Hence the vibrational motion of the molecules increases and the Cp value becomes less.

1. Introduction

The Differential Scanning Calorimeter (DSC) is employed to investigate the thermal behavior of the polymer samples. A study on the variation of the specific heat of the polystyrene (PS) sample of the present investigation as a function of temperature and electron beam irradiation has been carried out and the effect of electron irradiation on glass transition temperature (Tg) is also measured. The presence of benzene ring PS structure it is expected that it exhibits high radiation resistivity. The effect of high-dose electron and gamma irradiation on microstructure and thermal properties of PS was reported by several groups [1-3]. In these studies, the effect of high energy electron irradiation with low doses on the microstructure of PS in terms of free volume characterization was not done. Therefore, in this paper we report the free volume and thermal properties characterization after high energy electron irradiation at low doses in order to understand the microstructure of PS.

2. Experimental Details

Polystyrene samples, made by the BASF AG Ludwigshafen, Germany, are used for irradiation with 8MeV electron beam at doses 50, 75 and 100 KGy respectively 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.

The DSC measurements carried out by employing 2000F3 model of DSC with intra-cooler 70 versions in N2 atmosphere with constant pressure of 0.3bar to prevent any oxidation of the samples. The temperature has been varied up to 230^0C from ambient at a constant heating rate of 10^0C\min. Proteus analysis software is used to study the variation of specific heat (Cp) and glass transition temperature (Tg).

3. Results and Discussions

DSC measures the change in thermal properties and due to microstructural changes of any sample as a function of temperature The variation of specific heat (C_p) of electron irradiated Polystyrene (including the reference one) with temperature both above and below the glass transition temperature (T_g) are observed. The effect of irradiation dose on T_g and C_p are also observed but not pronounced.

In DSC measurement the specific heat of the sample can be determined by comparing it to that of a known sample. In our experiment we have considered sapphire as the standard known sample. The heat that flows into the sample is directly proportional to the specific heat. The equation is used to determines the specific heat of the sample 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 measured in centimeters [4-5].

Figure 1 shows the variation of specific heat (C_p) of PS with both temperature and irradiation dose. It is found that the glass transition of PS starts in the vicinity of 90 – 100^0 C with an endothermic enthalpic relaxation peak almost at the end of the glass transition process. It occurs immediately after the enthalpic relaxation, right after the glass transition process is complete. At a temperature around 115 – 120^0C, disordered PS chains start to order themselves in regular spherulitic structures. Spherulite is the basic higher order structure of crystalline polymers composed of lamellar structures filling in the inner part by the repetition or the re-orientation and branching on the growth in the radial direction. The variations of C_p values have interesting features; it increases with temperature up to the glass transition temperature and then decreases up to a certain temperature (~180^{o}C) and again increases with increase of temperature. It also shows a trend to give another peak at the temperature range 240-250^{o}C due to melting on heating and crystallization on cooling. But PS has a rather bulky pendant phenyl group at regular intervals;

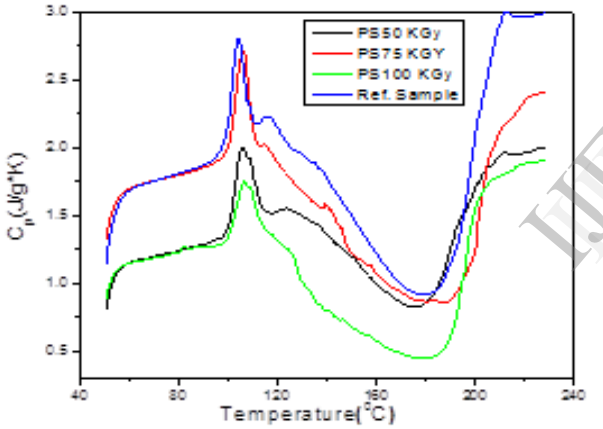

Figure 1. Variation of Specific Heat (C_p) of Polystyrene (PS) Samples With Temperature and Irradiation Doses(KGy)

steric hindrance makes it difficult to crystallize evenly and extensively. Thus its crystallization peak is not very sharp and is rather diffusively spread. High energy irradiation thus may be thought to set off two primary processes which may lead to structural changes in PS. They are chain scission and crosslinking. In effect, these are competitive processes, one leading to a lowering of molecular weight and the other increasing it. Both have a direct bearing on the packing and the crystallization of the polymer. In all probability, the process of chain scission turns out to be a dominating phenomenon. The overall effect of this is a decrease in the chain lengths as well as the molecular weight upon exposure to radiation and it also decreases the value of C_p. The variation of glass transition temperature (T_g) with irradiation doses are shown in the Table 1. At 50 KGy dose T_g increases by1.5 ^{o}C with respect to the reference sample. The T_g value at 75 KGy and 100 KGy are almost same and lesser than that of 50 KGy. The variation of T_g is negligible, thus it does not give any significant information on the microstructural changes in PS upon e-beam irradiation.

Table 1- Glass Transition Temperature at different Irradiation Doses (KGy)

Irradiation dose (KGy)	T_g (in ^{o}C)
Reference sample	99.1
50	100.7
75	99.6
100	99.9

4. Conclusion

In the DSC measurements, the variation in size of free volume influences very little on the value of T_g, it increases as the free volume size increases. It is also found that the specific heat at constant pressure and the rate of heat absorption decreases with the increase of electron irradiation dose. As the irradiation dose increases, the scission process becomes dominant and causes decrease of molecular weight and increase the amount of free volume in the sample. Hence the segmental motion of the molecules increases and the C_p value becomes less.

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