# Physical and mechanical behavior of electron-beam irradiated and ethylene oxide sterilized multiblock polyester

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The effect of two sterilization treatments (electron-beam radiation and ethylene oxide gas) on the structure and mechanical properties of a multiblock copolymer were investigated to establish the effects of the sterilizing procedures on potential biomedical material. The material was exposed for different radiation doses in order to find an optimum dose of electron-beam radiation. Characterization techniques employed include gel permeation chromatography, infrared spectroscopy, differential scanning calorimetry, dynamic mechanical thermal analysis and tensile testing. The optimal dose of radiation at which no change in structure and mechanical properties occurred was found as 25 kGy. Ethylene oxide gas treatment also did not affect the structure and properties of the polymer and it can be recommended as an alternative sterilization route for the studied polymer.


## 1. Introduction

Thermoplastic elastomers (TPE) are a rapidly developing class of polymeric materials, especially thermoplastic poly(ester-ether)s composed of hard and soft segments (blocks) randomly alternated along the polymer backbone [1]. This family of polyester elastomers exhibited outstanding elasticity, tear strength, solvent resistance, low-temperature flexibility, and strength at elevated temperatures. Equally important, they crystallize so rapidly from a melt that they can be processed by typical methods for forming plastics. Poly(ester-ether) elastomers are two-phase systems based typically on poly(butylene terephthalate)(PBT) polyester as well as aliphatic, most frequently amorphous oligoethers, i.e. poly(tetramethylene oxide) (PTMO) [2, 3].

Mody *et al*. [4] have replaced PTMO soft segment components by the unique polyether, namely poly-(ethylene oxide-5, 5-dimethyl-1, 3-hydantoin), which further was used as a component of segmented poly(ester-ether) commercial-ized under the trademark Polyactive by Holland Composites Implants, B.V. Leiden, The Netherlands. This polymer was found to be a degradable, biocompatible and bioerodible material, and by changing the weight ratio of soft/hard segments, a series of copolymers with different structures and properties was obtained [5–11] to find their end usage as an artificial tympanic membrane [7] and bone graft substitute [5, 6, 11].

Hoeschele [12] has introduced a dimer fatty acid (DFA) as a component of the soft segments in segmented polyesters improving the hydrolytic and oxidative stability of PBT (54 wt % of PBT)-dimer fatty acid material. This kind of nonlinear hydrophobic dimer (aliphatic dibasic acids) was successfully applied to a new class of biocompatible polyanhydride-based polymers developed for drug delivery [13].

However, the introduction of DFA into PBT-based copolymers was invented by Hoeschele [12], an original method for synthesis of this class of polyesters with variable soft/hard segments composition showing different structure and properties was elaborated in the Laboratory for Elastomers and Polymer Fibers, Technical University of Szczecin [14–18]. One of these polymers is extensively investigated now as the material for biomedical applications [19]. The aim of this article was to investigate such a multiblock polyester of PBT and DFA which, as far as the authors knowledge, has never been used in biomedical applications before. Therefore, prior to using the material for such applications a sterilization evaluation was required.

Several chemical and physical procedures can be chosen for sterilization purposes of biomedical devices. Use of ethylene oxide (EtO) and $\gamma$-irradiation are the two possible alternatives. The doses most commonly used for sterilization of the bulk materials for biomedical applications lie between 10 and 30 kGy (1–3 Mrad).

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Electron-beam radiation has been used successfully as a bactericide, and offers an attempt to develop sterilization techniques for different materials. The only disadvantage is that irradiation of polymers can promote chain scission, crosslinking or photo-oxidation reactions. Ethylene oxide gas treatment is also capable of degrading the polymer through hydrolysis, and presence of residual EtO may result in cytotoxicity after implantation.

In this work the effect of these two sterilization procedures on the physical and mechanical properties of multiblock polyester have been examined. The electron-beam irradiation from the accelerator instead of izotope method was used. The advantage of this method compared to the izotope method (with use of a $^{60}$Co-izotope source) is shorter exposition time (from 24 h for $^{60}$Co-irradiation up to 15 min for accelerator irradiation) due to the very high electron energy of 10 MeV, which is necessary for effective sterilization of the bulk polymer materials.

The effects of the radiation dose and the EtO treatment used in sterilization procedures on polymer properties was examined. It was of interest to evaluate the optimum radiation dose and the effect of EtO used in sterilization of this polymer.

## 2. Material and methods

### 2.1. Polymer

The material investigated was segmented polyester derived from a poly(butylene terephthalate)(PBT) extended with a dimerized fatty acid (DFA), which was obtained in the melt polycondensation reaction as reported elsewhere [14]. The composition of the polymer was 26 wt % of PBT and 74 wt % of DFA, respectively. At such a composition, the polymer appeared to be a flexible soft solid. The PBT was referred to as the hard segment phase, and DFA as the soft segment phase.

### 2.2. Sample preparation

Samples for dynamic mechanical and microcalorimetric examinations were prepared by press molding, carried out at a temperature 25 °C higher than the melting point $T_m$ determined from differential scanning calorimetry (DSC) (Table I). Samples for tensile testing were prepared by injection molding.

### 2.3. Sterilization procedure

Polymer samples were exposed to 25 kGy (2.5 Mrad), 50 kGy (5.0 Mrad) and 75 kGy (7.5 Mrad) electron-beam irradiation from the accelerator with an electron energy of 10 MeV. Ethylene oxide gas treatment was performed using a Steri-Vac 5 (3M) sterilization apparatus.

### 2.4. Gel permeation chromatography

An L-6000 (Hitachi Instruments, Tokyo, Japan) pump coupled with a Hitachi L-4000 UV detector operating at a wavelength of 254 nm were utilized in all experiments. A Shodex (JM Science, Grand Island, NY, USA) linear GPC 806L column $(0.8 \times 30\,\text{cm})$ packed with 10 μm polystyrene-co-divinylbenzene particles and a Rheodyne type 7725i valve (Cotati, CA, USA) with an injection loop of 20 μl were employed. The standard separation involved 1.0 ml/min flowrate, a solute concentration of 1.0 mg/ml. Polystyrene standards with a molecular weight range of 370–1 400 000 g mol$^{-1}$ (American Polymer Standards Corporation, Mentor, Ohio, USA) were used for column calibration and as relative reference for MM calculation of all samples.

### 2.5. Fourier transform attenuated total reflection infrared spectroscopy (ATR/FT-IR)

The IR spectra were obtained using the ATI Mattson Genesis FTIR spectrometer (ATI, Unicam, Great Britain) equipped with the Golden Gate Single Reflection Diamond ATR (Graseby Specac, Aatselaar, Belgium) scanning between 600 and 4000 cm$^{-1}$.

### 2.6. Differential scanning calorimetry

DSC scans were obtained from Seiko 120 DSC apparatus. The samples, whose weight varied between 7–10 mg, were dried in vacuum at 70 °C, and then kept in an exicator. The process was carried out in triple cycle heating-cooling-heating in temperature ranges $-100$ to 220 °C and $-50$ to 220 °C. The rate of heating and cooling was 10 °C min$^{-1}$. The glass transition temperature $(T_g)$ was determined from the temperature diagrams as the temperature corresponding to the upper infection point or maximum of the curve. The melting point $(T_m)$, and crystallization temperature $(T_c)$ were determined as corresponding to the maximum of the endothermic curve and the minimum of the exothermic curve, respectively.

### 2.7. Dynamic mechanical thermal analysis

Dynamic mechanical thermal tests were performed on a Rheometrix viscoelastometer in the temperature range $-80$ to 150 °C at frequency of 1 Hz. The storage modulus $(G')$, loss modulus $(G'')$, and loss tangent $(\tan\delta)$ were determined.

TABLE I Effect of radiation dose and EtO treatment on the molecular weight of polyester

| Dose (kGy) | $M_w$ [kD] | $M_n$ [kD] | $M_w/M_n$ | $[\eta]^a$ [dL/g] |
|---|---|---|---|---|
| 0 | 145.5 | 76.7 | 1.90 | 0.63 |
| 25 | 172.1 | 83.7 | 2.06 | 0.91 |
| 50 | 200.0 | 89.3 | 2.24 | 0.94 |
| 75 | 255.4 | 102.6 | 2.48 | * |
| EtO | 147.3 | 61.9 | 2.48 | 0.65 |

[a] Limiting viscosity number; *Sample swells in used solvent.

### 2.8. Tensile measurements

The tensile data were collected at room temperature with an Instron TM-II tensile machine, at a crosshead speed of 20 cm/min.

## 3. Results

### 3.1. Gel permeation chromatography (GPC)

GPC measurements of the multiblock copolymer samples evidenced (Table I) that the beam–irradiation sterilization indicate an increase on molecular weight with increasing radiation dose, but did not show any significant change on the $M_w$ for ethylene oxide sterilized sample. The trend in molecular weight changes results from structural modification (crosslinking) which has occurred along an increasing sterilization dose. This observation was confirmed by the limiting viscosity number [η] changes i.e. increase in the [η] values with increasing radiation dose up to swelling in the used solvent for the sample which was sterilized with a 75 kGy.

### 3.2. Fourier transform attenuated total reflection infrared spectroscopy

The ATR/FT-IR spectra (Fig. 1) show any significant changes in chemical composition and structure of samples during both sterilization processes.

### 3.3. Differential scanning calorimetry

The values for the thermal transitions were taken from the DSC scans from the second run (Table II). The sterilization treatment, up to 50 kGy, appeared to have no distinct influence on the glass transition temperature of the soft segments $(T_{g1})$ and the crystallization temperature $(T_{c2})$. However, increasing radiation dose decreased the melting point from 115.9 °C for non-sterile samples up to 111.3 °C for samples irradiated with a 50 kGy dose. The sample irradiated with a 75 kGy shows two crystalization and melting peaks. The peak melting temperature at 109.2 °C can indicate that some degradation occurs while the peak melting temperature at 119.1 °C appears to lead to crosslinking after such a high radiation dose treatment. EtO sterilization appears to affect the crystallization temperature (from 10.8 °C for the non-sterile sample to 21.2 °C after EtO sterilization), while melting point was found at same region as for the sample irradiated with a 25 kGy dose (112.4 °C). The crystalline phase content in the polymer $(\alpha_{tot})$ was calculated by assuming $\Delta H_f$ equal to 114.5 J/g [20] for 100% crystallinity of PBT homopolymer. As seen from Table II, the irradiation sterilization as well as gas treatment lead to the decrease in the crystallinity of the polymer.

### 3.4. Dynamic thermomechanical analysis (DMTA)

The storage modulus $(G')$, the loss modulus $(G'')$ and the loss tangent $(\tan\delta)$ of the studied polymers are plotted as

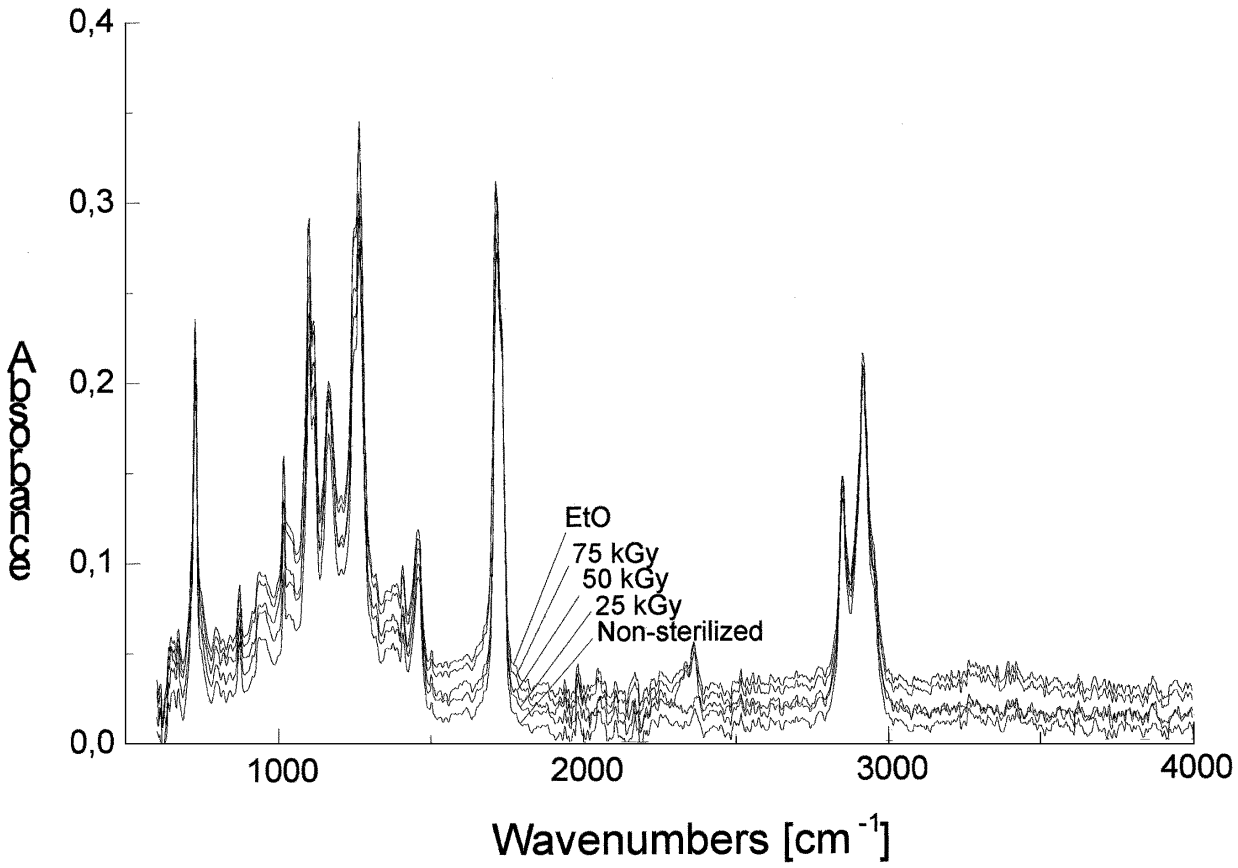


*Figure 1* ATR/FT-IR spectra of polymer.

TABLE II DSC results of the investigated polyesters

| Dose [kGy] | $T_{g1}$ [°C] | $\Delta C_p$[mJ/mg*deg] | $T_{g2}$ [°C] | $\Delta H$ [J/g] | $T_{c2}$ [°C] | $\Delta H_c$ [mJ/mg] | $T_{m2}$ [°C] | $\Delta H_m$ [J/g] | $\alpha_{tot}$ [%] | $T_{g1}, a$ [°C] |
|---|---|---|---|---|---|---|---|---|---|---|
| 0 | −42.1 | 0.391 | 58.9 | 1.4 | 10.8 | 7.2 | 115.9 | 11.3 | 7.8 | −39.8 |
| 25 | −41.8 | 0.348 | 61.0 | 1.5 | 10.4 | 7.1 | 112.4 | 11.4 | 7.8 | −37.9 |
| 50 | −41.9 | 0.375 | 61.8 | 1.4 | 10.3 | 6.8 | 111.3 | 10.1 | 6.9 | −39.7 |
| 75 | −42.0 | 0.380 | 45.8 | 0.2 | 9.6 | 6.8 | 109.2 | | 6.3 | −37.3 |
| | | | 60.0 | 0.6 | 10.3 | | 119.1 | 9.2 | | |
| EtO | −39.9 | 0.320 | 70.4 | | 21.2 | 7.6 | 112.4 | 6.9 | 4.7 | −40.3 |

$T_{g1}$-glass transition temperature of soft segments; $T_{g2}$, $T_{c2}$, $T_{m2}$, glass transition, crystallization and melting temperature of hard segments, respectively. $\Delta C_p$, heat capacity; $\Delta H$, melting entalpy of hard segments; $\Delta H_c$, crystallization enthalpy; $\Delta H_m$, melting ehthalpy of polymer; [a], determined by DMTA.

a function of the temperature in Figs 2–4. Peak maxima taken from $G''(T_{g1}, a)$ are summarized in Table II. The low-temperature peaks were attributed to the soft segment glass transition and all values are in good agreement with those determined by the DSC method. The higher temperature shoulder in $G''$ for the sample irradiated with a 75 kGy can be ascribed to structural changes like degradation and crosslinking. The rapidly decreasing values of $G''$ reveal the occurrence of the melting process.

### 3.5. Tensile properties

Table III shows the fundamental mechanical properties like stress at break ($\sigma_r$) and elongation at break ($\varepsilon$). Similarly to previous reported results a small radiation dose (25 kGy) does not affect the tensile properties. Increase in radiation dose influences increasing tensile strength and elongation. This is a consequence of the structural changes (intermolecular bonding, crosslinking within hard domains) upon high radiation dose (50 and 75 kGy). The EtO sterilized sample displayed slightly higher values of $\sigma_r$ and $\epsilon$ compared to the initial, non-sterilized sample.

TABLE III Results from mechanical tests of polymers

| Dose [kGy] | $\sigma_r$ [MPa] | $\epsilon$ [%] |
|---|---|---|
| 0 | 3.6 | 772 |
| 25 | 3.6 | 788 |
| 50 | 3.7 | 530 |
| 75 | 4.2 | 948 |
| EtO | 3.9 | 840 |

$\sigma_r$, stress at break; $\varepsilon$, elongation at break.

## 4. Discussion

The sterilization of multiblock copolymer can greatly influence the structure of the polymer, depending on the sterilization technique (gas or radiation treatment), as

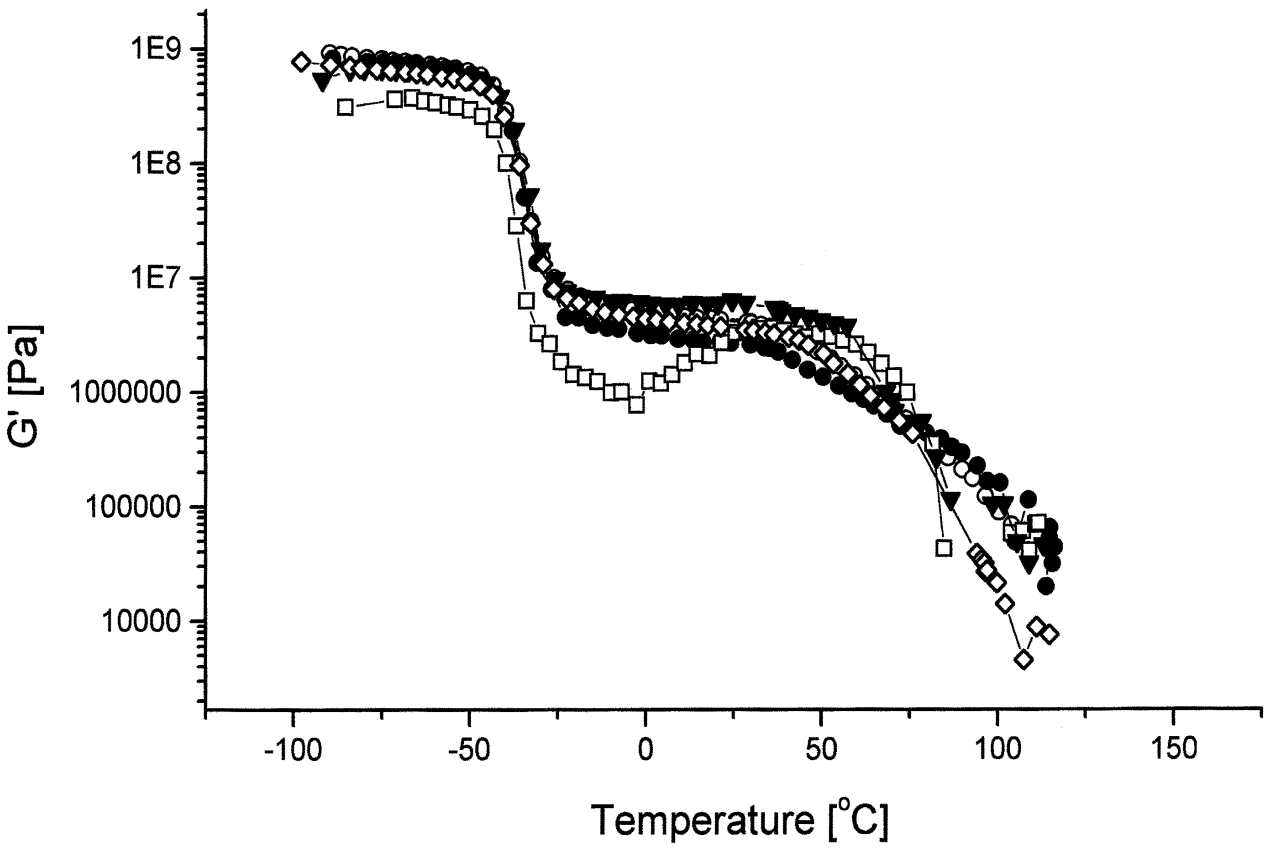


*Figure 2* The storage modulus ($G'$) versus temperature for polymer: ○ non-sterilized, ● 25 kGy, □ 50 kGy, ▼ 75 kGy, ◇ EtO.

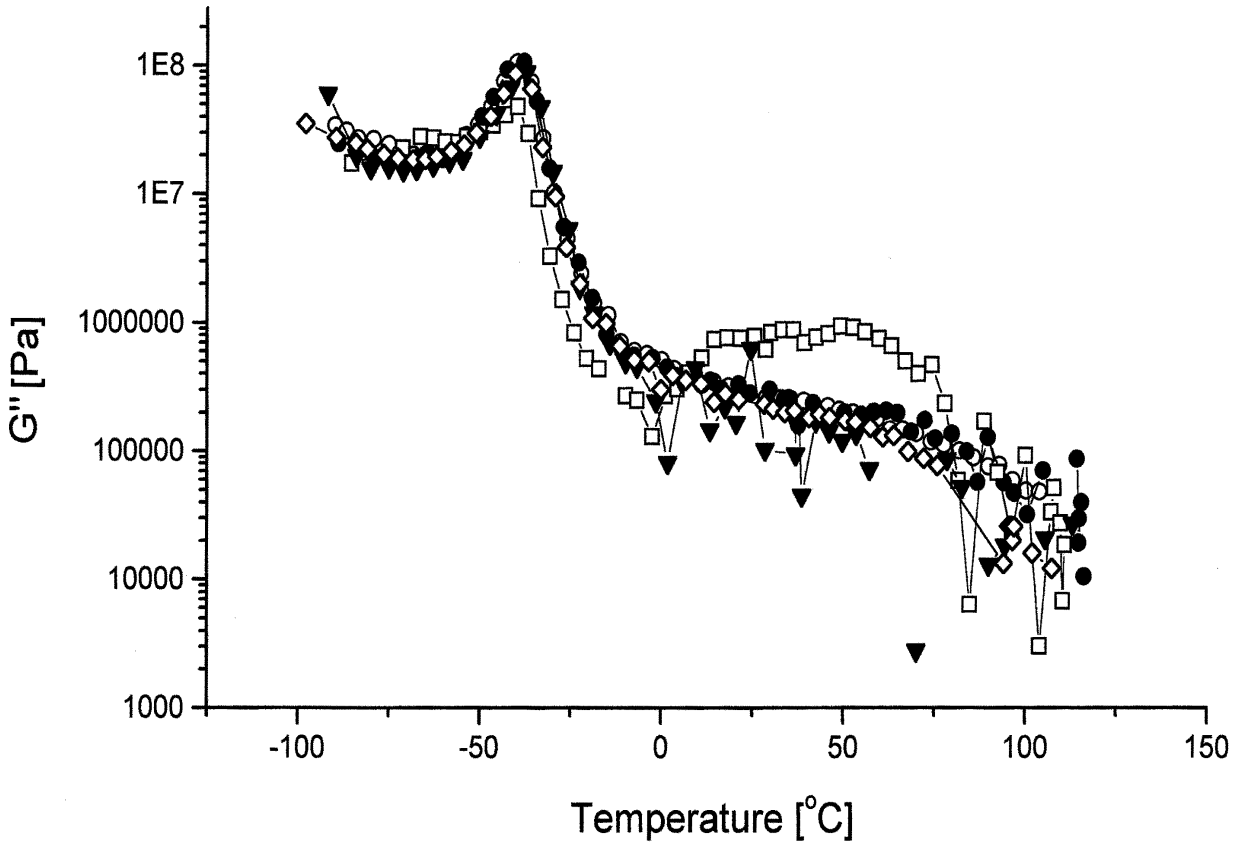


*Figure 3* The loss modulus ($G''$) versus temperature for polymer: ○ non-sterilized, ● 25 kGy, □ 50 kGy, ▼ 75 kGy, ◇ EtO.

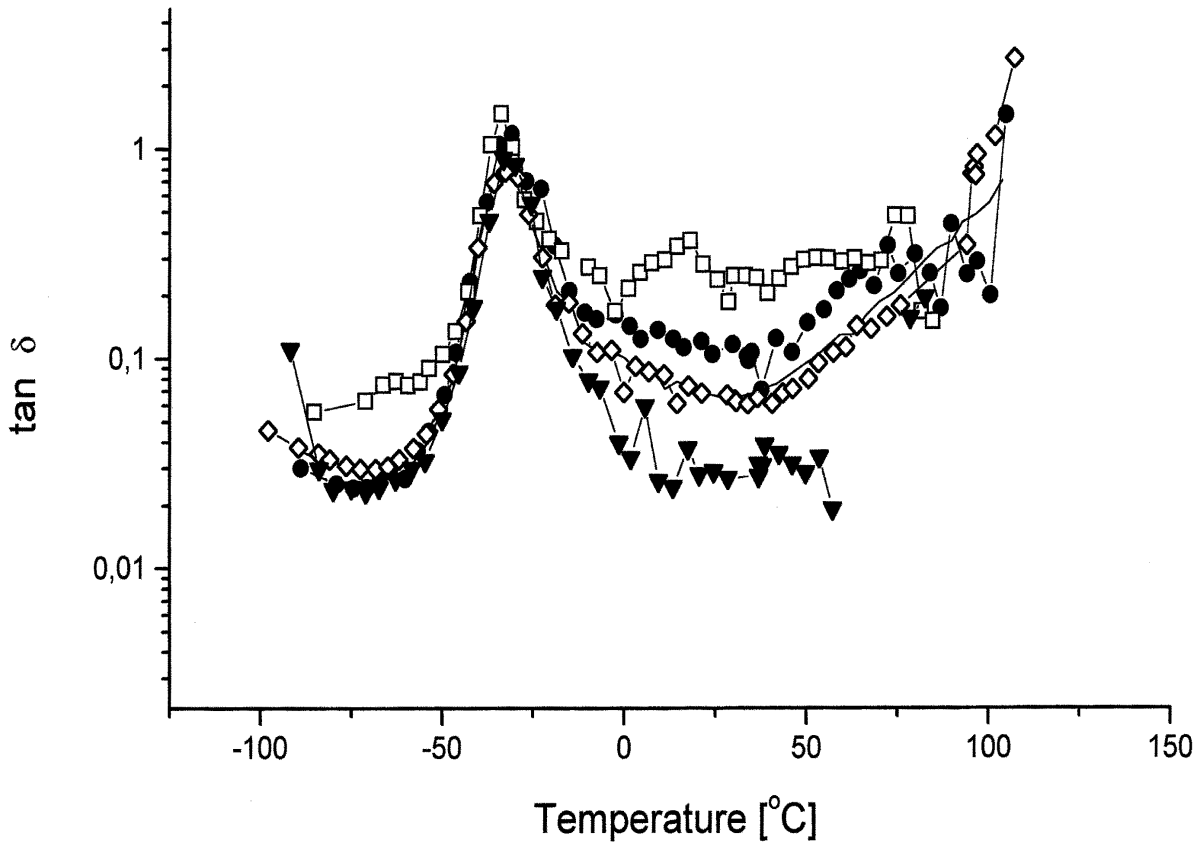


*Figure 4* The loss tangent ($\tan\delta$) versus temperature for polymer: ○ non-sterilized, ● 25 kGy, □ 50 kGy, ▼ 75 kGy, ◇ EtO.

well as from the radiation dose. Ethylene oxide gas sterilization does not appear to significantly alter the multiblock polymer properties and structure. Beam-radiation, on the other hand significantly changes polymer structure and properties with increasing radiation dose.

Irradiation of polymers results in either crosslinking or chain scission, depending on the chemical nature of the polymer and irradiation dose. Results from the present study indicate that the cross-linking mechanism seems to be dominating for the studied system due to the presence of the hard domains in the initial, non-crystallized material. These microdomains can form so-called physical crosslinks and their ''density'' increase with radiation dose. This evidence for crosslinking at an extremely high dose (75 kGy) was manifested in the GPC, limiting viscosity number, DSC and DMTA. Commonly recommended irradiation with a dose of 25 kGy was suitable for sterilization of bulk materials for biomedical applications and can also be applied for the studied polymer because this dose does not affect the polymer structure and mechanical properties.

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