

Thermal analysis of used and radiation treated polycarbonate (L-MW) biomaterial

M JAYABALAN†, K SREENIVASAN, P D NAIR and
K N JALAJAMANI*

Division for Technical Evaluation of Biomaterials, Sree Chitra Tirunal Institute for Medical Sciences and Technology, Biomedical Technology Wing, Trivandrum 695 012, India

*Department of Polymer Chemistry, Gandhiji University, Kottayam 686 002, India

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Abstract. γ -radiation treatment of radiation sterilized polycarbonate biomaterials has been carried out to ensure efficient disposal by incineration. Low molecular weight polycarbonate sterilized with 2.5 Mrad dose of γ -radiation was further treated with different doses of γ -radiation. The radiation-treated samples were subjected to thermogravimetry. The sterilized sample and the 7.5 Mrad-treated sample showed similar properties. These samples do not leave any residue during thermal decomposition.

Keywords. γ -radiation; sterilization; polycarbonate biomaterial; radiation treatment; thermal analysis.

1. Introduction

Synthetic polymeric materials are extensively used in medical applications. Polycarbonate is one of the toughest engineering thermoplastic. Its properties such as consistent clarity, excellent impact strength, dimensional stability, creep resistance, heat resistance, light and inert response to blood and body tissue make it useful for a variety of disposable medical devices like oxygenator, infusion and bypass filters, transfusion devices etc. Disposal of plastic waste is one of the primary concerns of the medical industry. Though modern synthetic plastics usually consist of the same elements and its structural arrangements are similar to biopolymers such as cellulose, collagen and keratin, these plastics are incompatible with natural environment. They degrade and lead to long-term ecological damage. Thermal decomposition has so far been tried for disposal. An attempt has been made in the present study to investigate the effect of radiation treatment of used polycarbonate for efficient disposal by incineration.

2. Experimental method

Medical grade Bisphenol-A polycarbonate (L-MW PC)(General Electric Company Ltd., USA) was used. The molecular weight of this sample was determined by gel permeation chromatography using polystyrene (Waters Associates Limited, USA) as standards. A calibration curve for elution time and molecular weight was generated using polystyrene standards. μ -styrigel columns (10^4 , 10^3 and 500 \AA pore size) were used and chloroform was used as the mobile phase. Absorbance was monitored at 254 nm using a UV absorbance detector. The molecular weight of the sample was 9368 ± 17 .

†To whom all correspondence should be addressed.

The samples were irradiated in the form of pellets using ^{60}Co source with a dose rate of 0.33 Mrads/h in a panoramic batch irradiator. Polycarbonate used as a connector for blood oxygenator for animal trials was treated for doses ranging from 2.5 Mrad to 7.5 Mrad (table 1).

Thermogravimetry was carried out in air using a Dupont 990 analyser. The radiation-treated samples were heated from ambient to 650°C at 10°C/min.

3. Results and discussion

Polycarbonate (PC), being aromatic with low lying electronic energy states (π electrons) can absorb the effects of γ -radiation reducing degradation (Golden and Hazell 1963; Golden 1966). Medium molecular weight polycarbonate (M-MW PC) however is stable only upto 8 Mrad dose of irradiation (Cohen 1983). The effect of γ -radiation of L-MW PC is different due to the degree of chain scission being lesser in low molecular weight material. Long chain molecules are susceptible to chain scission at more points.

The radiation treatment of candidate sterilized L-MW PC alters macromolecular structure. The degradation reaction during sterilization and radiation treatment can be visualized by a mechanism proposed for radiation-induced degradation of polycarbonate (Davis and Golden 1968). This was confirmed by changes in the molecular weight (table 2). The trend in the change of molecular weight for the sterilized and radiation-treated samples shows that L-MW PC undergoes chain scission and recombination. According to the mechanism (Davis and Golden 1968) chain scission leads to formation of two types of end-capped radicals, (i) phenyl end-capped (with liberation of carbon dioxide) and (ii) the phenoxy end-capped (with liberation of carbon monoxide). When the G value of carbon monoxide (0.36) and carbon dioxide

Table 1. Radiation treatment schedule of L-MW PC.

Sample code	Radiation dose (Mrad)	Remarks
J ₀	0	Control
J ₁	2.5	Sterilization before use
J ₂	2.5	Radiation treatment after use
J ₃	5.0	-do-
J ₄	7.5	-do-

Table 2. Changes in molecular weight of L-MW PC.

Sample code	Type of reaction	Molecular weight		Dispersity Mw/Mn
		Number average (Mn)	Weight average (Mw)	
J ₀	—	9368 ± 17	23732 ± 25	2.53 ± 0.002
J ₁	A	10333 ± 21	23639 ± 37	2.29 ± 0.001
J ₂	B	9060 ± 29	20763 ± 27	2.29 ± 0.001
J ₃	B	7909 ± 24	20019 ± 19	2.53 ± 0.01
J ₃	A	8098 ± 26	19779 ± 18	2.44 ± 0.009

Note: A, chain scission and recombination; B, chain scission only

(0.19) is higher than the G value for chain scission (0.14) cage recombination of radicals occurs (Golden and Hazell 1963; Golden 1966).

The yield of a reaction induced by ionizing radiation, expressed as G value is the number of events produced per 100 eV absorbed in the system. Recombination is further found from the graph showing variation of weight average molecular weight with irradiation dose (figure 1). From the steady state nature obtained for 2.5 and 10.0 Mrad dose it is clear that cage recombination of radicals takes place for these doses of irradiation (table 2) leading to the formation of diphenyl ether linkage in the polycarbonate backbone when the phenyl and phenoxy radical recombines. On the other hand 2-hydroxy diphenyl ether linkage is formed in the polycarbonate when two phenoxy radicals are recombined.

One can decide from the molecular weight data that chain scission and recombination of radicals are simultaneous events for a sterilized sample (J_1). Chain scission alone predominates during further treatment with 2.5 and 5.0 Mrad (J_2 and J_3). Molecular weight increases from 9368 ± 17 for L-MW PC to 10333 ± 21 for sterilized L-MW PC and also from 7909 ± 24 for J_3 to 8098 ± 26 for J_4 . The decrease in macromolecules leads to an increase in the number-average-molecular weight (\bar{M}_n).

The thermal data of the sterilized and radiation-treated samples are given in table 3. The TGA thermogram is given in figure 2. The J_2 and J_3 values of L-MW-PC exhibit similar thermogravimetric characteristics. However, these two-phase decompositions of J_1 and J_4 leave only ash in the end. But J_2 and J_3 leave some residue for carbonization.

The difference in the decomposition of these sterilized and radiation-treated samples is attributed to changes in macromolecular structure. Since the radiation yield for carbon monoxide (G 0.36) is higher than that of carbon dioxide, the

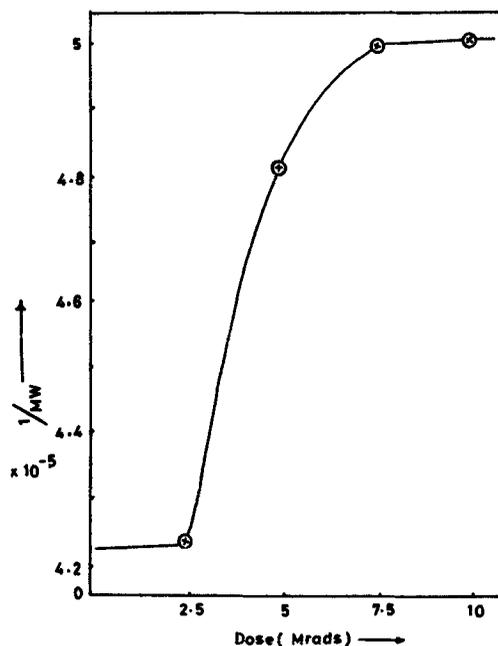


Figure 1. Variation of weight average molecular weight with irradiation dose.

Table 3. Thermal data of L-MW PC.

Sample code	Type of reaction	Decomposition temperature (°C)		% weight remaining after decomposition
		Td_1	Td_2	
J_0	—	410	505	20.0
J_1	A	425	515	0.8
J_2	B	430	517.5	18.4
J_3	B	437.5	535	21.2
J_4	A	410	507.5	0.0

Note: A, chain scission and recombination; B, chain scission only.

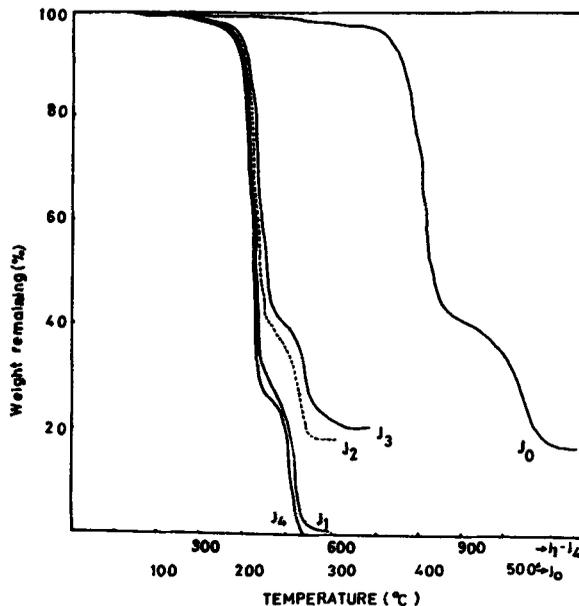


Figure 2. TGA curve of irradiated samples.

formation of 2, hydroxy diphenyl ether linkage is more favourable during recombination of radicals. Recombined macromolecules (as in sterilized PC and J_4) are liable to undergo a higher degree of chain scission during thermogravimetric analysis because of increase in chain length. Moreover the recombined macromolecule is susceptible to greater degradation irrespective of its molecular weight. Therefore these materials do not leave any residue. The lower decomposition temperature of J_1 and J_4 is due to the changes in stereo-regularity and also due to flexibility of chain by $-OH$ substituent.

The decomposition temperatures of J_2 and J_3 are higher for gas evolution and main chain degradation in thermal analysis. Some percentage of residual material remains for the third phase of decomposition. The residue is formed by the gelation of the degraded L-MW PC molecules during pyrolysis of J_2 and J_3 . Davis and Golden (1969) proposed a mechanism by which J_1 and J_4 do not exhibit such residue in the TGA curves. This indicates the absence of such gelation.

4. Conclusion

The radiation treatment of used (sterilized) L-MW PC favours efficient disposal by heat when the radiation dose is confined to 7.5 Mrad. Moreover a dose of 2.5 Mrad can either be used for waste and/or unused L-MW PC for treatment before incineration. It is also clear that incineration of unirradiated L-MW PC and also radiation treatment with doses lesser than 7.5 Mrad for the used L-MW PC may lead to a residual deposit in the incinerator.

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