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Effects of Electron Beam Irradiation on the Thermal Properties of Scrap Polytetrafluoroethylene

(Kesan Sinaran Elektron ke atas Sifat Terma Pepejal Politetrafluoroetilena)

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ABSTRACT

This study is focused on analyzing the effects of electron beam (EB) irradiation at high doses and normal atmospheric conditions on the thermal stability of scrap polytetrafluoroethylene (PTFE) solid to facilitate the recycling process of the material by grinding it into micro-powder additives for various applications. In this work, PTFE scrap with thickness not exceeding 1 mm was irradiated in doses between 0 - 1500 kGy using an electron beam accelerator machine (EBM) with a voltage energy of 3 MeV and current of 10 mA and grinded into powder by using a laboratory mill. The changes in morphology of the grinded powder, crystallinity and thermal properties of PTFE with increasing irradiation dose was studied by using scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The photomicrographs obtained from SEM showed that the particle size of the grinded micro-powder decreases with increasing irradiation dose with best results observed at 1500 kGy dose. DSC analysis showed that the crystallization temperature (T_c) and melting temperature (T_m) decreases with increasing irradiation doses as a result of lower molecular weight. XRD analysis of the irradiated PTFE indicated that the intensity of the peak had increased with increasing doses of irradiation due to the increase in crystallinity of the material. The distinctly shorter derivative thermogravimetric (DTG) peak height at 1500 kGy shows higher rate of mass loss at that dose due to the rapid loss of mechanical properties caused by degradation.

Keywords: Degradation; electron beam; irradiation; micro-powder; polytetrafluoroethylene

ABSTRAK

Kajian ini ditumpukan kepada analisis kesan sinaran elektron (EB) pada dos sinaran yang tinggi dan dalam keadaan atmosfera biasa terhadap kestabilan terma sisa bahan pepejal politetrafluoroetilena (PTFE) untuk memudahkan proses pengitaran semula dengan mengisarkannya kepada bahan tambahan dalam bentuk serbuk bersaiz mikron untuk digunakan dalam pelbagai jenis aplikasi. Sisa bahan PTFE dalam bentuk kepingan dengan ketebalan tidak melebihi 1 mm disinarkan pada dos antara 0 - 1500 kGy dengan menggunakan mesin pemecut alur elektron (EBM) dengan tenaga voltan sebanyak 3 MeV dan arus alur elektrik 10 mA dan dikisarkan menjadi serbuk dengan menggunakan mesin pengisar makmal. Perubahan morfologi serbuk yang dikisarkan, sifat kehabluran dan sifat terma bahan PTFE dengan peningkatan dalam dos sinaran dikaji dengan menggunakan mikroskop elektron pengimbasan (SEM), analisis pembelauan sinar-X (XRD), analisis termogravimetri (TGA) dan kalorimetri pengimbasan pembezaan (DSC). Fotomikrograf yang diperoleh daripada analisis SEM menunjukkan bahawa saiz partikel serbuk mikro yang dikisar menjadi lebih kecil dengan peningkatan dalam dos penyinaran sehingga 1500 kGy. Analisis DSC menunjukkan bahawa suhu penghabluran (T_c) dan suhu lebur (T_m) berkurangan dengan peningkatan dalam dos penyinaran disebabkan nilai berat molekul yang menjadi lebih rendah. Analisis XRD bagi bahan PTFE yang disinarkan menunjukkan bahawa keamatan puncak meningkat dengan peningkatan dalam dos penyinaran disebabkan oleh peningkatan dalam sifat kehabluran bahan tersebut. Keamatan puncak termogravimetrik terbitan (DTG) yang jauh lebih rendah pada 1500 kGy juga menunjukkan kadar kehilangan jisim yang lebih tinggi disebabkan oleh degradasi serta kehilangan sifat mekanikal yang ketara pada dos berkenaan.

Kata kunci: Alur elektron; degradasi; penyinaran; politetrafluoroetilena; serbuk bersaiz mikro

INTRODUCTION

Polytetrafluoroethylene (PTFE) is a fluoropolymer with a long chain $(CF_2–CF_2)_n$ molecular structure with some interesting properties such as its hydrophobicity, resistance to high temperatures, non-stick characteristics, chemical stability and low friction coefficient (Barylski et al. 2020a; Goel et al. 2011; Liu et al. 2015; Vijay et al. 2020). Its specialty compared to other polymers is due to the presence of fluorine atoms in its chemical structure because fluorine is the most electronegative element among all chemical elements. These attractive properties make PTFE one of the most widely used polymeric materials in various industries such as in aerospace, electronics and for household equipment and utensils (Dhanumalayan & Joshi 2018; Ebnesajjad 2013).

Previously, there have been many studies done on the effect of irradiation on the chemical structure of PTFE under various irradiation conditions and parameters (Lappan, Geißler & Lunkwitz 1999; Lunkwitz, Lappan & Scheler 2004; Oshima et al. 1997, 1995). Depending on factors such as dose rate and range, temperature and atmospheric conditions such as in presence of oxygen, PTFE irradiation by electron beam (EB) or gamma rays changes the morphology, mechanical and chemical structures of the material significantly (Chai et al. 2019; Mohammadian-Kohol, Asgari & Shakur 2018; Su et al. 2006; Voronova et al. 2020). Previous studies done on PTFE have shown that depending on the irradiation parameters and conditions such as in air, vacuum state or in the presence of inert gases, changes in the chemical structure occurs whereby either cross-linking or chain-scission of the long-chain becomes the dominant process (Khatipov, Serov & Buznik 2020). Chain-scission of PTFE predominantly occurs when irradiated in air at room temperature while cross-linking and branching is the dominant process when irradiated in molten state or under oxygen-free vacuum state or inert gases (Lunkwitz, Lappan & Scheler 2004). Radiation-induced radicals react with oxygen if the partial degradation of PTFE takes place in air leading to the formation of acid fluoride groups (COF) within the polymer and in the presence of atmospheric humidity, and the COF groups hydrolyzes to form carboxylic acid groups (COOH) (Lappan, Geißler & Lunkwitz 2000; Lappan, Geißler & Scheler 2007; Lappan et al. 2002; Tabata, Ikeda & Oshima 2001; Tabata, Suzuki & Ikeda 2013). According to Oshima et al. (1995), degradation of PTFE occurs after irradiation at room temperature because the radicals formed had restricted mobility and could not go through the recombination processes.

PTFE still retains the intrinsic properties of the material even after irradiation, thus, can be modified to be used in composite materials or as additives in rubber and synthetic elastomers where it functions as an internal solid lubricant that improves the friction and wear properties of the base material (Barylski et al. 2020b; Dubey et al. 2013; Khan, Lehmann & Heinrich 2008; Khan et al. 2009). Generally, a material with higher molecular weight increases the impact resistance of the material. This is due to the higher degree of entanglement of polymeric chains where more polymer bonds need to be broken to cause rupture. Thus, irradiation processing can be used in the recycling of scrap PTFE material by reducing the molecular weight to a range in which it could be converted into micro-powder by mechanical processing, and which subsequently can be used as a dry lubricant to enhance the properties of various industrial products such as in inks, plastics and coatings (Lappan, Geißler & Lunkwitz 1999). According to Ebnesajjad and Morgan (2012), degradation of PTFE molecular chains starts to occur at a dose range of above 500 kGy at normal conditions. While the effects of irradiation on the changes in chemical structure of PTFE under various temperature and atmospheric conditions have been studied extensively by many researches, the effects of irradiation-degradation on the thermal stability and microstructural changes of PTFE material for the purpose of recycling into micro-powder have not been fully investigated. Hence, the motivation of this work is to study the effects of EB irradiation at a wide range of doses on the thermal and microstructural properties of scrap PTFE under normal atmospheric conditions.

MATERIALS AND METHODS

PTFE scrap material with thickness not exceeding 1 mm was irradiated at doses from 0 to 1500 kGy and grinded into micro-powder with an IKA-M20 laboratory mill with a cutting speed of 20,000 rpm in 20 min. Irradiation of the PTFE scraps was done with an EPS-3000 electron beam accelerator machine (EBM) with a voltage processing parameter of 3 MeV, 10 mA electric current and dose rate of 50 kGy per pass. Differential scanning calorimetric (DSC) analysis of the samples was performed using the Mettler Toledo STAR^e to obtain a thermogram in the temperature range from 30 °C to 400 °C with a heating rate of 10 °C per min. From analysis of the DSC exothermic and endothermic thermograms, the melting temperature (T_m) and crystallization temperature (T_c) of the samples can be obtained. Thermogravimetric analysis (TGA) tests were performed using the Netzsch TG209 equipment in the temperature range from 35 °C to 700 °C to determine the thermal stability of the samples at various irradiation doses. X-ray diffraction (XRD) analysis of the samples was obtained using a PANalytical PW3040/60 X'Pert PRO MPD XRD. The radiation source used in XRD is CuK$_\alpha$ with a wavelength of 1.5418 Ǻ. Morphological study of PTFE micro-powder samples after grinding was analyzed using a scanning electron microscope (SEM) model Zeiss Gemini 500.

RESULTS AND DISCUSSION

DIFFERENTIAL SCANNING CALORIMETRIC (DSC) ANALYSIS

DSC 1st heating and cooling scans of the PTFE samples were used to determine the T_m and T_c peaks, respectively, and to calculate the percentage of crystallinity (X_c) based on the value of the enthalpy of fusion of the polymer sample in J/g. Thus, the X_c percentage value is calculated as the ratio of ΔH_c obtained from the thermogram peak area with ΔH_c of PTFE at 82 J/g. The DSC exothermic and endothermic curves are shown in Figures 1 and 2, respectively. From the heating exothermic peaks in Figure 1, it can be observed that T_m decreases only slightly at 250 kGy, indicating that cross-linking of the molecular chain is the dominant process and decreases in value rapidly from 500 kGy onwards where chain-scission dominates with the peaks shifting further left where the lowest T_m is observed at 1500 kGy dose. From the endothermic scan in Figure 2, with increasing doses of irradiation, the crystallization peak T_c decreased with the peaks shifting further to the left of the thermogram where the crystallization process happens at much lower temperatures in comparison to the unirradiated PTFE sample.

The heating and cooling scans from the DSC

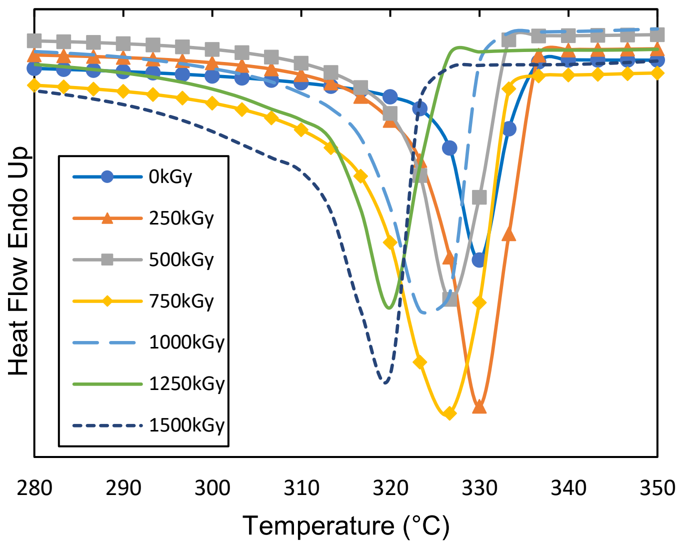

FIGURE 1. DSC heating thermogram of PTFE at irradiation doses of 0 -1500 kGy

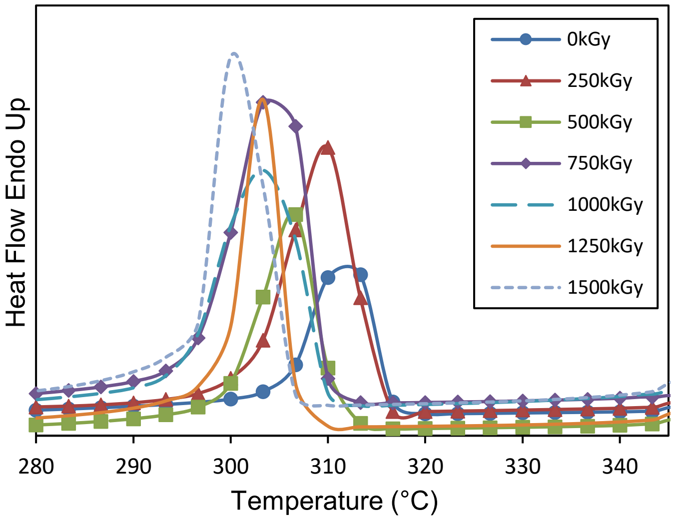

FIGURE 2. DSC cooling thermogram of PTFE at irradiation doses of 0 -1500 kGy

thermogram provides information about the effect of irradiation on the molecular chain crystallization process and the final crystallinity (Frick et al. 2013). When the molecular weight of PTFE decreases, it results in thermally less stable semi-crystalline structure which melts at a lower temperature due to the disentanglement of polymer chains leading to the formation of a more disordered structure. Figure 3 and Table 1 shows that the heat of crystallization, ΔH_c and percentage of crystallinity, X_c (%) calculated from the cooling thermogram peak area shows maximum values at 750 kGy and decreases at higher doses. However, according to Lappan et al. (2004), the number-average molecular weight, M_n reduces with increasing doses of irradiation as PTFE undergoes predominantly chain scission at higher doses which leads to shorter molecular chains. Shorter chains result in greater mobility of PTFE and less intra and intermolecular entanglements. This results in occurrence of a more complete crystallisation by the melt crystallisation process during the cooling scan. Therefore, ΔH_c of PTFE should theoretically be influenced by the molecular weight because the crystallisation process of molten PTFE during cooling is increasingly hindered if cross-linking is dominant due to the intensified entanglement of PTFE chains with increasing molecular weight. Therefore, the Suwa equation, $M_n = 2.1 \times 10^{10} \times (\Delta H_c)^{-5.16}$ (Suwa, Takehisa & Machi 1973), which is dependent on the value of ΔH_c is commonly used by previous researches to calculate M_n since PTFE is an insoluble material where the molecular weight cannot be determined by direct analytical methods such as by using gel permeation chromatography (GPC) analysis.

From ΔH_c values in Table 1 and based on the Suwa equation, the calculated M_n value will be lower at the 750 to 1000 kGy irradiation dose range ($M_n = 1.50 \times 10^4$ and 1.58×10^4 g/mol, respectively) and increases again at 1250 and 1500 kGy ($M_n = 1.79 \times 10^4$ and 2.11×10^4 g/mol, respectively). However, we observed that with increasing irradiation doses the mechanical properties of the material had decreased due to degradation which can only be possible due to dominance of chain-scission process and a decrease in the molecular weight as reported by Forsythe and Hill (2000). Therefore, a better hypothesis for the decrease in values of ΔH_c and X_c at the 1250 and 1500 kGy dose range can be attributed to modifications or damage within the molecular microstructure of PTFE leading to a less orderly structure hindering the crystallisation process during cooling rather than a decrease in the molecular weight. This trend can also be observed during the melting phase where ΔH_m reaches maximum at 1000 kGy dose and thereafter decreases. Furthermore, studies done by Lappan et al. (2004) have shown that estimation of molecular weight by quantitative relationship between M_n and ΔH_c might not be suitable if the calculated M_n is $< 10^5$ g/mol.

TABLE 1. Thermal transitions of PTFE material at E-beam irradiation doses of 0 – 1500 kGy

Dose (KGy)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	X_c (%)
0	329.98	24.09	312.46	31.48	38.39
250	329.69	60.95	311.99	58.68	71.56
500	326.57	63.40	307.23	60.57	73.86
750	324.84	66.24	305.74	64.95	79.21
1000	323.98	67.90	304.02	64.36	78.49
1250	320.72	60.99	304.06	62.75	76.52
1500	319.10	61.07	302.37	60.81	74.15

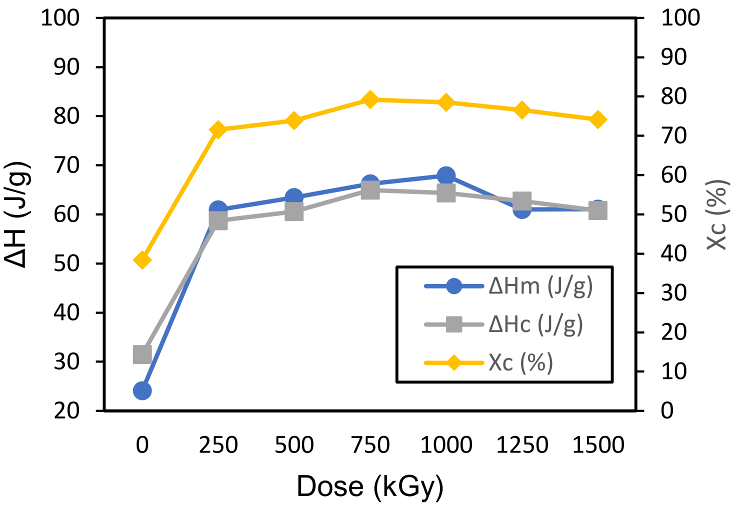

FIGURE 3. DSC melting heats compared with the crystallization heat and percentage of crystallinity of PTFE at irradiation doses of 0 -1500 kGy

X-RAY DIFFRACTION (XRD) CHARACTERIZATION

XRD characterization of the PTFE samples are shown in Figure 4(a) with Figure 4(b) showing the peak intensity at 2θ angles between 17.5° and 18.5° for better clarity. Brown et al. (2008) has suggested that PTFE is a semi-crystalline polymer with the crystalline domains separated by regions of amorphous PTFE molecule with helical coil structure within the individual polymer chains and hexagonal packing structure between chains in the crystalline state.

From the results, it can be observed that the intensity of main peak (100) had increased with increasing doses of EB irradiation with the peaks shifting slightly to a lower degree due to increase in the crystallinity of PTFE as a result of polymer chain-scission at higher doses. The only exception for this trend is seen at the 1000 kGy

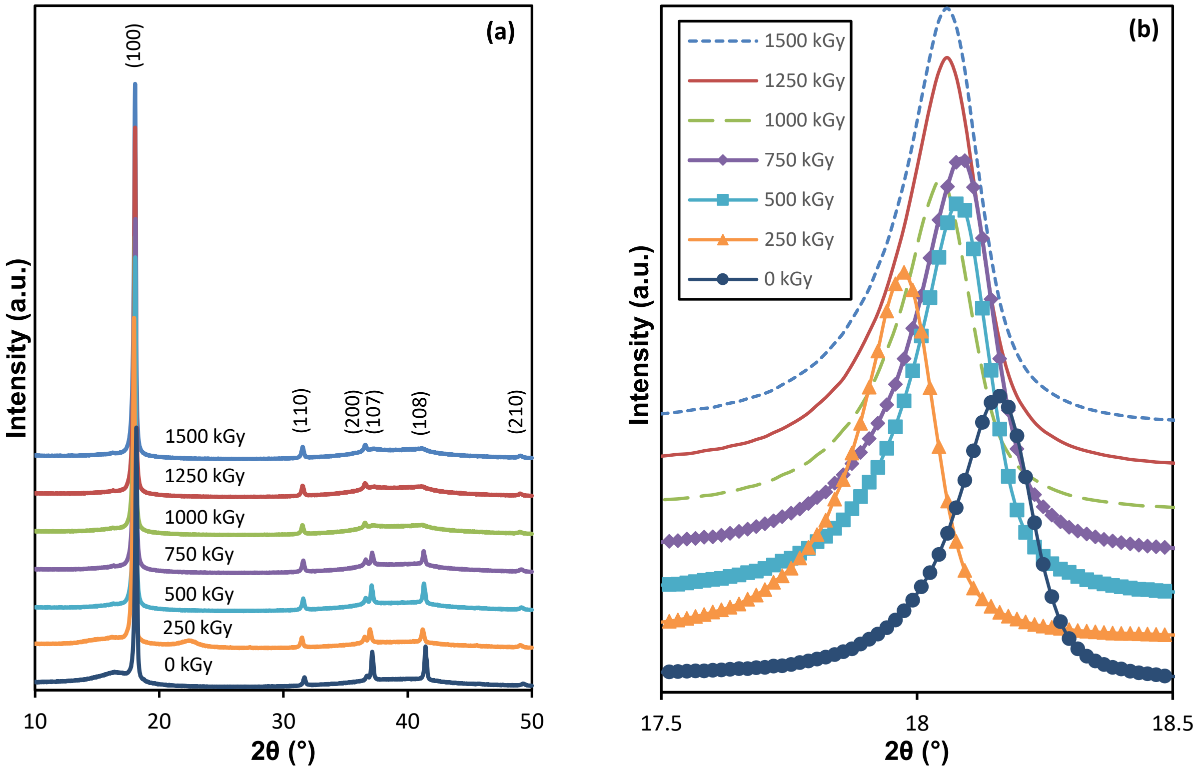

FIGURE 4. (a) Comparison of XRD intensity of PTFE at irradiation doses of 0 -1500 kGy and (b) peak intensity at 2θ angles between 17.5° and 18.5°

dose where there is a slight decrease in the intensity of the peak. As for the peaks in the higher degrees, except for (110) plane, the (200), (107), (108) and (210) plane peaks decreased in intensity or disappeared. The lattice spacing (d-spacing) of the main peak can be obtained from Bragg's formula $n\lambda = 2d\sin\theta$, where θ = maximum peak intensity diffraction angle, λ = wavelength of the XRD source and n = integer number of wavelengths. D-spacing can be described as the distance between planes of atoms that give rise to diffraction peaks. For the unirradiated PTFE sample the calculated d-spacing was 4.8807 Å and increased to 4.9311 Å at 250 kGy. The d-spacing values obtained from XRD analysis was 4.9035 Å, 4.8989 Å, 4.9126 Å, 4.9081 Å and 4.9081 Å, respectively, at 500 kGy, 750 kGy, 1000 kGy, 1250 kGy and 1500 kGy irradiation dose as shown in Figure 5.

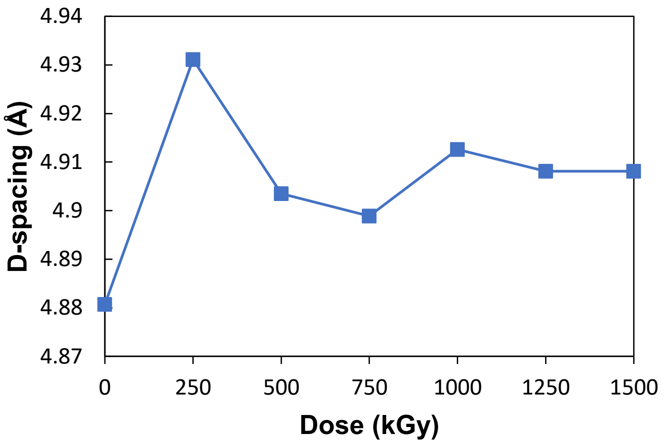

FIGURE 5. XRD d-spacing values of PTFE obtained at irradiation doses of 0 -1500 kGy

For PTFE irradiated at 250 kGy, the increase in d-spacing of the main peak compared with the unirradiated sample can be suggested to be caused by mainly cross-linking and branching of the molecular chain. Degradation of PTFE molecular chains starts to occur at a dose range of above 500 kGy (Ebnesajjad & Morgan 2012). The d-spacing value decreases at the 500 kGy dose where chain-scission is the dominant process. As observed also in the DSC analysis with regards to ΔH_c, ΔH_m and X_c values at the 750 -1500 kGy dose range, the d-spacing value does not decrease linearly with degradation of the PTFE material. Therefore, the changes in d-spacing after the 500 kGy dose can be postulated to be caused by modifications or damage within the molecular microstructure of PTFE leading to a less orderly crystalline structure caused by degradation with increasing irradiation dose.

THERMOGRAVIMETRIC ANALYSIS (TGA)

TGA weight loss curves are shown in Figure 6, where the unirradiated PTFE sample shows a single-step degradation pattern, with no weight loss up to 569 °C beyond which thermal decomposition of molecular chains of PTFE occurs in the range of 569-627 °C. The initial decomposition temperature (T_{onset}) decreased from 569 °C for the unirradiated sample to 517 °C at 1500 kGy. It can also be observed from the weight loss curves that T_{onset} is distinctly lower at 1500 kGy dose compared to the other irradiated samples due to an increase in degradation of the sample at that particular dose. At 1500 kGy dose, PTFE also showed a single step degradation pattern with a distinct reduction of the derivative thermogravimetric (DTG) peak to 565 °C from 602.5 °C for the unirradiated PTFE. The shorter DTG peak height at 1500 kGy from Figure 7 also shows that the rate of mass loss is higher at that dose compared to the other samples. This result is consistent with our observation for the PTFE scrap sample irradiated at 1500 kGy where the material breaks in to pieces when removed from the irradiation tray due to a steep reduction in mechanical properties caused by degradation.

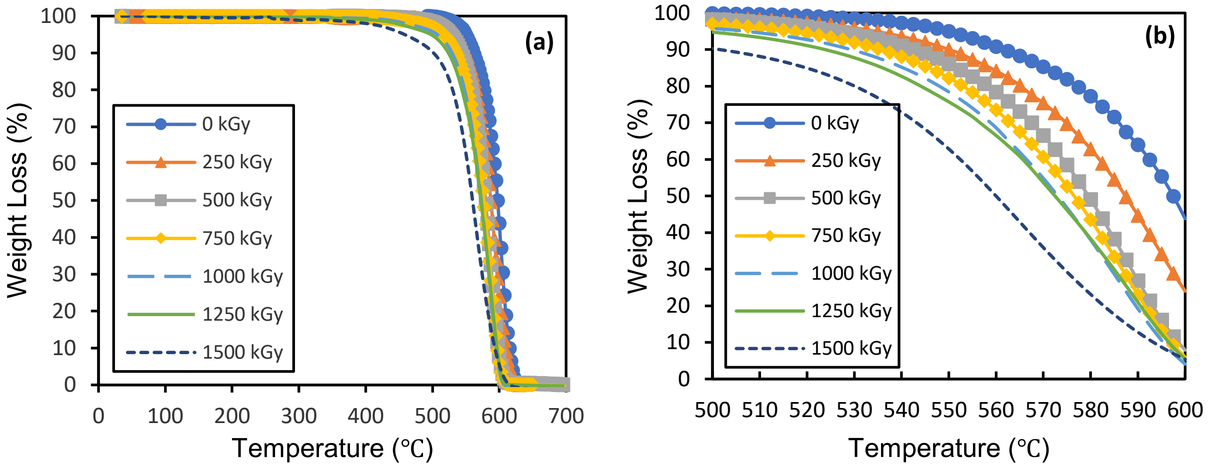

FIGURE 6. (a) TGA weight loss curves of PTFE at irradiation doses of 0 -1500 kGy and (b) initial decomposition curves

MORPHOLOGICAL ANALYSIS OF GRINDED PTFE POWDER

SEM micrographs of the irradiation-degraded PTFE samples in the range of 500-1500 kGy after grinding are shown in Figure 8(a) to 8(e). SEM studies were not conducted for samples irradiated at 0 and 250 kGy due to grinding limitations as they were found to be very tough and difficult to be grinded. Such observation could be associated with the improved mechanical properties due to occurrence of predominantly radiation-induced cross-linking at 250 kGy. Similar observation of improved mechanical properties for cross-linked PTFE was reported by Oshima et al. (1999). The SEM images with a magnification of 50× show that the particle size

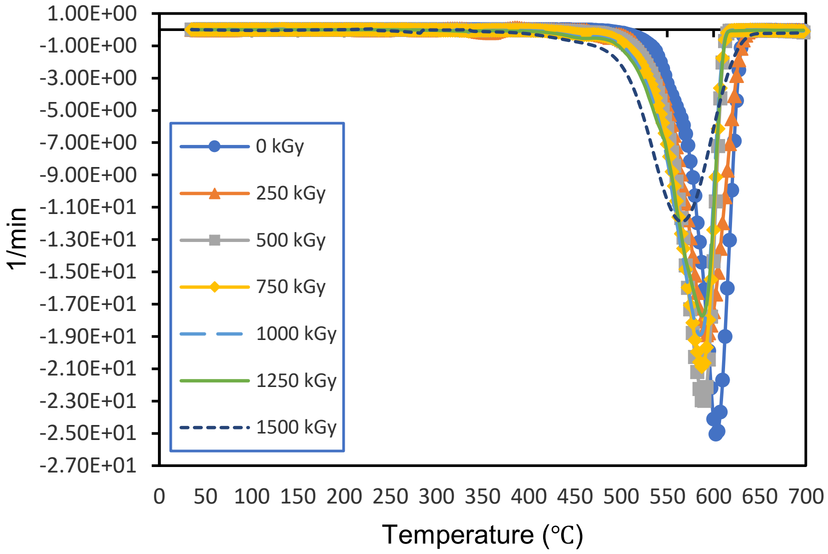

FIGURE 7. DTG peaks of PTFE at irradiation doses of 0 -1500 kGy

of the powder decreases with increasing EB irradiation dose due to an increase in the degradation of the material which makes it highly crystalline and brittle, which facilitates the grinding process into smaller particles. From observation of the SEM images, the distribution of smaller particle size is observed to be more prevalent at 1500 kGy dose while the presence and distribution of larger particles (exceeding 100 µm) is more random compared to the other doses.

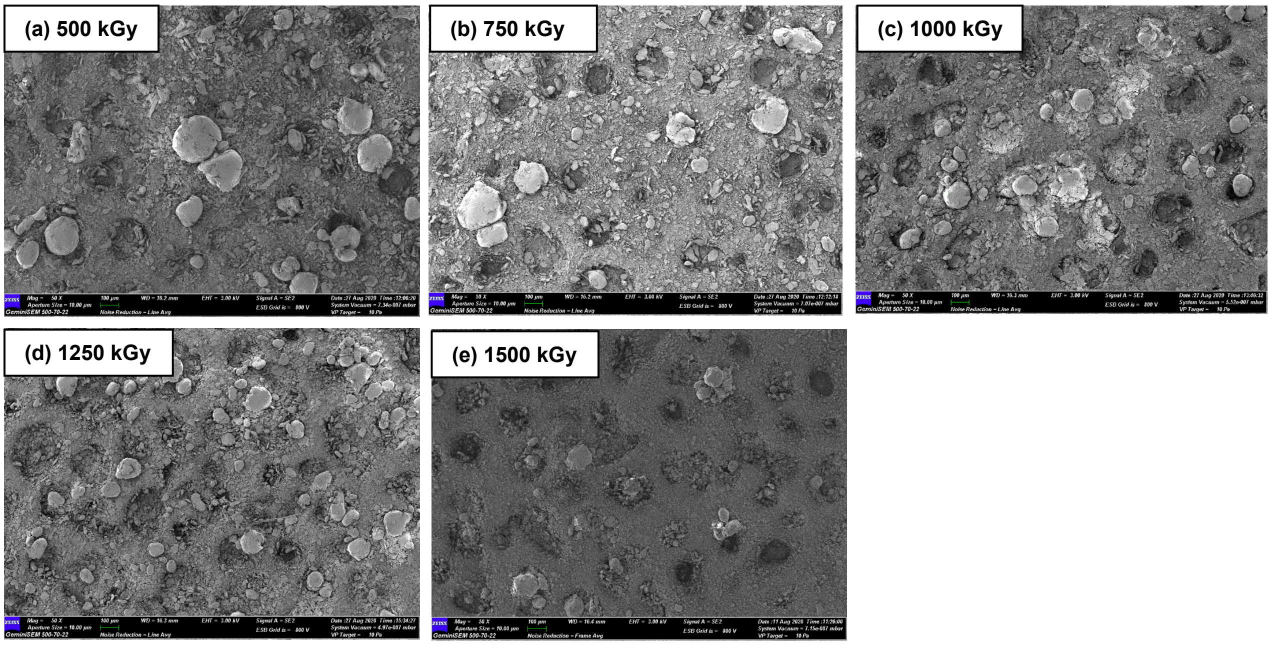

FIGURE 8. SEM morphological images of grinded PTFE micro-powder samples irradiated at 500 -1500 kGy are shown in micrographs (a) to (e)

CONCLUSION

Estimation of molecular weight by Suwa equation which depends on the quantitative relationship between M_n and ΔH_c obtained from DSC analysis shows discrepancies where the theoretically calculated molecular weight is shown to be higher at 1250 and 1500 kGy. However, we postulate that by analysis of the d-spacing results obtained from XRD, that changes in ΔH_c could also be attributed to modifications or damage within the molecular microstructure of PTFE at higher irradiation doses leading to a less orderly structure hindering the recrystallisation process during cooling rather than just the effects of the molecular weight. It can be concluded that EB irradiation dose of up to 1500 kGy in normal atmospheric conditions reduces the thermal stability of PTFE material where T_m,T_c and T_{onset} decreases with increasing dose. The distinctly shorter DTG peak height at 1500 kGy shows higher rate of mass loss at the dose. This result is consistent with our observation for the PTFE scrap sample irradiated at 1500 kGy where the material had become very brittle and breaks when removed from the irradiation tray. SEM images have shown that the size of powder particles obtained after the mechanical grinding process of degraded PTFE scrap for a constant time period correlates with the irradiation dose given.

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