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LETTER

Effect of proton irradiation on multiple melting peaks of polyethylene terephthalate

B. Mallick · R. C. Behera · S. Panigrahi · T. N. Tiwari

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The study of effects induced by keV or MeV heavy ions irradiation on polymers has attracted attention 1–4 both for fundamental interest and for potential technological applications in various fields such as dosimeters, biomaterial for implantation, composites, conducting polymers, electroactive polymers, textile industry, surgical polymeric textiles, etc. The polyethylene terephthalate (PET) material gets damaged while irradiating (in vacuum) with different ions and fluences as confirmed from the differential scanning calorimetry (DSC) by different researchers 5–11. An interesting result has been observed when PET microfibre is subjected to 3-MeV proton irradiation in air with two different fluences, viz. 1×10^{13} p/cm^2 and 1×10^{15} p/cm^2 and studied under DSC. The multiple melting endotherm is found to be shifted towards higher temperature with higher enthalpy change as compared the to pristine microfibre, which indicates the modification of PET for higher thermal stability and enhancement of its crystallinity.

The phenomenon of multiple melting endotherms seems to exist with most polymers including PET 5–7. It is well confirmed that the observation of multiple melting phenomena in PET is because of recrystallisation 7. In the present study, the PET microfibre (of denier value 1.5 denier per filament) has been irradiated with a proton beam, extracted to air from a 9SDH-2 tandem type pelletron accelerator (National Electrostatic Corporation, USA), at the Institute of Physics, Bhubaneswar, India 4. The irradiated microfibre has been studied using a Netzsch STA 409C simultaneous thermal analyzer (NETZSCH-Gerätebau, GmbH). The multiple melting transition temperature T_m of virgin and proton-irradiated PET microfibers are shown in Fig. 1. The DSC thermogram of virgin microfibre shows superimposed (two peaks) endotherms. The first endotherm (sharp) is observes at 253.9 °C (T_m^s) and the second peak (broad) endotherm at 254.75 °C (T_m^b). In the irradiated samples, it is observed that the sharp endotherm obtained at T_m^s remains constant (unmodified) for the two proton fluences used, viz. 1×10^{13} p/cm^2 and1×10^{15} p/cm$^{2.}$ However, the broad endotherm (modified), observed at T_m^b, is shifted to 256 °C and remains constant for both the proton fluences. It is also observed that the total change in enthalpy of fusion ($\Delta H_f = \Delta H_f^s + \Delta H_f^b$) varies with proton fluence and found higher in the case of irradiated samples. As reported by Calcagno 9, the semi-crystalline polymers, when subjected to ion irradiation at low fluence, mainly suffer a transformation from their semi-crystalline structure to a damaged one. The damaged material is still semi-crystallne, but is characterized by a low melting temperature and a broad melting behaviour. Similar phenomenon was also observed by many researchers using protons 10 and silicon ions 11 for irradiating polymeric materials.

The interesting result observed in the present study is that the ion-induced, modified semi-crystalline peak of PET is shifted towards higher temperature instead of lower temperature, as reported by others 5–11. This

B. Mallick (✉) · S. Panigrahi · T. N. Tiwari
Department of Physics, National Institute of Technology, Rourkela 769 008, India
e-mail: bmallick_iopb@scientist.com

R. C. Behera
Department of Metallurgical and Materials Engineering, National Institute of Technology, Rourkela 769 008, India

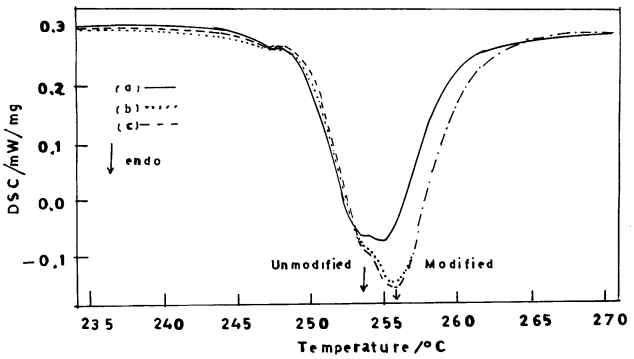

Fig. 1 DSC thermograms of the pristine and 3-MeV proton irradiated PET microfibres: (**a**) pristine (——), (**b**) irradiated with 1×10^{13} p/cm^2 (- - -) and (**c**) irradiated with 1×10^{15} p/cm^2 (·····)

shift of broad endotherm is probably due to recrystallization of the new phase (modified material) formed due to simultaneous action of the cross-linking effect 12 and sponge effect 13, since it is well known that the crosslinking of irradiated polymers takes place in the amorphous phase only. Again, irradiation of the polymer (PET) having benzene ring in its structure shows sponge effect when irradiated in air (oxygen). Also, the percent crystallinity ($\%C$) of the virgin sample; and samples irradiated at 1×10^{13} p/cm^2 and 1×10^{15} p/cm^2, measured by DSC, are found to be 24.01%, 30.06% and 28.78% respectively. Hence increase of ΔH_f, T_m and $\%C$ of irradiated sample is related to the modified PET material with improved thermal characteristics.

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References

1. Venkatesan T, Calcagno L, Elman BS, Foti G (1987) In: Mazzoldi P, Arnold G (eds) Ion beam modification of insulators. Elsevier, Amsterdam
2. Brown WL (1989) Nucl Instrum Methods Phys Res B 37/38:270
3. Davenas J, Stevenson I, Celette N, Cambon S, Garddette JL, Rivaton A, Vignoud L (2002) Nucl Instrum. Methods Phys Res B 191:653
4. Mallick B, Patel T, Behera RC, Sarangi SN, Sahu SN, Choudhury RK (2006) Nucl Instrum Methods Phys Res B 248:305
5. Fava RA (1980) In: Polymers: crystal structure and morphology. Academic Press, New York
6. Hodsworth PJ, Turner-Jones A (1971) Polymer 12:195
7. Miller GW (1974) Thermochim Acta 8:129
8. Papaleo RM, De Araujo MA, Livi RP (1992) Nucl Instrum Methods Phys Res B 65:442
9. Calcagno L (1995) Nucl Instrum Methods Phys Res B 105:63
10. Singh NL, Shah N, Singh KP, Desai CF (2005) Radiat Meas 40:741
11. Singh V, Singh T, Chandra A, Bandyopadhyay SK, Sen P, Witte K, Scherer UW, Srivastava A (2006) Nucl Instrum Methods Phys Res B 244:243
12. Charlesby A (1960) In: Atomic radiation and polymers. Pergamon press, Oxford
13. Kuleznev VN, Shershney VA (1990) In: The chemistry and physics of polymers. Translated by G. Lebib, MIR Publishers, Moscow