EFFECT OF IONIZING RADIATION ON DIFFERENT POLYMERS AND POSSIBLE USE OF POLYMERS IN RADIOACTIVE (NUCLEAR) WASTE MANAGEMENT

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TONGUÇ ÖZDEMİR

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Prof. Dr. Canan ÖZGEN
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Doctor of Philosophy.

Prof. Dr. Ali USANMAZ
Head of Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Doctor of Philosophy.

Prof. Dr. Ali USANMAZ
Supervisor

Examining Committee Members

Prof. Dr. Kemal ALYÜRÜK	(METU, PST)	
Prof. Dr. Ali USANMAZ	(METU, PST)	
Prof. Dr. Olgun GÜVEN	(Hacettepe Univ., CHEM)	
Prof. Dr. Güngör GÜNDÜZ	(METU, CHE)	
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Name, Last name: Tonguç ÖZDEMİR
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ABSTRACT

EFFECT OF IONIZING RADIATION ON DIFFERENT POLYMERS AND POSSIBLE USE OF POLYMERS IN RADIOACTIVE (NUCLEAR) WASTE MANAGEMENT

Özdemir, Tonguç
Ph.D., Polymer Science and Technology Department
Supervisor: Prof. Dr. Ali USANMAZ

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In this study three polymers, namely poly(carbonate urethane), poly(bisphenol-a-epichlorohydrin) and poly(methyl methacrylate), were selected and change of properties with gamma treatment were studied. Two different dose rates were used for irradiations and the properties of the irradiated polymers exposed to same total absorbed dose were compared. In addition, long irradiations of up to about six months with high dose rate were done in order to understand the radiation stability of the polymers, which may be possible candidates for embedding media for low and intermediate level radioactive (nuclear) waste before their final disposal.

Tensile, DSC, DMA, TGA, FTIR-ATR, FTIR tests were completed to understand the degradation of the polymers as a function of dose rate and total absorbed dose.

The DSC and FTIR results showed that there was not much structural chemical changes in polymer chains with irradiation. However, the changes in mechanical properties were recorded.

It was concluded that poly(carbonate urethane) and poly(bisphenol-a-epichlorohydrin) can possibly be used in conditioning of radioactive waste, as they are radiation stable polymers. However, due to the moderate resistance of poly(methyl methacrylate) to ionizing radiation, it can be used for low level radioactive waste conditioning.

Keywords: Polymer, Radiation, Degradation, Radioactive Waste

ÖZ

İYONLAŞTIRICI IŞIMANIN DEĞİŞİK POLİMERLER ÜZERİNE ETKİSİ VE POLİMERLERİN RADYOAKTİF (NÜKLEER) ATIK YÖNETİMİNDE OLASI KULLANIMI

Özdemir, Tonguç
Doktora, Polimer Bilimi ve Teknolojisi Bölümü
Tez Yöneticisi: Prof. Dr. Ali USANMAZ
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Bu çalışmada poly(carbonate urethane), poly(bisphenol-a-epichlorohydrin) ve poly(methyl methacrylate)'dan oluşan üç tür polimer seçilmiş ve özelliklerinin gama ışınım etkisi altındaki değişimi çalışılmıştır. Söz konusu çalışmada iki değişik doz hızı kullanılmıştır. İki değişik doz hızında ışınlanmış ancak toplam soğurulan (absorplanan) dozu eşit olan polimerlerin özellikleri karşılaştırılmıştır. Bunun yanında, altı ay kadar uzun süreli yüksek doz hızlı ışınlamalar yapılarak düşük ve orta düzeyli radyoaktif (nükleer) atıkların şartlandırılmasında (conditioning) kullanılması olası polimerlerin gama ışınımına karşı dayanıklılıkları saptanmaya çalışılmıştır.

Mekanik, DSC, DMA, TGA, FTIR-ATR, FTIR testleri yapılmış ve polimerlerin bozunmasının doz hızı ve soğurulan doza bağlı değişimi anlaşılmaya çalışılmıştır.

DSC ve FTIR analiz sonuçlarından seçilen polimerlerin gama ışınımı ile çok büyük miktarda yapısal değişikliğe uğramadıkları anlaşılmış ancak söz konusu polimerlerin mekanik özelliklerinde gama ışınımı etkisinden kaynaklanan değişiklikler kaydedilmiştir.

Gama ışınımına karşı dayanıklılıkları bakımından poly(carbonate urethane) ve poly(bisphenol-a-epichlorohydrin)'nin düşük ve orta seviyeli radyoaktif atıkların şartlandırılmasında kullanılmalarının olası olduğu ancak poly(methyl methacrylate)'ın gama ışınımına karşı orta düzeyde dayanıklılığı bakımından düşük seviyeli radyoaktif atıkların şartlandırılmasında kullanılmasının olası olduğu anlaşılmıştır.

Anahtar sözcükler: Polimer, Işıma, Radyasyon, Degradasyon, Radyoaktif atık

TO

MY PARENTS, MY BROTHER and MY WIFE

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CHAPTER I

INTRODUCTION

Polymers having wide-range of applications in daily life are degraded due to the environmental effects and degradation is non evitable for polymers facing with hard environmental conditions during their usage and applications.

1.1. SELECTED POLYMERS

Three polymers namely, poly(carbonate urethane) (PCU), poly(bisphenol-a-epichlorohydrin) (PBEH) and poly(methyl methacrylate) (PMMA), frequently used in the daily life, have been selected in this study to understand the gamma irradiation effect on them and the possibility of their usage in radioactive waste management.

1.1.1. Poly(carbonate urethane)

A special group of polyesters of carbonic acid are known as polycarbonates. Polycarbonate resin, an amorphous thermoplastic material, has outstanding impact strength, superior dimensional stability, glass-like transparency, excellent thermal resistance and low-temperature toughness. Polycarbonate resin is widely used in a broad range of industries, including automotive and transportation, building and construction, electrical and electronics, telecommunication, packaging, medical, optical/opthalmic and optical media.

The first polycarbonates were prepared as early as 1898 by Einhom, by reacting phosgene with hydroquinone and resorcinol. There are two main methods for preparing polycarbonates, the first is via direct reaction of phosgene with the diphenol and the second is via an ester interchange [1].

The reaction may be carried out in the presence of pyridine that acts as a catalyst and an HCl scavenger. Often, a chlorinated solvent is used as a diluent for the pyridine. Phosgene is bubbled through a solution of the diphenol at 25-35 °C. The pyridine hydrochloride precipitates out and after washing the pyridine solution with dilute HCl and water, the polymer is precipitated with a non-solvent.

An interfacial polymerization procedure is also employed in direct phosgenations. A caustic solution of the diphenol is dispersed in an organic chlorinated solvent containing small quantities of a tertiary amine. Phosgene is bubbled through the reaction mixture at 25 °C. When the reaction is complete, the organic phase contains the polymer. It is separated and the product is isolated as above. The ester interchange method is carried out between the diphenol and diphenyl carbonate (Figure 1) [1]:

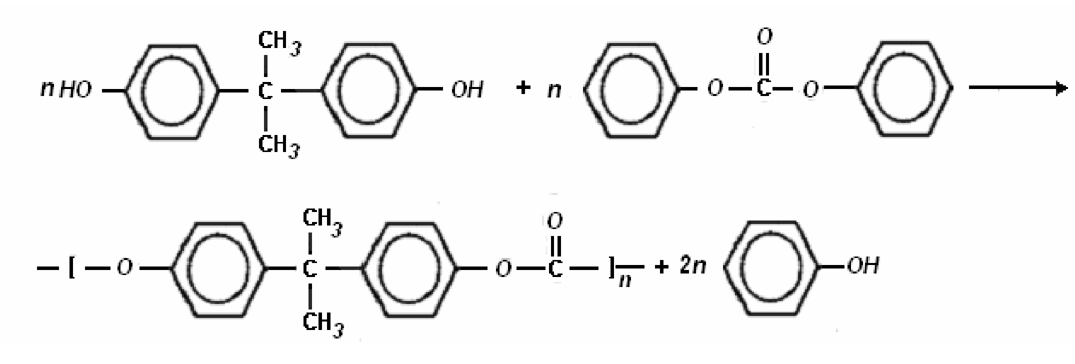


Figure 1. Ester interchange of diphenol and diphenyl carbonate

Polycarbonate urethane is a thermoplastic elastomer formed as the reaction product of a hydroxyl terminated polycarbonate with an aromatic diisocyanate and a low molecular weight glycol used as a chain extender. Carbonate linkages adjacent to hydrocarbon groups give this family of materials oxidative stability, making these polymers attractive in applications where oxidation is a potential mode of degradation. Polycarbonate urethanes were the first biomedical polyurethanes promoted for their biostability. Crosslinked, nonconjugated poly(carbonate urethane) can conduct electricity upon doping with iodine [2].

Polyurethanes are very hygroscopic materials. The pellets should be dried in a forced air dehumidifying dryer at 82 °C for at least four hours prior to processing. The moisture content prior to processing should be below 0.01%. It is recommended that polycarbonate urethane be filtered during extrusion. Mesh packs should include three filters, one 350 mesh and two 500 mesh. Extrusion equipment should be set with crosshead temperatures of approximately 200 °C to 215 °C to initiate the flow. Once flow is established, the crosshead temperature should be decreased until steady, viscous flow is achieved. For softer grades the annealing (stress relaxation, crystallization) step should be considered. It is recommended either annealing the molded part overnight in a nitrogen-purged oven at 60 °C or aging at least seven days at room temperature [4].

1.1.2. Poly(bisphenol-a-epichlorohydrin)

Epoxies are formed in two-stage process. In the first step, a low-molecular-weight prepolymer is prepared by a base catalyzed step growth reaction of dihydroxy compound (bisphenol-a) with an epoxide (typically epichlorohydrin). The prepolymer’s molecular weight is increased and the network is formed during a separate cure step. Amines, usually aromatic, may be used to cause ring opening of the end epoxide groups through nucleophilic addition. Carboxylic acid anhydrides such as phthalic acid anhydride can react with pendant hydroxyl to give ester acids, which can then react with epoxide or other hydroxyl groups to create additional ester groups. Epoxy resins have high chemical and corrosion resistance, outstanding adhesion properties and low shrinkage upon curing and good electrical properties [5]. The structure of the bisphenol - a- epichlorohydrin is shown in Figure 2.

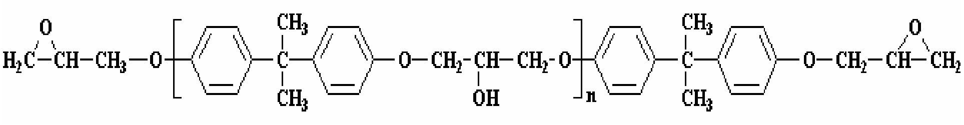


Figure 2. Prepolymer formed from bisphenol-a and epichlorohydrin

The epoxy resins can be produced in various forms, ranging from low viscosity liquids to high melting solids, by varying the ratio of epichlorohydrin to bisphenol-a. Typically this prepolymer has a molecular weight of approximately 1500-2000. The mechanism for the formation of the prepolymer (Figure 3) begins with the formation of phenolate anion, which reacts with the epichlorohydrin in a nucleophilic reaction bonding the two together and opening the epoxide ring. A new epoxide ring then formed by nucleophilic reaction of the resulting alkoxide with the carbon bearing the chloride. This sequence repeats forming a prepolymer containing 25-50 repeating units. Crosslinking starts when the hardener is mixed with the prepolymer [6].

Cycloaliphatic epoxides respond only to acidic hardeners, such as polycarboxylic acid or acid anhydrides. Because of the compact structure of these resins, systems cured with hexahydrophthalic anhydride have heat deflection temperatures above 190℃. Epoxy resins are rarely used alone because the development of the required properties generally necessitates several additives. Hardeners, which are required to produce thermoset compositions from the epoxy resin intermediates, must be carefully selected because they can have a significant effect on the properties, the processing and the cure rates [7].

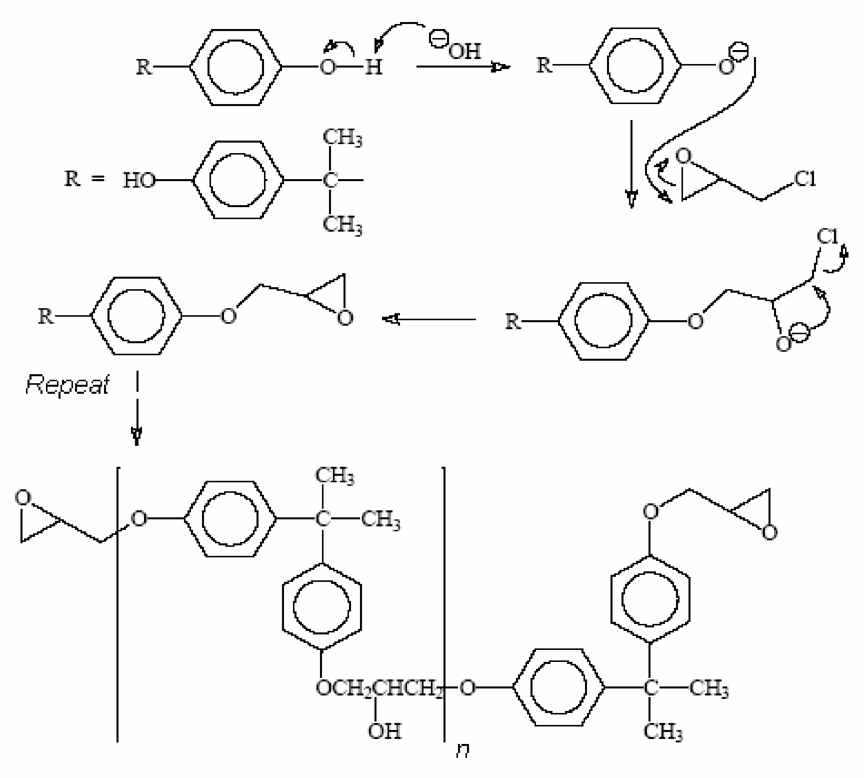


Figure 3. The mechanism for the formation of the prepolymer

Some of the mechanical properties of the epoxies are given in Table 1 [5].

Table 1. The mechanical properties of the epoxies

Modulus, GPa	2.8-4.2
Tensile strength, MPa	55-130
Compressive strength, MPa	140
Density, $g.cm^{-3}$	1.15-1.2
Thermal expansion coefficient, 10^{-6} per °C	45-65
Tg, °C	130-250

A very large excess of epichlorohydrin in the reaction leads to liquid resins of lower molecular weight, which may be used for waste immobilization [7].

1.1.3. Poly(methyl methacrylate)

Commercial grade poly(methyl methacrylate), (PMMA), is an amorphous polymer of moderate Tg (105℃), with high light transparency and good resistance to acid and environmental deterioration. It is commercially polymerized by free radical initiators such as peroxides and azo compounds in suspension or in bulk (e.g., cast polymerization). PMMA may also be polymerized anionically at low temperatures to give highly isotactic (Tg is 45℃ and Tm is 160℃) or highly syndiotactic (Tg is 115℃ and Tm is 200℃) polymers. PMMA finds major applications in the automotive industry (e.g., rear lamps, profiles, and light fixtures) as acrylic sheet for bathtubs, advertisement signs, and lighting fixtures, and as composite materials for kitchen sinks, basins and bathroom fixtures. Some of the mechanical properties of the PMMA are tabulated in Table 2 [5].

Table 2. The mechanical properties of the PMMA

Elastic Modulus (GPa)	2.4-2.8
Yield Strength (MPa)	48-62
Ultimate Strength (MPa)	48-69
Elongation at Break (%)	2-10
Poisson’s ratio	0.4

PMMA has been widely employed in industrial and domestic appliances since it was commercialized in the beginning of the 1930s. PMMA may be produced and formed into rigid bodies showing attractive features, excellent transparency (92%), good mechanical properties and high resistance to atmospheric agents [8].

1.2. POLYMER DEGRADATION

Polymer degradation is the common name given to various processes deteriorating polymers' properties [9]. Effects of degradation are discernible in the reactor where polymer is synthesized, in the extruder where it is fabricated, during its service life when it gives its useful performance, and after its failure when it is either recycled or discharged to the environment [10].

Types of chemical degradation can be listed as:

- Thermal degradation
- Photo-oxidative degradation
- Hydrolytic degradation
- Environmental stress cracking
- Chemical degradation
- Mechanochemical degradation
- Radiation induced degradation
- Biodegradation
- Degradation due to weathering
- Degradation during storage

Effects of degradation on polymers may be assessed from the following items.

1. Changes in chemical structure: Weathering leading to oxidative degradation generally produces conjugated double bonds, carbonyl groups and hydroxyl groups
2. Changes on the surface
3. Loss in mechanical properties
4. Embrittlement
5. Changes in molecular weight
6. Generation of free radicals
7. Toxicity of products formed due to thermal degradation, pyrolysis or combustion of polymers
8. Loss of additives and plasticizers
9. Discoloration

Examples of polymers that are particularly susceptible to attack of naturally occurring and or man-made agents are listed in Table 3 [10].

Table 3. Effects of Environmental Agents on Polymers [10]

Agent	Susceptible Polymers	Examples
Biodegradation	Short-chain polymers, nitrogen-containing polymers, Polyesters	Polyurethanes, Polyether-polyurethane
Ionizing radiation	Aliphatic polymers having quaternary carbon atoms	PMMA, Polyisobutylene
Moisture	Heterochain polymers	Polyesters, Polyamides Polyurethanes
Organic liquids and vapors	Amorphous polymers	Polystyrene, PMMA
Ozone	Unsaturated elastomers	Polyisoprene, Polybutadiene
Sunlight	Photosensitive polymers	Polyacetals, Polycarbonate

Multiple exposures, such as a combination of moisture and heat or oxygen and light (photooxidation), can result in accelerated deterioration. Deterioration of plastics to normal environmental conditions is called weathering. Factors that contribute to weathering include radiation (UV, visible, and near-infrared), moisture, temperature cycling and wind [10].

During degradation, chain scission can occur by one of three mechanisms. These include (1) random degradation, where the chain is broken at random sites, (2) depolymerization, where monomer units are released at an active chain end and (3) weak-link degradation where the chain breaks at the lowest-energy bonds. In addition to thermal energy, degradation may be initiated by photochemical action, irradiation or mechanical action.

Non-chain scission reactions; one example of a common non-chain scission reaction is dehydrohalogenation, which results from the breakage of a carbon-halogen bond and the subsequent liberation of hydrogen halide. The most important example of a polymer that degrades by dehydrohalogenation is poly(vinyl chloride) (PVC) [5].

1.3. OXIDATIVE DEGRADATION OF POLYMERS

Although the term polymer degradation is widely used, in practice, degradation always takes place in the presence of a certain amount of oxygen and therefore, in hydrocarbon polymers, oxidation reactions are the most important means of structural breakdown [10].

1.4. STABILITY OF POLYMERS UNDER IONIZING RADIATION

Ionizing radiation is a powerful source of energy for chemical processing applications, thus; it can be applied in different industrial applications. Due to the fact that, irradiation can initiate chemical reactions or destroy microorganisms, radiation is used in various industrial processes. Gamma irradiation is ionizing, which on passage through matter, gives positive ions, free electrons, free radicals and excited molecules. The capture of electrons by molecules can also give rise to anions. Thus, a whole range of reactive species becomes available [11].

Radiation chemistry is the study of chemical changes that occur when ionizing radiation interacts with matter and there have been extensive studies on the changes produced by irradiating polymers [12]. The physical and chemical properties of polymeric materials could be modified by treatment with ionizing radiation in the form of gamma rays, X-rays and energetic electrons [13]. The role of oxygen in degradation studies is crucial for materials exposed to low dose rates over long periods, as it is the case in nuclear power plants or for the storage and disposal of radioactive wastes.

The effects of radiation on polymers depend strongly on the molecular structure, for instance, the presence of tertiary or quaternary carbon and as well as the presence of oxygen in the structure, the presence of additives and the radiation environment itself. The presence of aromatic rings in the polymer backbone, such as phenoxy resins, has a radiation-stabilizing effect on the polymer [14].

Moreover, dose rate is an important parameter when considering the effect of ionizing radiation on polymers. In general, when the total absorbed dose is same and the dose rate is sufficiently different; the rate of radical formation is progressively slower and depth of oxygen diffusion is progressively greater in the low dose rate irradiations compared to high dose rate irradiation and in the case of low dose rate irradiation homogeneous radiation-oxidation is the potential mode of degradation [15]. However, the thickness of the polymer being irradiated is also the important parameter on which the homogeneous radiation-oxidation type of degradation depends.

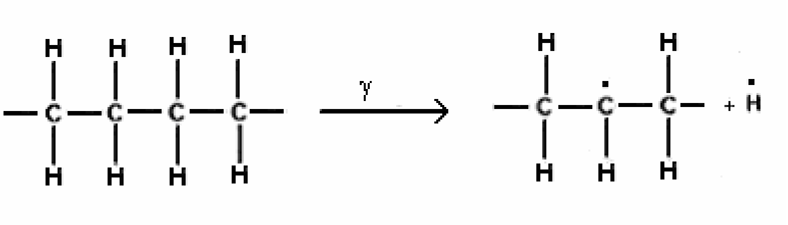
Half value dose (HVD) of elongation or tensile strength is defined as the doses (Gy) at which elongation or tensile strength reaches their half values respectively. Since elongation strongly depends on the molecular mass, HVD (elongation) is more sensitive measure of the degradation than that of tensile strength [16].

1.4.1. Elementary Radiolysis Processes in Polymers

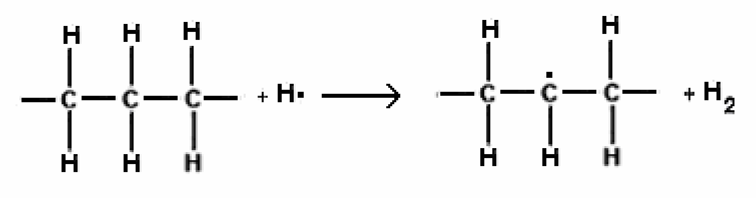
Primary radiation reactions can be observed at very low temperatures in the absence of oxygen, where other ways of energy conversion such as molecular movements or formation of oxidized species are blocked. Polyethylene illustrates the different modifications resulting at the molecular level from the energy transferred upon irradiations. It must be pointed out that radiolysis leads to the scission of the chemical bonds (C–H) whereas (C–C) bonds appear less affected. Partridge has attributed this behavior to excitation energy transfers along the macromolecular chain preventing main chain scission, whereas C–H bond scission is favored by the localization of the excitation [17]. The reactions of the radiolysis of polyethylene are given below.

Reaction I: Hydrogen abstraction

The free radical ($H^{\cdot}$) released in the initial radiolysis reaction has enough kinetic energy to eject another hydrogen atom to produce a hydrogen molecule.

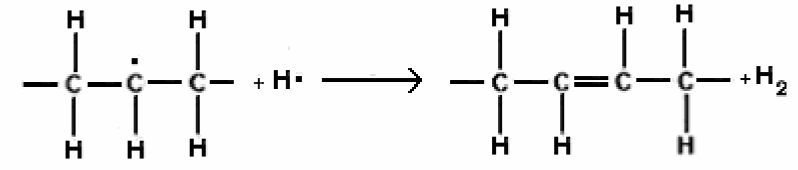


Reaction II: Formation of molecular hydrogen

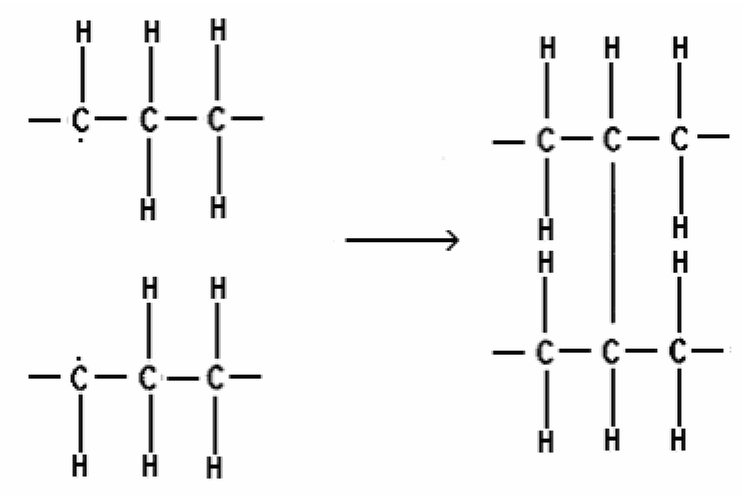


Different recombination pathways follow the irreversible loss of hydrogen molecule:

Reaction III: double bond formation results from two events occurring on the same chain



Reaction IV: Recombination leading to crosslinking



Hydrogen evolution – formation of unsaturated bonds and cross-linking are the main changes induced at the molecular level in PE. In addition to these elementary modifications other polymers may also show scissions on the main chain inducing degradation.

Reaction V: Main chain scission

The radiochemical yield for chain scission becomes significant when four carbons surround a carbon of the main chain. The presence of bulky side groups in particular inhibits the restoration of main chain scissions. The empirical rule of quaternary carbon allows the distinction between polymers whose evolution is controlled by cross-linking or degradation.

1.5. RADIATION EFFECTS ON SELECTED POLYMERS

Literature review of the radiation effects on the selected polymers are given in this section.

1.5.1. Poly(carbonate urethane)

Wiggins et. al. [18] studied the effect of soft-segment chemistry on biostability of polyurethane elastomers under conditions of static and dynamic loading and this study used an accelerated in vitro test. It was demonstrated that segmented polyurethane with a polycarbonate soft segment (PCU) was more stable toward oxidative degradation than polyurethane with a polyether soft segment (PEU).

Bonin et al. [19] have focused on determining the effects of radiation on the properties of the materials: polypropylene, nylon 66, polycarbonate, and polyurethane, with and without glass fiber reinforcement. It was concluded that the investigated polymers could potentially be used for disposal containers due to their abilities to resist radiation adequately.

Effect of ionizing radiation on PCU and its radiation stability have not been encountered in the literature.

1.5.2. Epoxies

Damian et. al. [20] studied three types of ageing (thermal oxidation, radiochemical ageing and hydrolytic ageing) for a series of epoxy networks which was aimed to be used for the embedding of low activity radioactive wastes, the effects on the chemical composition and structure were studied and related to the evolution of the gas diffusion properties of these networks.

Sakr et. al. [21] studied improving the characteristics of cement-waste forms, such as strength and leachability, either by mixing epoxy with cement-clay at predetermined ratios or by coating cement-clay mixtures with an epoxy layer. Experimental results of immobilization into a mixture of cement, kaolinite, and epoxy polymer were reported. The ideal ratio of mixture of cement, waste, water, kaolinite and epoxy was reported for immobilizing media for radioactive waste. Compressive strength values increased, and the leachability value of radionuclides were decreased with the increase of epoxy composition between 2% and 6%.

Gilfrich and Wilski [22] studied changes in flexural strength and dielectric properties of an epoxy plastic (bisphenol a-based epoxy resin cured with aromatic diamines) with inorganic fillers via irradiation at high dose rates up to 10 MGy. They observed the properties remained unchanged. However, the measurements of heat deflection temperature and sol fraction indicated deterioration. The same results obtained after irradiation with the presence of air at extremely low dose rate (irradiation time 10 years).

Nicaise et. al. [23] studied diffusion of water into typical epoxide and polyester materials as a function of temperature, temperature cycles and polymer structure. The factors of thickness involved in the actual waste drums, temperature and hygrometry of the levels typical of shallow and land burial sites, the delays related to the water migration towards the embedded radioactive wastes were taken into consideration. It was concluded that the subsequent release would fall within the required norms. Moreover, Nicaise et. al. [24] studied diffusion of water into epoxide composites containing sand and glass beads as a function of temperature, type of filler and its surface treatment. It was reported that adhesion of epoxide polymer is better on siliceous sand than on glass beads and moreover, the amount of water absorbed by the sand filled materials are lower than that of unfilled ones during the extended periods of water immersion. In addition, it was concluded that the use of epoxide polymers filled up to 30% by volume of sand of 30 mm mean particle size would yield a more convenient product than that of unfilled in terms of resistance to leaching for nuclear waste management.

Baluch M.H. et. al. [25] concluded that based on a chemical stability criteria of less than 50 percent compressive strength loss at room temperature in a corrosive environment, the epichlorohydrin/bisphenol resin polymer concrete developed and investigated exhibited a sufficient degree of stability and it may prove beneficial for use in underwater structures, long term storage of radioactive nuclear waste material, tunnel lining, pavements and bridge deck lining to prevent corrosion of reinforcement.

Davenas et. al. [17] have performed a study of the relations between the modifications induced at the molecular level and the resulting properties of elastomers, which are used as seals and also for electrical cable insulation, and epoxy resins which are used for nuclear waste storage. It was reported that the epoxy resins can be used in the nuclear waste storage.

1.5.3. Poly(methyl methacrylate)

PMMA known as a positive photo-resist for its degradation upon irradiation has been the subject of more investigations in radiolysis than many other polymers. This was partly due to a growing interest in the application of PMMA in ion beam lithography in the semiconductor industry [26] and partly due to the non-gelling of PMMA at low dose irradiation, which allowed investigators to study the irradiation mechanisms of scission and crosslinking. Both crosslinking and chain scission occur simultaneously during irradiation of polymers, but the relative magnitude of cross-linking (gelling) to scission (degradation) depends upon polymer structure [27].

Gamma irradiation of PMMA causes main chain scission (MCS), which might be desired depending of the type of application. Hydrogen abstraction from an α-methyl or methylene group also occurs upon irradiation, particularly with ultraviolet light, producing carbon-carbon double bonds in either the main chain (M=) or a side group (S=) by cleavage of methyl ester groups but without causing main chain scission (Figure 4). Formation of M= and S= double bonds is undesirable because fragments of PMMA with substantially increased solubility are not produced. The extent of formation of each of the derivatives resulting from irradiation depends on the physical state of the PMMA. In solution all three products are observed, while in the solid, where two and three-dimensional structures must be considered, MCS and S= predominantly are observed. In summary, the PMMA is excited (*) and then undergoes decomposition to several products [28].

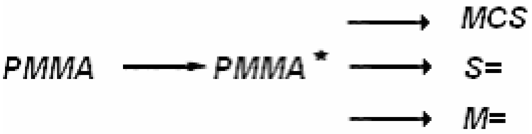


Figure 4. Irradiation of PMMA [28]

PMMA can also be used in the radiation dosimeter applications. The active substance of the PMMA film dosimeters is a dye dispersed in the PMMA. Ionizing radiation leads to the ionization of the PMMA and the added dye. Creation of excited molecules, free electrons and positive ions are observed. The de-excitation of the molecules results in the production of free radicals via electron transfer [29]. The radicals of ionized polymer react with the dyed molecules to produce an optical absorption in the visible spectrum. The ejection of an electron out of the PMMA involves the division of a radical and the resulting excitation involves the scission of the principal PMMA chain. The diffused oxygen in the plastic matrix attacks the radicals until its disappearance and as a result of oxygenation a stable product is formed. The stable product can be read from the spectrophotometer.

The radiation chemical yield of scission (degradation), G_s, defined as the number of chain scissions per 100 eV of the absorbed energy. G_s of PMMA is 1.6 and composition of the gas product of radiolysis includes H_2 (18%), CH_4 (15%), CO (36%), CO_2 (25%), C_3H_8 (5.3%) [30].

The use of PMMA as an embedding matrix for spent ion exchange resins with low specific radioactivity was investigated in Egypt. Solid homogeneous cylindrical blocks are obtained by incorporating 50 wt% ion exchange resins into PMMA. The dry resin particles are added to an equal amount of matrix solution. After settling, polymerization is initiated with benzoyl peroxide at room temperature, by heat or by irradiation in a gamma cell (0.5 Gy/s) [7].

1.6. RADIOACTIVE WASTE MANAGEMENT

1.6.1. Classification of Radioactive Waste

Radioactive waste is classified based on the different criteria and each country has their own waste classification. However, up to now, the widely accepted waste classification is the classification made by the International Atomic Energy Agency. In this classification, wastes are mainly classified into three as exempt waste, low and intermediate level waste (with two sub categories short lived and long lived) and high level waste [35]. The low and intermediate level-short lived waste category has the characteristics of restricted long-lived radionuclide content and limited amount of long-lived alpha emitting radionuclides.

1.6.2. Radioactive Waste Conditioning

Radioactive waste means any material which contains or is contaminated by radionuclides and for which no use is foreseen. The nuclear industry generates considerable amounts of radioactive wastes that require advanced treatment. Evaporation, precipitation, ion exchange or adsorption on clay surface may be used to concentrate wastes for further treatment and/or disposal. Common immobilization methods include solidification of wastes in cement, polymer or bitumen [21]. The conditioning of treated radioactive wastes by solidification to obtain stable forms is an important step in the predisposal waste management because in this way the potential for radioactivity release to the environment during storage, transport and disposal can be minimized. A number of materials have been employed for the solidification of low and intermediate level radioactive wastes in different countries. Although safety is the primary requirement in the selection of a suitable solidification system, there are also other aspects to be considered; some of these are:

-Volumetric efficiency

-simplicity of process operation and maintenance

-quality control requirements

-process economics

-waste form properties [7].

Although cementation is widely used method for the conditioning of radioactive waste, it is stated that the radiation field can assist in the formation of complexing agents from cemented organic wastes and these complexing agents are water soluble that enhances the migration of radionuclides from the disposal site [15].

Soundararajan et. al. [31] states that when the contaminants present are heavy metal ions simple cement/pozzolone based binders will be sufficient for immobilization however when the waste content is radioactive and organic species, these binders would not be adequate. In addition, it is stated that the structural damage to the matrix by the radioactive isotopes and the poor leaching of cement-based binders deters the use of it as a binder.

Polymers, both thermoplastics and thermosets, can be used as a matrix for the conditioning of radioactive waste and as a packaging material during the disposal and transport of radioactive waste as well.

Thermoplastic polymers, such as polyethylene, can be heated above melting point, mixed with powdered waste, and poured into a disposal container, where solidification occurs while the melt cools. No interaction occurs between the waste and the polymer. For the thermoset polymers, powdered waste is mixed with monomer and curing agent, as the liquid monomer and curing agent react, solidification occurs. A major disadvantage of this process for conditioning of waste is that waste constituents can react with the monomer and curing agent thus may interfere with solidification. Although thermoset polymers are a good option for macroencapsulation of debris and radioactive lead wastes, the potential for interference of the solidification reaction makes thermoset polymers a less desirable solution than thermoplastic [34].

1.6.3. Regulatory issues

Countries' Regulatory Authorities determine the criteria for the radioactive waste disposal and the radioactive waste is controlled for 300 years after disposal. US Code of Federal Regulation 10 PART 61 "Licensing Requirements for Land Disposal of Radioactive Waste" regulates the requirements for the land disposal of radioactive waste. 56th item of this regulation [36] explicitly gives the details of waste characteristics in two main categories,

(a) Minimum requirements for all classes of waste, intended to facilitate handling at the disposal site and provide protection of health and safety of personnel at the disposal site.

(b) Requirements to provide stability of the waste. Stability is intended to ensure that the waste does not structurally degrade and affect overall stability of the site through slumping, collapse or other failure of the disposal unit and thereby lead to water infiltration. Stability is also a factor in limiting exposure to an inadvertent intruder, since it provides a recognizable and nondispersible waste.

There is no final disposal facility in Turkey at the moment and the required norms for the final disposal have not been officially published.

1.7. AIM OF THE STUDY

In this study, change of properties with gamma treatment for the above mentioned polymers were studied. Two different dose rates were used for irradiations and the mechanical properties of the irradiated polymers exposed to same total absorbed dose were compared. In addition, long term irradiations times to about six months with high dose rate were done in order to understand the radiation stability of the polymers in the long term, some of the selected polymers may be possible candidates for embedding media for low and intermediate radioactive (nuclear) waste before their final disposal.

Due to the potential for interference of the solidification reaction of thermoset polymers, the radiation resistance of the epoxy polymer was studied in order to see the change in the radiation stability due to non usage of hardener.

CHAPTER II

EXPERIMENTAL STUDIES

2.1. MATERIALS

The polymers (PBEH, PCU) were supplied from Aldrich and have not been purified or processed further, they were melted up to 175 °C and then molded, the molded polymer were cut as dog bone for the tensile test. On the average three to four dog bone samples were used for each irradiation. In total, about 190 dog bones with thickness of 1.7 ± 0.2 mm were prepared, irradiated and tested.

Poly(carbonate urethane) has number average molecular weight of about 76.000 and weight average molecular weight of about 256.000 as determined by GPC [3]. PCU is copolymer of poly(1,6-hexyl-1,2-ethyl carbonate) diol, 4,4′-methylenebis(phenyl isocyanate) and 1,4-butanediol and has softening point 81 °C (Vicat, ASTM D 1525) [3]. PCU contains 4,4′-methylenebis(phenyl isocyanate) as hard segment and chain extended with 1,4-butanediol and a poly(1,6 hexyl 1,2-ethyl carbonate) as soft segment. Two sets of PCU samples with different mechanical properties were prepared. One set was used for high dose rate long term irradiations (irradiations with absorbed dose from 523 to 6240 kGy) and the other was used for the short term high dose rate irradiations (irradiations with absorbed dose from 35 to 357 kGy) and for all low dose rate irradiations.

Denture base PMMA was used for the experiments. The powder–liquid mixtures were prepared according to the manufacturer’s instruction. The dough prepared from the powder–liquid was first polymerized for 20 minutes at 60 °C by peroxide initiation present in the powder fraction; then, the temperature was increased to 90 °C to carry out further polymerization and curing was done for 45 minutes.

Poly(bisphenol a-co-epichlorohydrin) as the weight average molecular weight about 40.000 was in the pellet form with density of 1.18 g/ml [37]. The used bisphenol-a-epichlorohydrin has the degree of polymerization of approximately 63.

2.2. IRRADIATIONS

The samples of the polymers were irradiated with two gamma sources, one was relatively high dose rate and the other was emitting relatively low dose rate. Tenex Issledovatel model Co-60 (half life 5.27 years, 1.173 and 1.332 MeV/dis) source with activity of 2516 Ci (as of February 2005), dose rate chart given in Appendix A, was used for high dose rate irradiations which is hereinafter abbreviated as HDR. Gammacell 220 model including Co-60 source, initial activity of 12400 Ci (as of March 1968), with the dose rate of 0.0828 kGy/h (as of September 2005) was used for the low dose rate irradiations and hereinafter abbreviated as LDR. Irradiations were done in the presence of oxygen.

Irradiation periods for both high and low dose rate irradiations are tabulated in Table 4 and Table 5. The dose rate ratio of high and low dose irradiation source was 18, in other words 18 times of the irradiation period for high dose rate was required for low dose rate irradiation in order to have equal amount of total absorbed dose.

Table 4. HDR Irradiation periods and corresponding absorbed dose (kGy) to the polymers

	Short-term						Long-term						
Day(s)	1	2	3	4	5	10	14	30	45	57	100	130	175
PCU	35	71	107	143	178	357	523	1140	1690	2150	3630	4590	6240
PBEH	35	71	107	143	178	357	523	1100	1690	2150	3630	4590	X
PMMA	35	71	107	143	178	357	523	X	X	X	X	X	X

Table 5. LDR Irradiation periods and corresponding absorbed dose (kGy) to the polymers

Days	18	36	47	54	72	90	180
Polymers	35	71	94	107	148	178	357

2.3. TESTS

Mechanical and thermal tests were made for the non-irradiated and irradiated samples. Mainly tensile, TGA, FTIR, DSC, DMA and ATR-FTIR tests were carried out for the samples.

Computer controlled Lylod LR 50 K mark test machine with the load cell of 5 kN was used for the mechanical tests. Mechanical test were done according to ASTM D638, standard test method for tensile properties of plastics. Mechanical tests were performed at a constant crosshead displacement rate at 10 mm.min^{-1} for PBEH, PMMA and 50 mm.min^{-1} for PCU.

Two TGA instruments were used during the thermal gravimetric analyses. One of them was Thermal Analyst SDT Q600. The other was Perkin Elmer Pyris 1 TGA which connected to a FTIR spectrometer, Perkin Elmer Spectrum 1 FTIR Spectrometer, and the FTIR spectroscopy of the gas effluents from the TGA analysis were taken by this spectrometer and this instrument would hereinafter be stated as TGA-FTIR. TGA studies were carried out under N_2 atmosphere

Differential scanning calorimetry (DSC) thermograms of the polymers were taken on Dupont Thermal Analyst 2000 Differential Scanning Calorimeter 910 S and dynamic mechanical analysis (DMA) was carried out on a Thermal Analyst Dynamic Mechanical Analyzer model 983.

The DSC thermograms for 5-10 mg of samples in aluminum pans were taken under N_2 atmosphere in a temperature range of -100–300 °C with 10 °C/min heating rate and the same temperature range and heating rate were used for DMA. DMA test were also carried out under N_2 atmosphere. ATR-FTIR analyses were done via Bruker Vertex 70.

CHAPTER III

EXPERIMENTAL RESULTS

3.1. HIGH DOSE RATE EXPERIMENTAL RESULTS

3.1.1. Poly(carbonate urethane)

PCU was irradiated up to absorbed dose of 6240 kGy (duration of this irradiation was about six months) in the high dose rate gamma irradiation source. Another set of PCU samples were irradiated up to absorbed dose of 357 kGy (duration of this irradiation was six months) in the low dose rate gamma irradiation source.

3.1.1.1. Non-Irradiated

Tensile, DMA, DSC and TGA tests have been carried out for the non-irradiated PCU. Tensile test results are given in Section 3.1.1.5, HDR (high dose rate) all mechanical test results section. The stress-strain diagram for non-irradiated PCU is given in Figure 5 where the average strain at break is about 2.45.

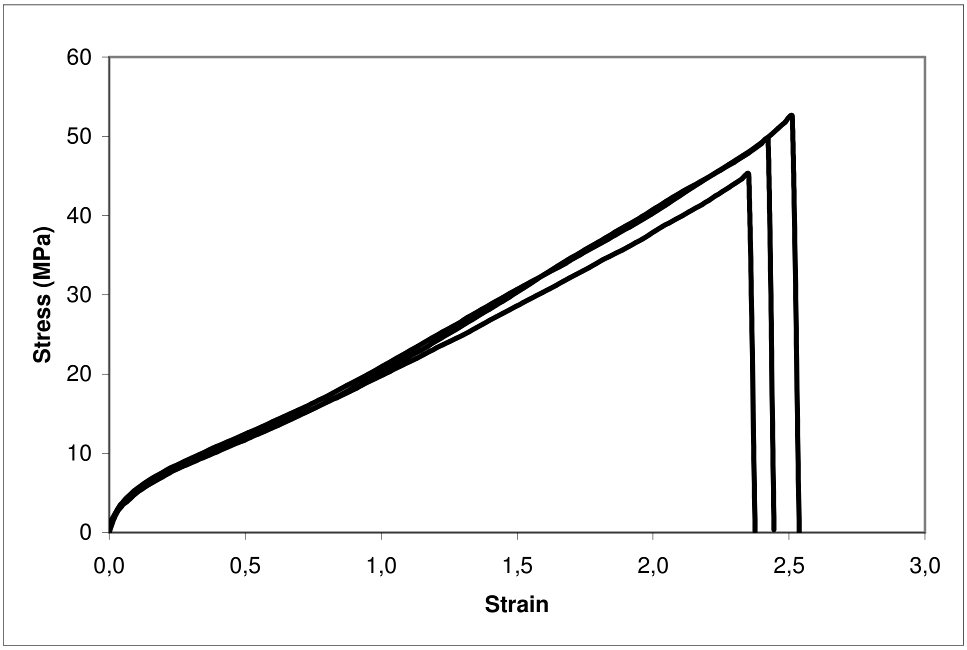


Figure 5. Stress- strain diagram of non-irradiated PCU

DMA and DSC thermograms of the non-irradiated PCU are given in Figures 6 and 7. From the DMA diagram, it is seen that the damping peak occurs at about 92 °C and damping factor is 0.83 at the peak point.

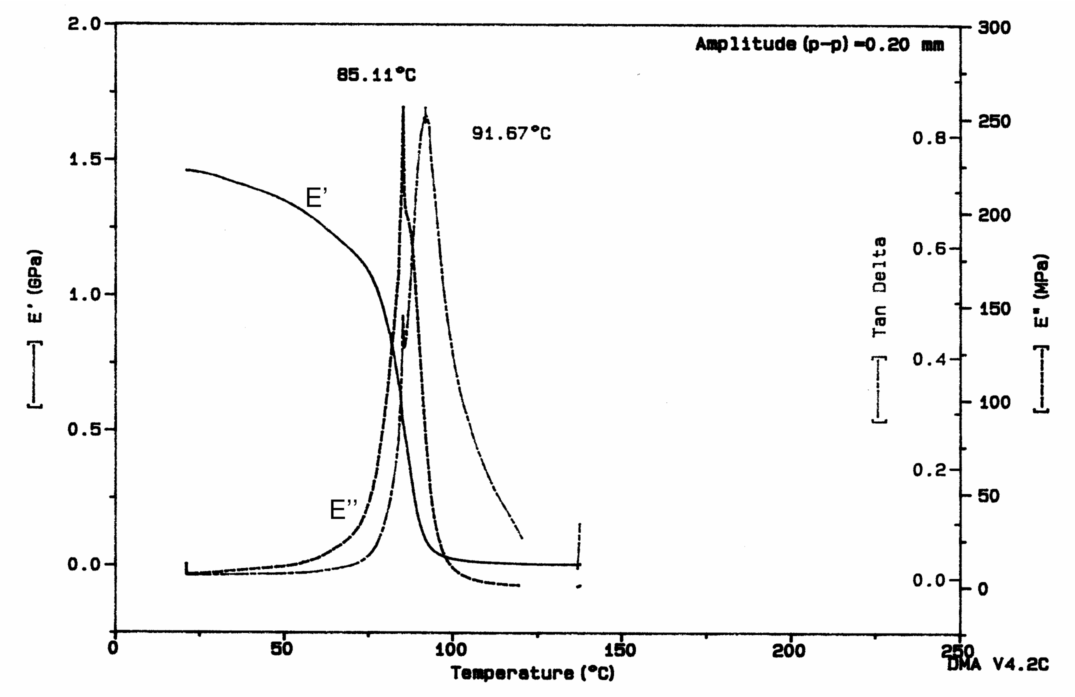


Figure 6. DMA of the non-irradiated PCU

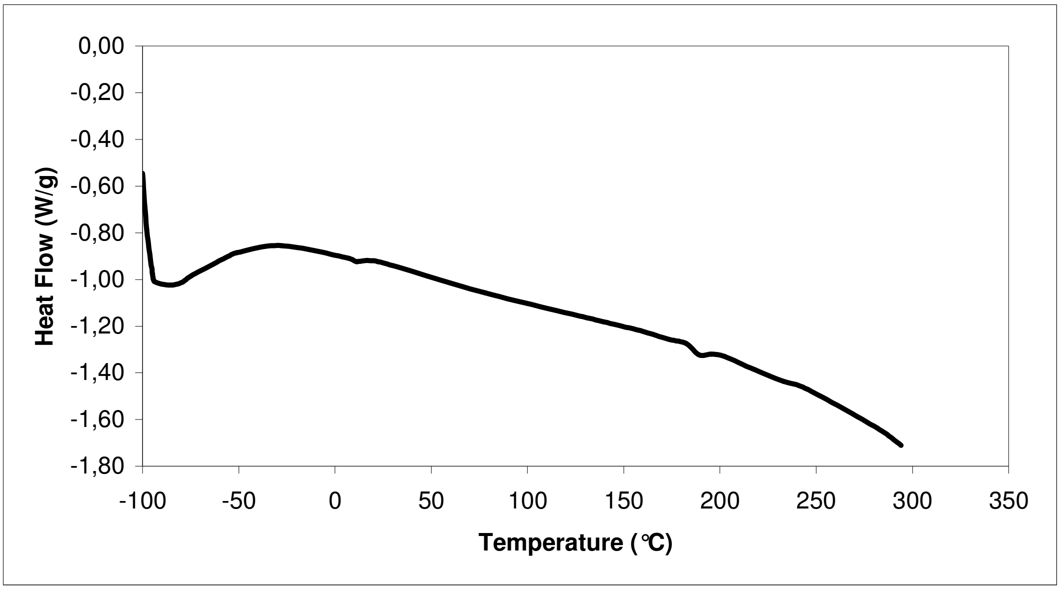


Figure 7. DSC thermogram of the non-irradiated PCU

TGA thermogram and ATR-FTIR spectrum for the non-irradiated PCU are given in Figures 8 and 9. From the TGA thermogram, it is seen that non irradiated PCU starts to degrade at 270 °C.

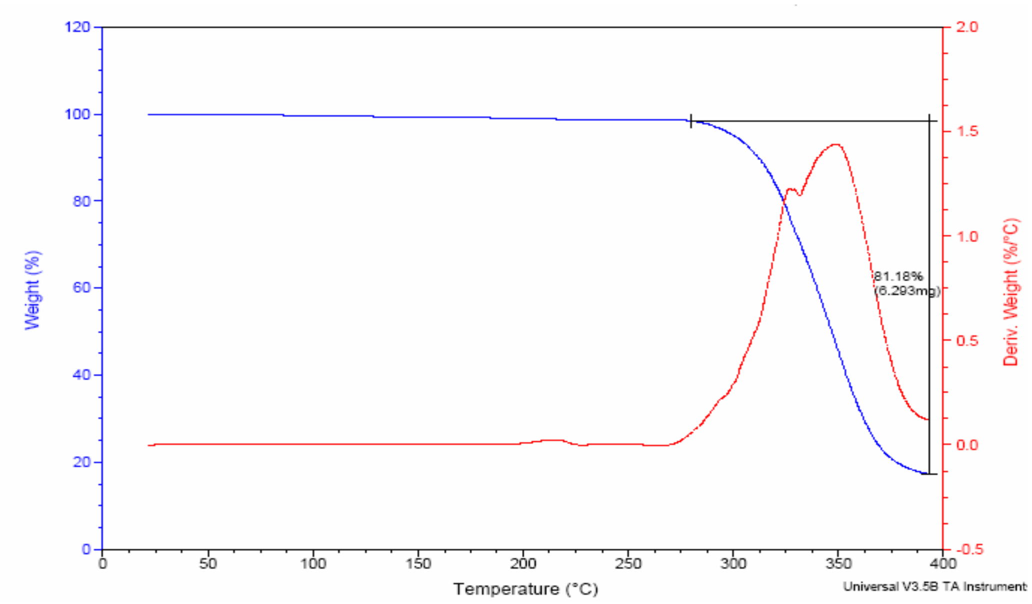


Figure 8. TGA thermogram for non-irradiated PCU

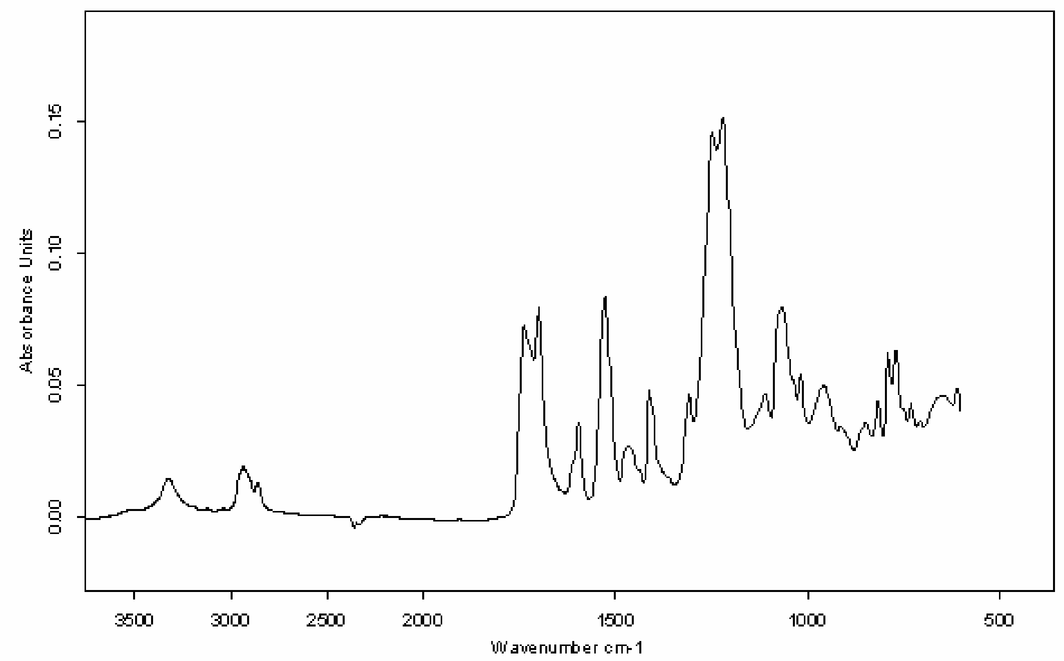


Figure 9. ATR-FTIR spectrum for non-irradiated PCU

3.1.1.2. Short term irradiations

During the short term irradiations, samples were irradiated with 35, 71, 107, 143, 178 and 357 kGy of absorbed doses. Tensile tests have been made for the short term irradiated PCU samples.

In addition, DSC, DMA, TGA-FTIR and ATR-FTIR tests have been completed for the irradiated PCU with 107 kGy. Tensile test results are given in Section 3.1.1.5. Comparisons of the experimental results are given in Section 3.3.

3.1.1.3. Long term irradiations

During the long term irradiations, the samples were irradiated with 523, 1140, 1690, 2150, 3630, 4590 and 6240 kGy of absorbed doses.

All tensile test results are given in Section 3.1.1.5. Comparisons of the experimental results are given in Section 3.3.

DMA tests have been carried out for the irradiated PCU with 1140 and 3630 kGy absorbed dose. DSC, TGA-FTIR and ATR-FTIR tests have been made for the irradiated PCU with 4590 kGy. TGA thermogram for the irradiated PCU with absorbed dose of 4590 kGy is given in Figure 10 where it is seen that the degradation starts at about 200 °C.

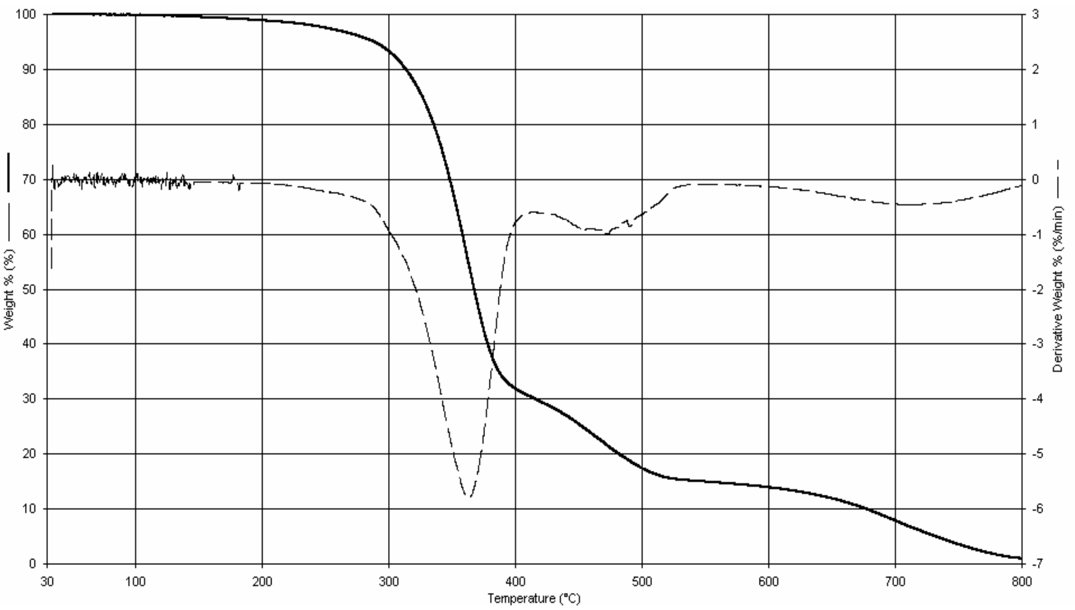


Figure 10. TGA thermogram for PCU with abs. dose of 4590 kGy

3.1.1.4. Color formation

Radiation induced color change from transparent to yellow then to brown was observed. Table 6 gives the change of color with the irradiation.

Table 6. Change of color of PCU with irradiation

Absorbed Dose (kGy)	Color
0	Transparent
107	Yellow
1107	Brown
3630	Dark Brown

3.1.1.5. HDR all mechanical test results

The mechanical test results for all high dose rate irradiated and non-irradiated PCU samples are given in Table 7. The changes of the mechanical properties with the absorbed dose are shown in the Figures 11-15.

Table 7. Comparison of the mechanical test results for PCU

	SHORT TERM							LONG TERM						
Absorbed Dose (kGy)	0	35	71	107	143	178	357	0	523	1690	2150	3630	4590	6240
Stiffness (N/m)	11239	8040	9328	12484		12611	10685	7037	8500	13130	13577	17692	14644	19950
Young's Modulus (MPa)	65.0	58.7	61.9	80.6		76.2	71.3	33.50	57.1	65.7	63.9	98.7	95.4	124.0
Load at Ultimate TS (N)	264.6	226.0	234.7	279.8	248.5	268.4	224.9	244.76	248.4	201.8	190.8	142.3	110.1	90.6
Extension at Ultimate TS (mm)	75.8	71.5	76.9	86.7	80.6	78.8	77.9	63.10	81.8	53.3	46.4	36.5	24.9	11.3
Ultimate Tensile Strength (MPa)	49.6	47.7	50.3	58.6	48.8	52.3	48.4	37.71	49.2	32.3	29.2	25.6	23.1	18.1
Load at Break (N)	264.6	226.5	234.6	279.6	248.4	268.4	224.9	239.57	248.4	201.7	190.8	142.3	110.0	90.6
Extension at Break (mm)	75.8	71.5	76.9	86.8	80.7	78.8	77.9	63.64	81.8	53.4	46.4	36.5	25.0	11.3
Stress at Break (MPa)	49.6	47.7	50.3	58.6	48.7	52.3	48.4	36.91	49.2	32.2	29.2	25.6	23.1	18.1
Strain at Break	2.45	2.31	2.48	2.80	2.60	2.54	2.51	2.06	2.37	1.72	1.50	1.18	0.081	0.36
Work to Break (J)	10.2	7.9	9.2	12.1	10.0	11.1	9.1	7.46	10.3	6.1	5.0	3.1	1.7	0.7

Change of the PCU’s tensile strength with absorbed dose is given in Figure 11. Ultimate tensile strength increases in the initial part of irradiation after which it decreases at high irradiation doses. Half value of the non-irradiated samples’ average ultimate tensile strength is shown as dotted line in Figure 11where it is seen that HVD (tensile strength) is 6010 kGy for high dose rate irradiation at 1485 Gy/h.

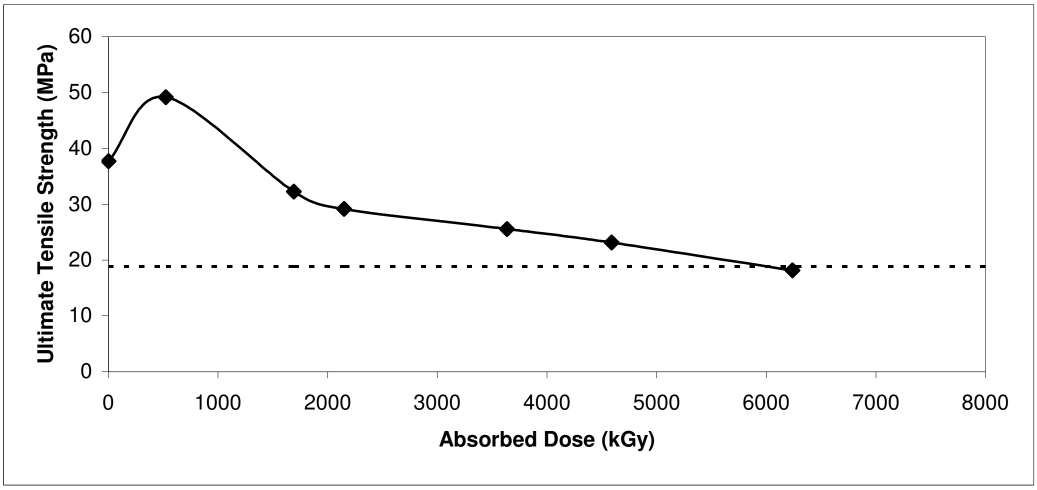


Figure 11. Change of the PCU’s tensile strength with abs. dose

Change of strain at break with absorbed dose is given in Figure 12 and the last two data of experimental points were extrapolated linearly as shown in the figure, in order to predict the maximum resistible dose by the PCU and it was found as 7500 kGy from the extrapolation of strain at break diagram. Half value of the non-irradiated samples’ average strain at break is shown as dotted line in Figure 12 where it is seen that HVD (elongation) is 4010 kGy for high dose rate irradiation at 1485 Gy/h.

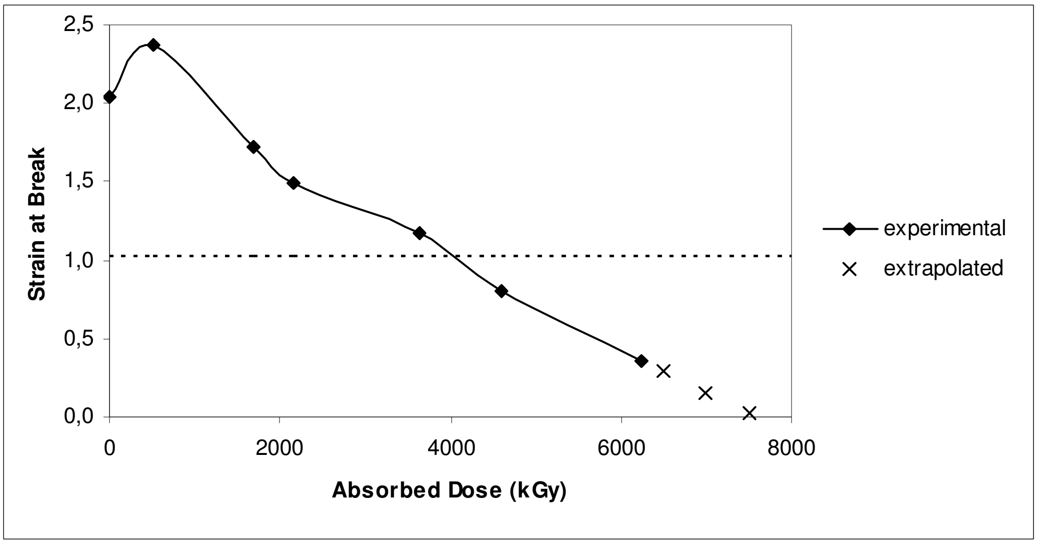


Figure 12. Change of the PCU's strain at break with abs. dose

Change of the PCU's Young modulus with absorbed dose is given in Figure 13 where it is seen that Young's Modulus increases with irradiation.

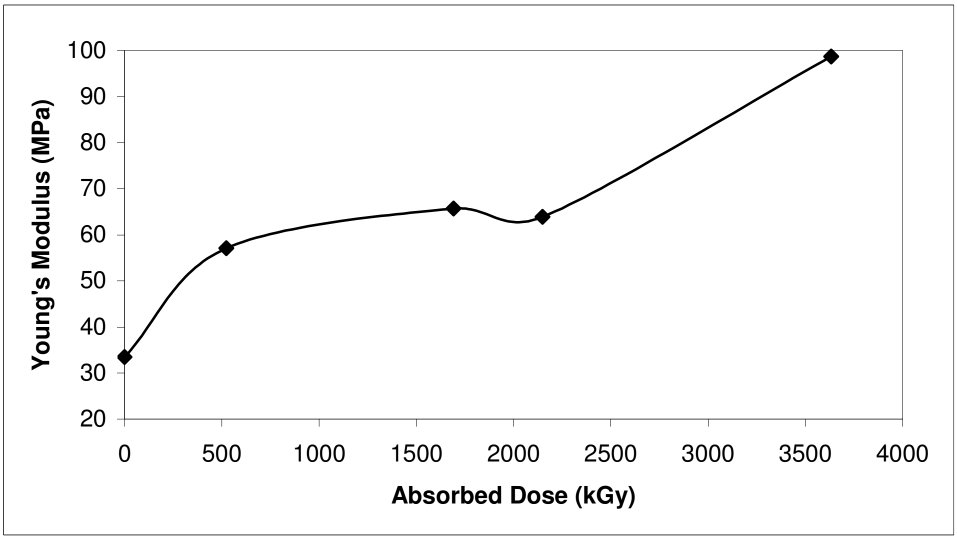


Figure 13. Change of the PCU's Young Modulus with absorbed dose

Change of the PCU’s stiffness with absorbed dose is given in Figure 14. PCU becomes stiffer with high dose irradiation.

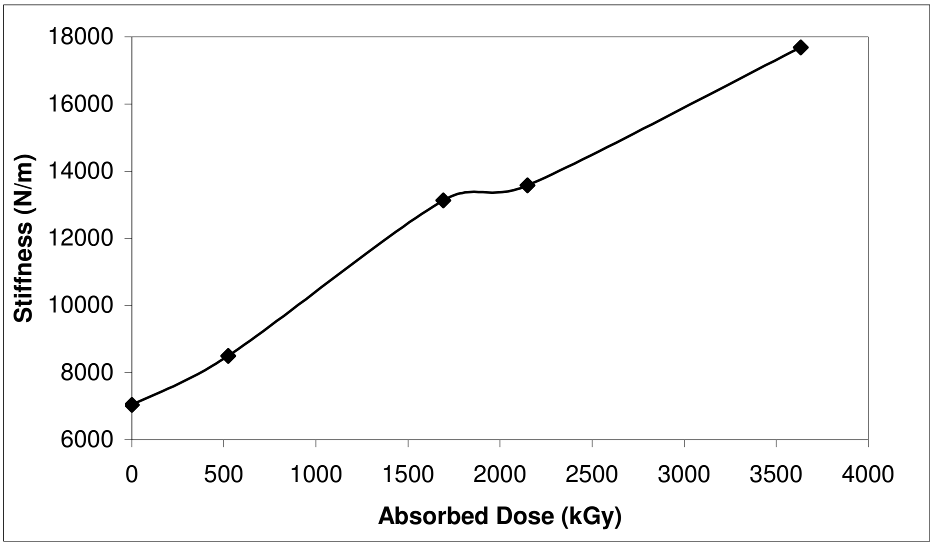


Figure 14. Change of the PCU’s stiffness with absorbed dose

Toughness was calculated from the stress-strain curve, which was curve fitted and the relating function was integrated. Change of the PCU’s toughness with absorbed dose is given in Figure 15. Toughness has the same behavior, increases in the initial part and has a peak point after which it decreases.

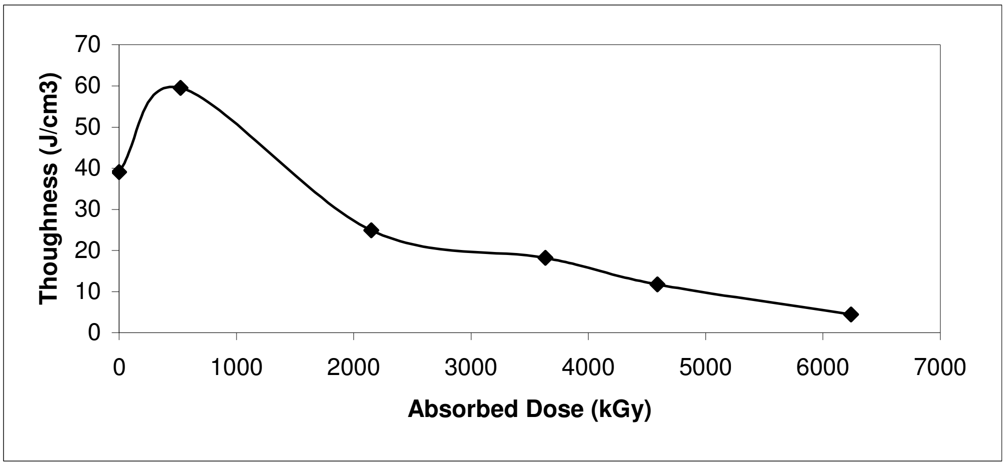


Figure 15. Change of the PCU’s toughness with absorbed dose

3.1.2. Poly (bisphenol –a – epichlorohydrin)

Tensile, DSC, DMA and TGA tests have been made for the irradiated PBEH with up to 1100 kGy, tensile test results are given in section 3.1.2.4. Moreover, the irradiations were done up to 4590 kGy but the tensile tests could not be done for these samples due to their brittleness.

3.1.2.1. Non Irradiated

The stress- strain diagram for non-irradiated PBEH is given in Figure 16. The average tensile strength of the samples at yield point was found as 49.2 MPa and average strain at break was 0.48.

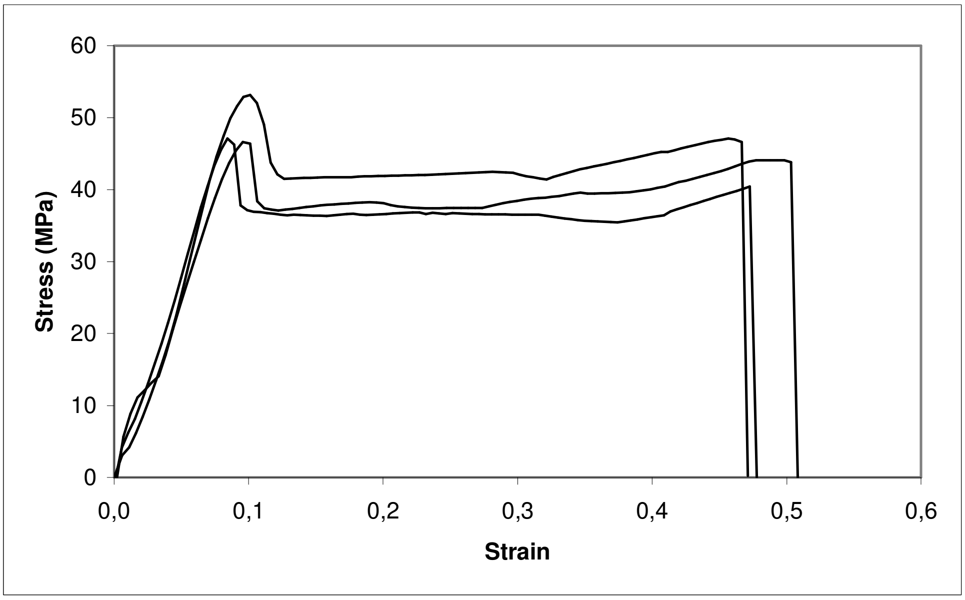


Figure 16. Stress-strain diagram of non-irradiated PBEH

ATR-FTIR spectra of the poly(bisphenol-a-epichlorohydrin) is given in Figure 17.

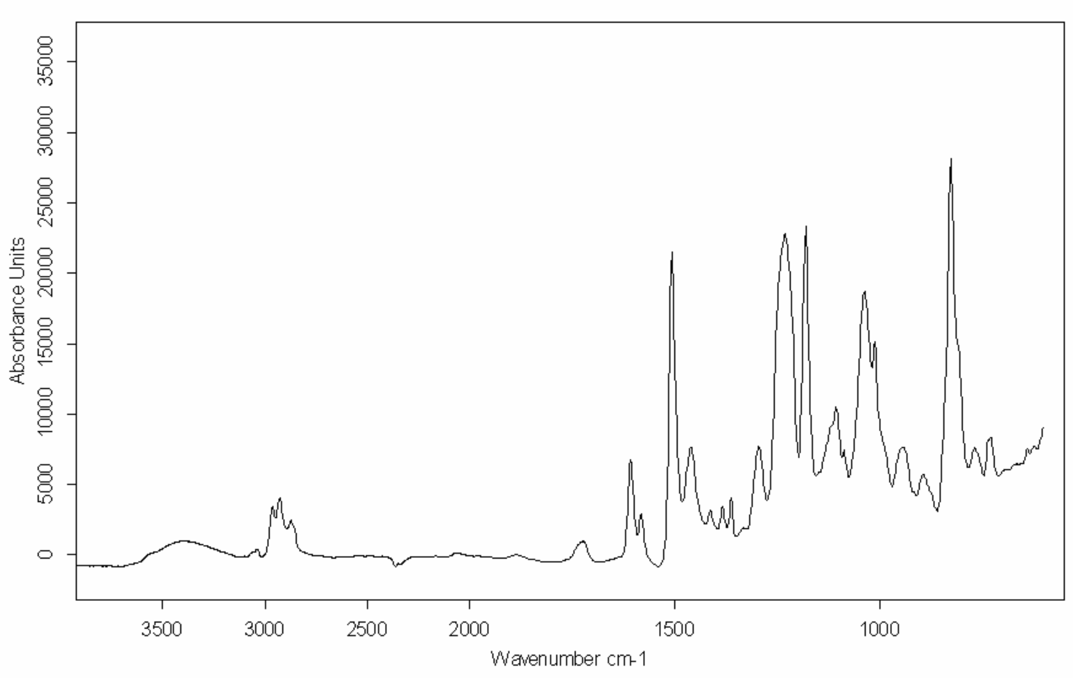


Figure 17. ATR-FTIR spectra of non-irradiated PBEH

DMA and DSC thermogram for the non-irradiated PBEH are given in Figures 18-19. From DMA diagram it is seen that the damping peak occurs at about 94 °C.

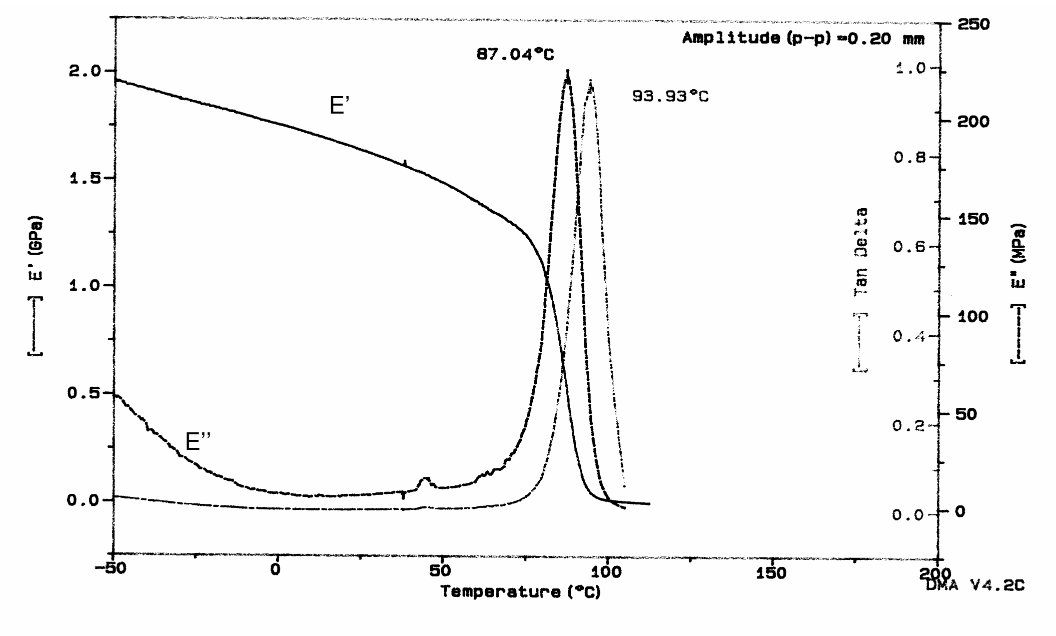


Figure 18. DMA of non-irradiated PBEH

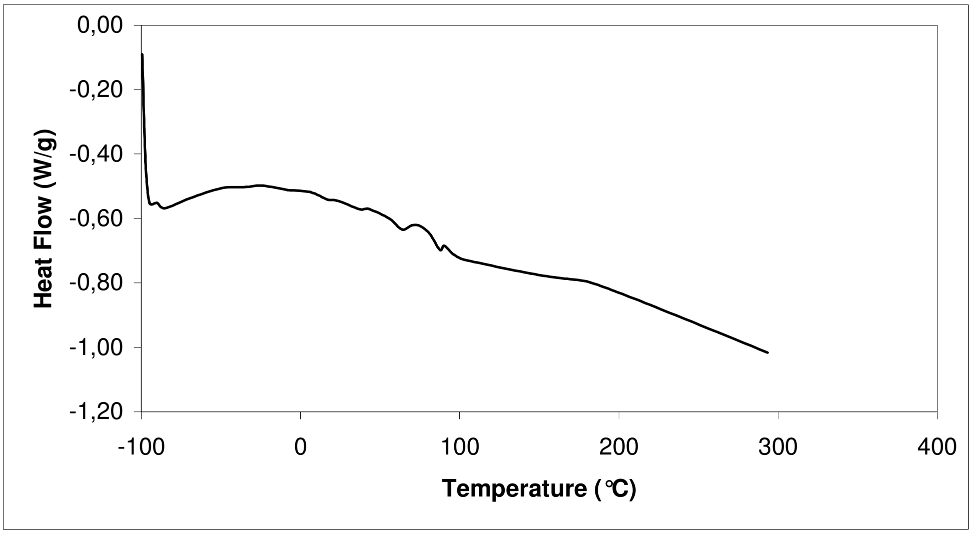


Figure 19. DSC thermogram for non-irradiated PBEH

TGA thermogram for non-irradiated PBEH is given in Figure 20 and it is seen from the figure that the degradation starts at about 375 °C and derivative weight loss over temperature data has peak point at 445 °C.

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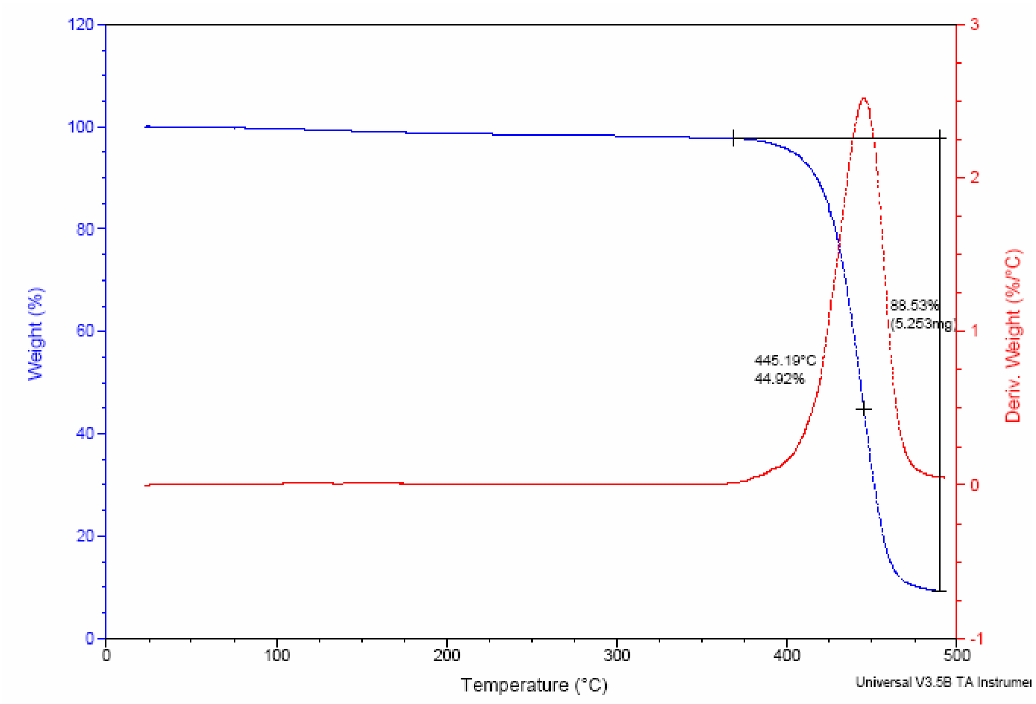

Figure 20. TGA thermogram for non-irradiated PBEH

3.1.2.2. Short term irradiations

During the short term irradiations, the samples were irradiated with 35, 71, 107, 143, 357 kGy of absorbed doses. Tensile tests have been made for the short term irradiated PBEH samples.

DSC tests have been made for the irradiated PBEH with 35 and 107 kGy. Tensile test results are given in Section 3.1.2.4. Comparisons of the experimental results are given in Section 3.3.

3.1.2.3. Long term irradiations

During the long term irradiations, the samples were irradiated with 523, 622, 1100, 1690, 2150 and 4590 kGy of absorbed doses. Tensile tests have been carried out for the irradiated PBEH with 622 and 1100 kGy, tensile test results are given in Section 3.1.2.4. Comparisons of the experimental results are given in Section 3.3.

Since the PBEH has broken down due to the irradiation, tensile test could not be made for the PBEH irradiated with absorbed dose of 1690 kGy and higher. DSC tests have been carried out for the irradiated PBEH with absorbed doses of 1100 kGy. DMA test have been made for the irradiated PBEH with absorbed dose of 1690 kGy. ATR-FTIR and TGA-FTIR tests have been done for the irradiated PBEH with absorbed dose of 2150 kGy.

3.1.2.4. HDR all mechanical test results

Change of the PBEH's tensile strength at yield point with absorbed dose is given in Figure 21 where it is seen that the tensile strength increases at the initial part of the irradiation and decreases again then it starts to level off after which the tensile strength decreases with the high irradiation dose. Half value of the non-irradiated samples' average tensile strength at yield point is shown as dotted line in Figure 21 where it is seen that HVD (tensile strength) is 885 kGy for high dose rate irradiation at 1485 Gy/h.

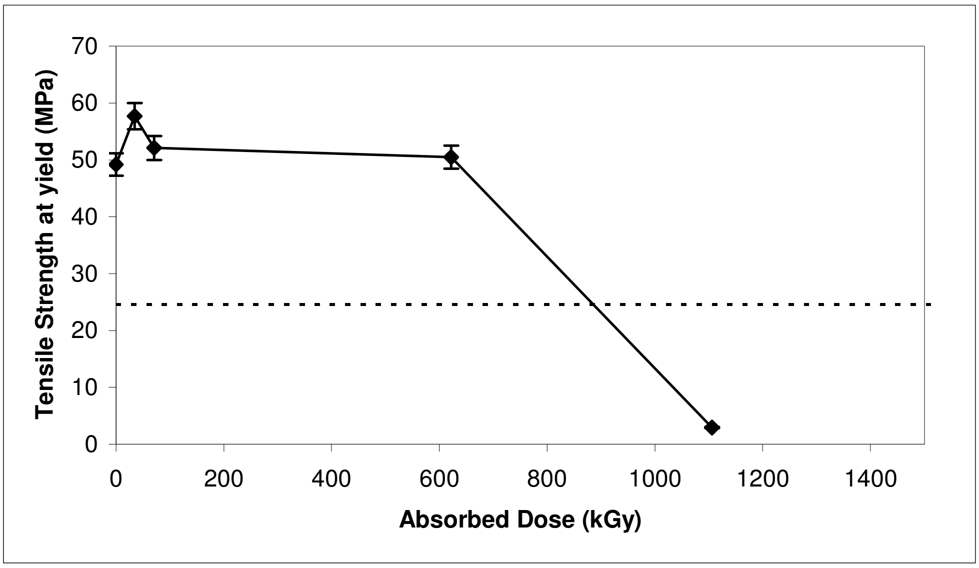

Figure 21. Change of the PBEH's tensile strength with absorbed dose

Change of the PBEH’s strain at break and strain at yield with absorbed dose is given in Figure 22 where it is seen that the strain at break decreases suddenly with relatively small amount of absorbed radiation dose. The difference between the two lines decreases. Half value of the non-irradiated samples’ average strain at break is shown as dotted line in Figure 22 where it is seen that HVD (elongation) is 29 kGy for high dose rate irradiation at 1485 Gy/h.

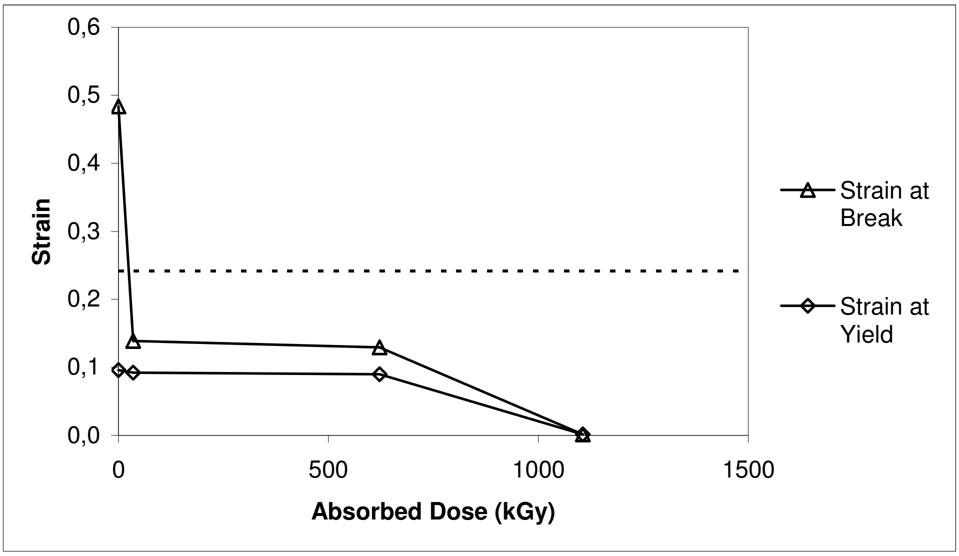

Figure 22. Change of the strain with absorbed dose for PBEH

Change of the PBEH’s young modulus with absorbed dose is given in Figure 23 where it is seen that the Young’s modulus increases at the initial part of the irradiation.

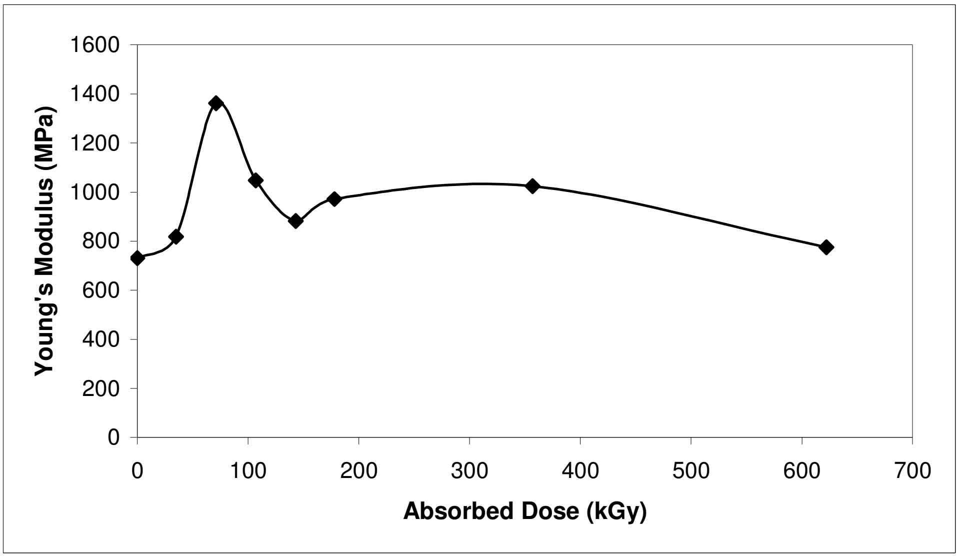

Figure 23. Change of the PBEH's young modulus with absorbed dose

Change of the PBEH's stiffness with absorbed dose is given in Figure 24 where it is seen that stiffness increases at the initial part of the irradiation and decreases again then it starts to level off.

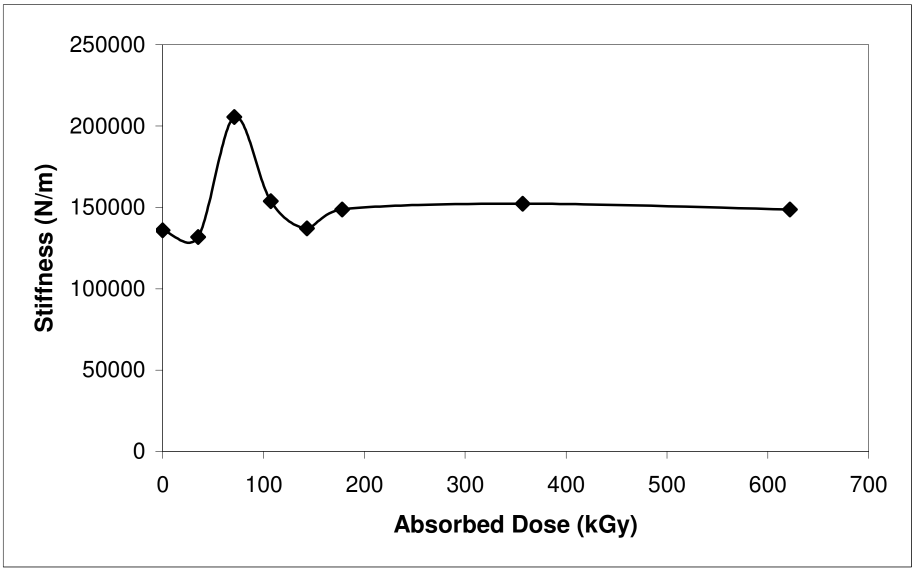

Figure 24. Change of the PBEH's stiffness with absorbed dose

Toughness was calculated from the stress-strain curve for each tensile test and change of the PBEH's toughness with absorbed dose is given in Figure 25. Toughness decreases suddenly in the initial part of irradiation and it level off and starts to decrease with high irradiation dose.

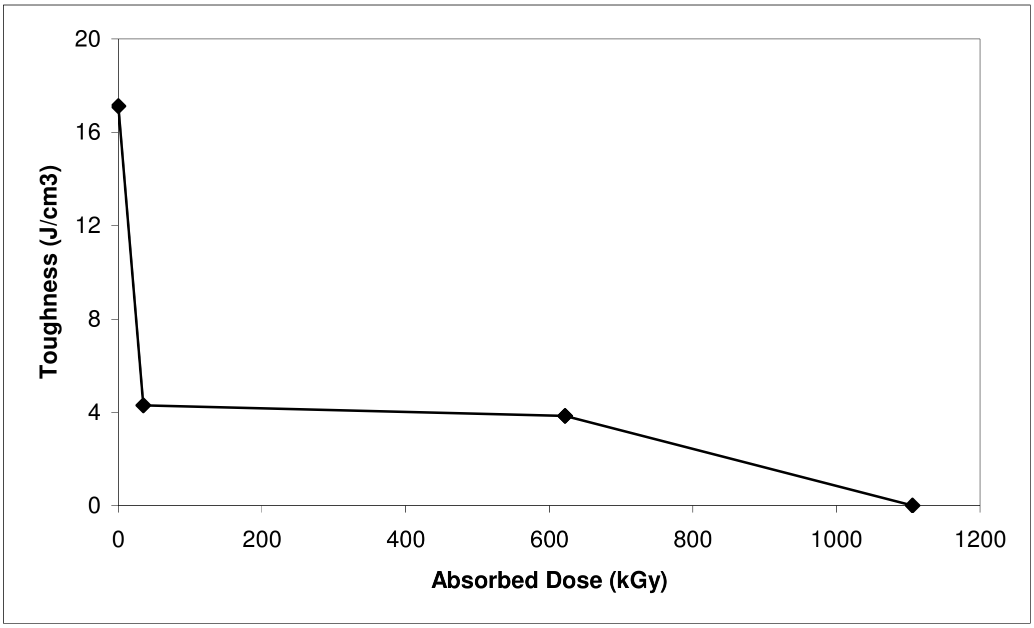

Figure 25. Change of the PBEH's toughness with absorbed dose

Mechanical test results of the irradiated and non-irradiated PBEH are given in Table 8.

Table 8. Comparison of Mechanical Test Results for PBEH

Absorbed Dose (kGy)	0	35	71	107	143	178	357	622	1100
Stiffness (N/m)	135930	131810	205570	153880	137060	148790	152380	148800	
Young's Modulus (MPa)	730.4	818.4	1361.5	1048.1	881.6	971.6	1023.8	775.3	
Load at yield (N)	243.1	269.1	243.5	228.8	239.2	233.3	240.5	229.2	13.12
Extension at yield (mm)	2.5	2.7	1.7	1.9	2.4	2.1	2.1	2.0	0.35
Tensile Strength at yield (MPa)	49.2	57.7	52.1	50.3	49.8	52.8	52.1	50.5	2.94
Work to yield (J)	0.3	0.3	0.2	0.2	0.3	0.2	0.2	0.2	2.3E-03
Load at Break	209.8	127.8	135.7	126.3	156.0	148.7	149.6	113.5	13.12
Extension at Break (mm)	12.8	4.0	2.2	2.4	2.8	2.8	2.7	2.9	0.35
Stress at Break (MPa)	42.5	27.0	29.1	27.6	32.4	33.6	32.4	25.0	2.94
Strain at Break	0.48	0.14	0.07	0.08	0.09	0.1	0.088	0.13	0.013
Work to Break (J)	2.34	0.62	0.29	0.29	0.35	0.34	0.37	0.39	2.3E-03

3.1.3. PMMA

3.1.3.1. Non Irradiated

Tensile, DSC, DMA, ATR-FTIR and TGA tests have been made for the non-irradiated PMMA, tensile test results are given in the HDR all mechanical test results (3.1.3.4) section. The stress-strain diagram for non irradiated PMMA is given in Figure 26 and the average ultimate tensile strength of the samples was found as 28.2 MPa.

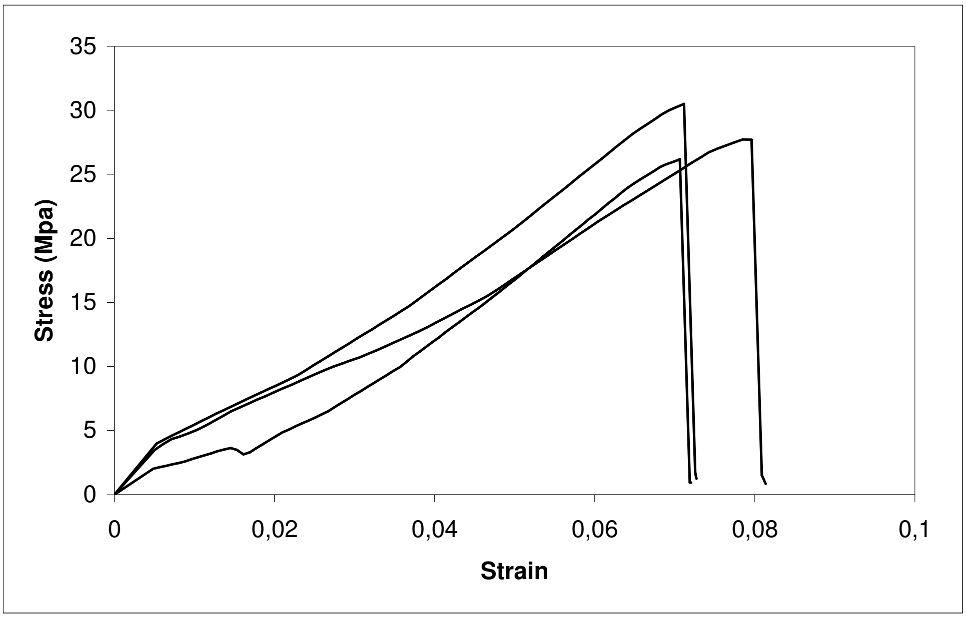

Figure 26. Stress- strain diagram of non-irradiated PMMA

DMA, DSC, TGA and ATR-FTIR diagrams for the non-irradiated PMMA are given in Figures 27-30. It is seen from the DMA graph that the alpha transition starts at about 97 °C and the beta transition starts at about 41.5 °C. From the DSC thermogram, it is observed that there is a further polymerization of PMMA with a peak point at about 119 °C.

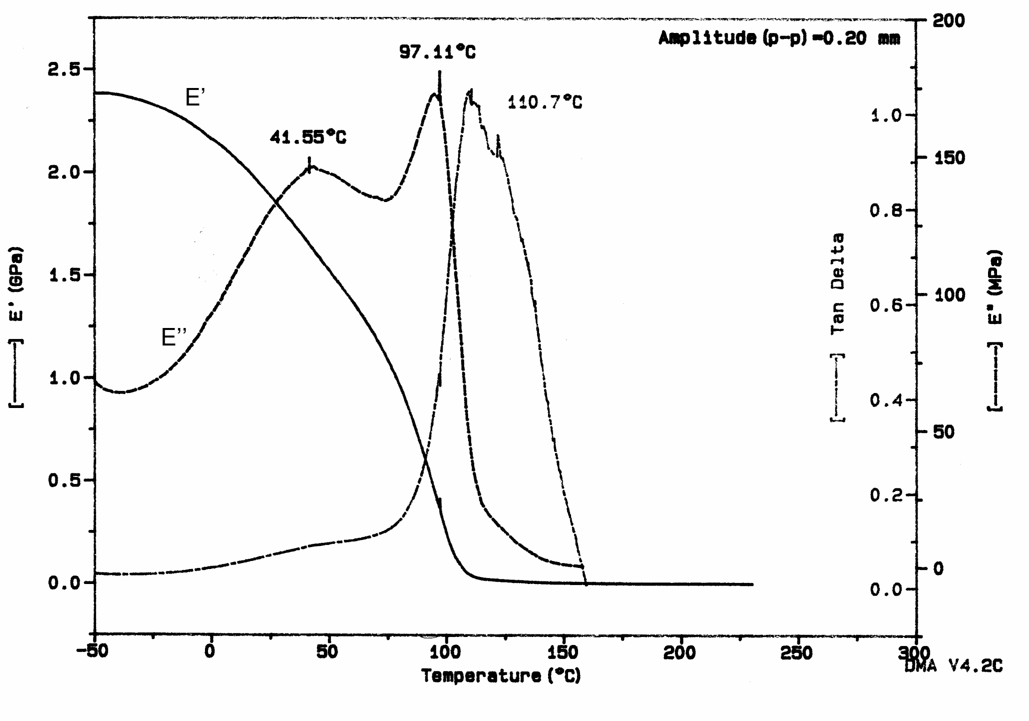

Figure 27. DMA of non-irradiated PMMA

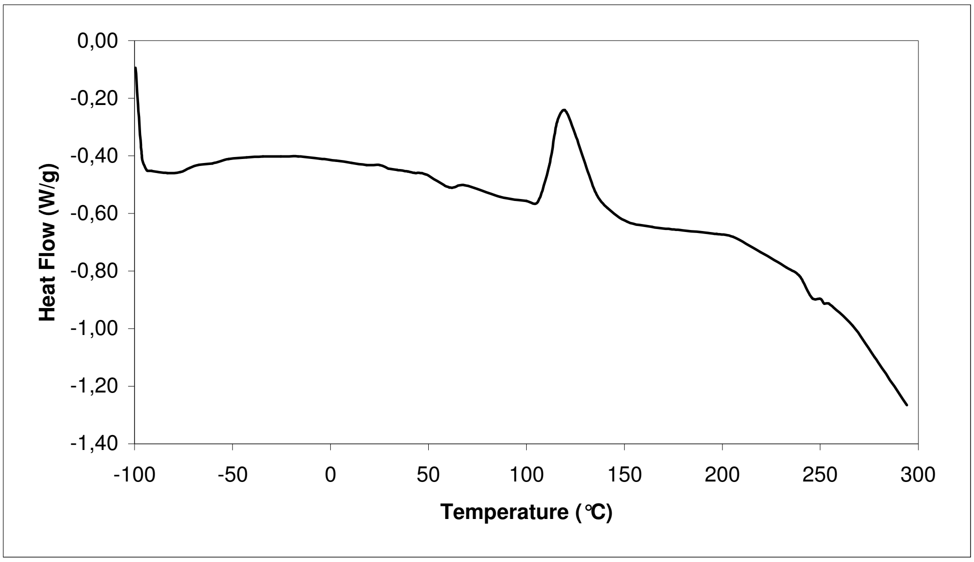

Figure 28. DSC thermogram for non-irradiated PMMA

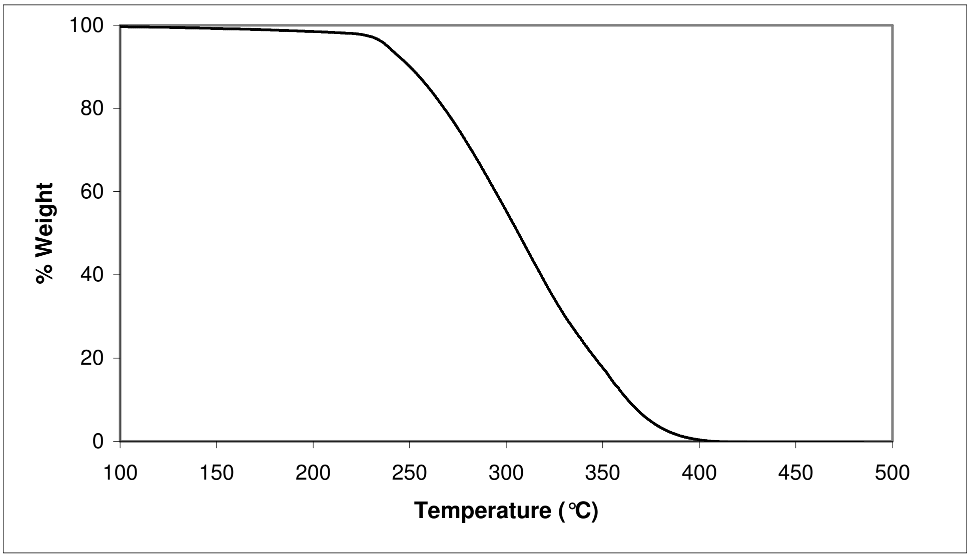

Figure 29. TGA thermogram for non-irradiated PMMA

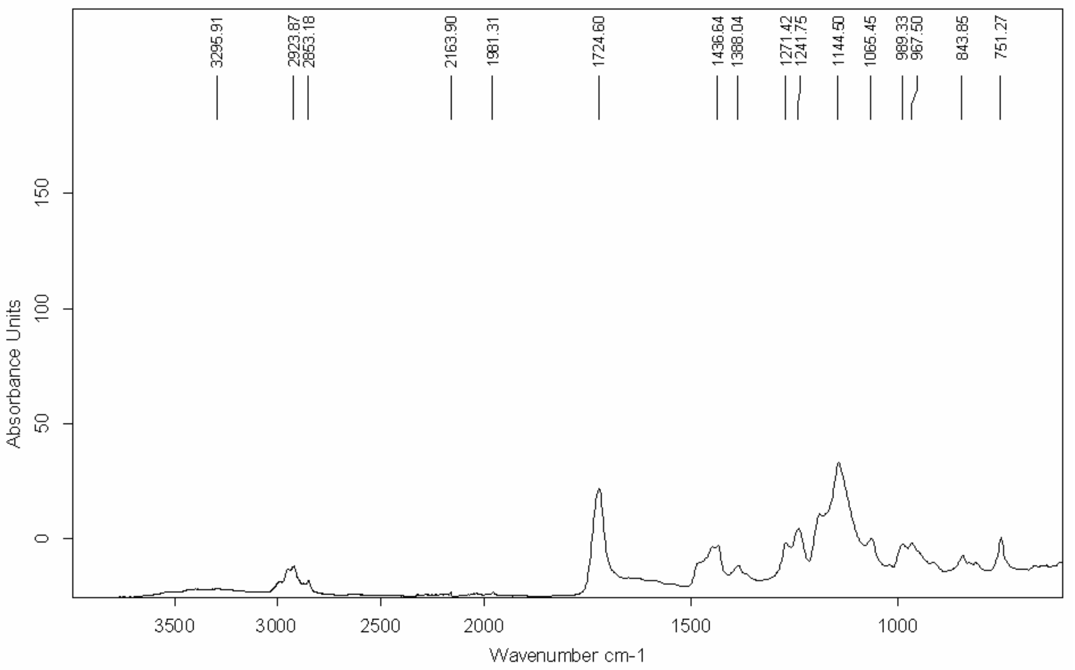

Figure 30. ATR-FTIR spectra for non-irradiated PMMA

3.1.3.2. Short term irradiations

During the short term irradiations, the samples were irradiated with 35, 71, 107, 178 and 357 kGy of absorbed dose.

DSC and DMA tests have been done for the irradiated PMMA with 35 kGy. TGA, DSC and DMA tests have been done for PMMA irradiated with 107 kGy. DMA test have been done for the PMMA irradiated with 178 kGy. TGA-FTIR, ATR-FTIR and DMA tests have been done for PMMA irradiated with 357 kGy.

TGA thermogram for PMMA irradiated with absorbed dose of 357 kGy is given in Figure 31. Tensile test results are given in Section 3.1.3.4. Comparisons of the experimental results are given in Section 3.3.

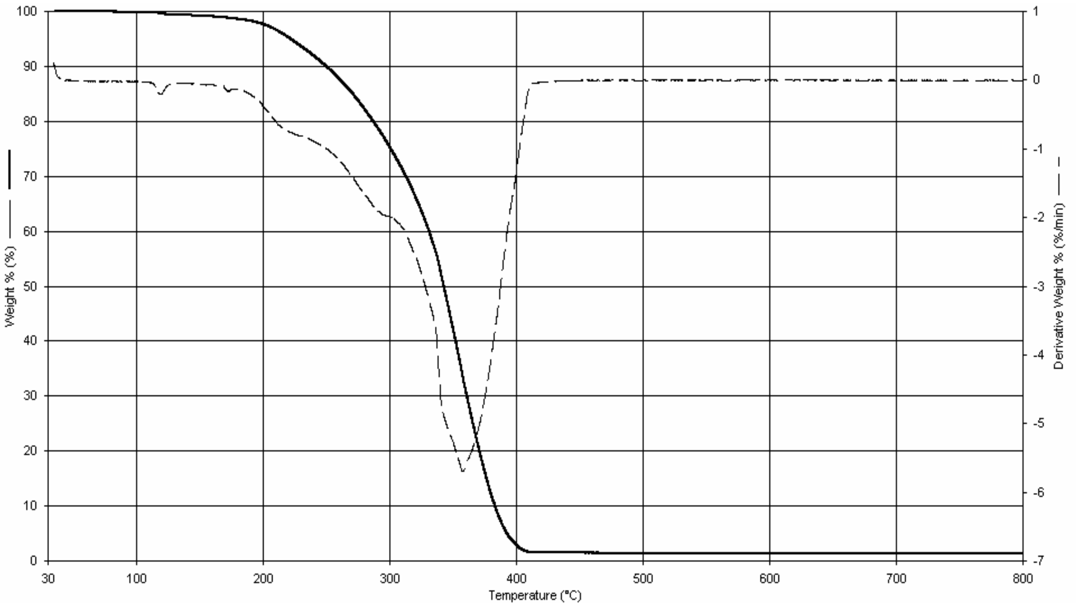

Figure 31. TGA thermogram for PMMA with abs. dose of 357 kGy

3.1.3.3. Long term irradiations

Since the PMMA has broken down due to the irradiation, tensile test could not be done for the PMMA irradiated with 523 kGy. Higher dose irradiations were not done due to PMMA's lack of resistance.

3.1.3.4. HDR all mechanical tests results

All Mechanical tests results of PMMA are given in Table 9. The changes in the mechanical properties are given in Figures 32-35.

Table 9. Mechanical properties of PMMA

Absorbed Dose (kGy)	0	35	71	107	178	357
Stiffness (N/m)	9.0E+04	2.3E+05	2.4E+05	1.8E+05	1.4E+05	1.3E+05
Young's Modulus (MPa)	476.7	1103.8	1053.9	787.5	661.0	643.8
Ultimate Tensile Strength (MPa)	28.2	34.9	30.3	23.1	13.9	4.5
Work to Maximum (J)	0.2	0.1	0.1	0.1	0.0	0.0
Load at Break (N)	161.8	215.1	208.1	155.9	84.7	24.4
Extension at Break (mm)	2.3	1.5	1.2	1.2	0.7	0.3
Stress at Break (MPa)	28.2	34.9	30.3	23.1	13.9	4.5
Strain at Break	0.07	0.05	0.04	0.04	0.03	0.01
Work to Break (J)	0.18	0.13	0.11	0.08	0.03	0.01

Tensile strength and strain at break increases in the initial part of the irradiation then decreases continuously with the increase of the absorbed dose. Experimental data for both ultimate tensile strength and strain at break were extrapolated in order to determine maximum resistible absorbed dose to PMMA as shown in Figures 32-33. Half value of the non-irradiated samples' average ultimate tensile strength is shown as dotted line in Figure 32 where it is seen that HVD (tensile strength) is 178 kGy for high dose rate irradiation at 1485 Gy/h. HVD (elongation) was found as 148 kGy following the same procedure for Figure 33.

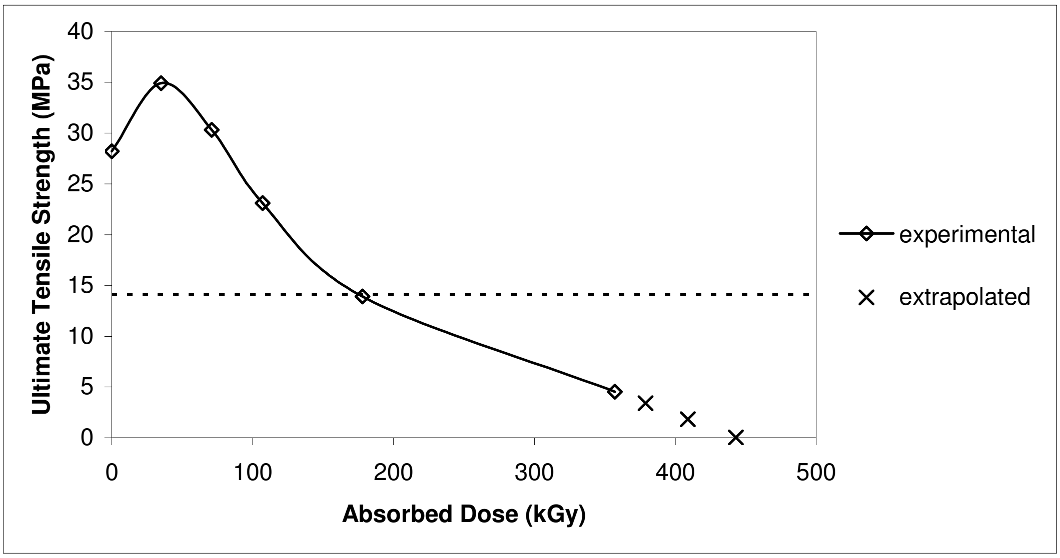

Figure 32. Change of PMMA's ultimate tensile Strength with abs. dose

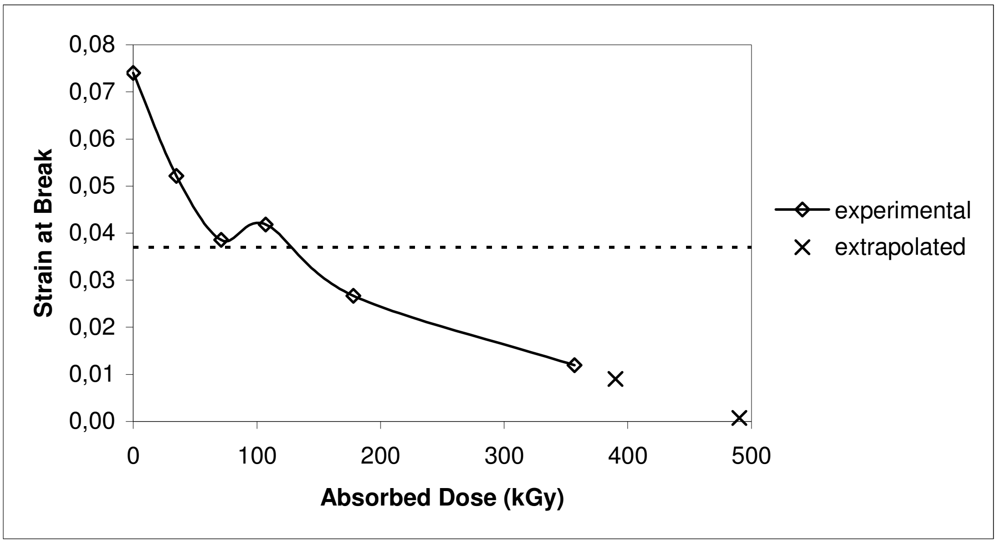

Figure 33. Change of PMMA’s strain at break with abs. dose

Young’s modulus increases in the initial part of the irradiation then it starts to decrease and level off between 178-357 kGy absorbed dose. Stiffness increases in the initial part of the irradiation then it starts to increase slightly after which decreases with the increase of the absorbed dose and the PMMA samples irradiated with 523 kGy absorbed dose becomes brittle.

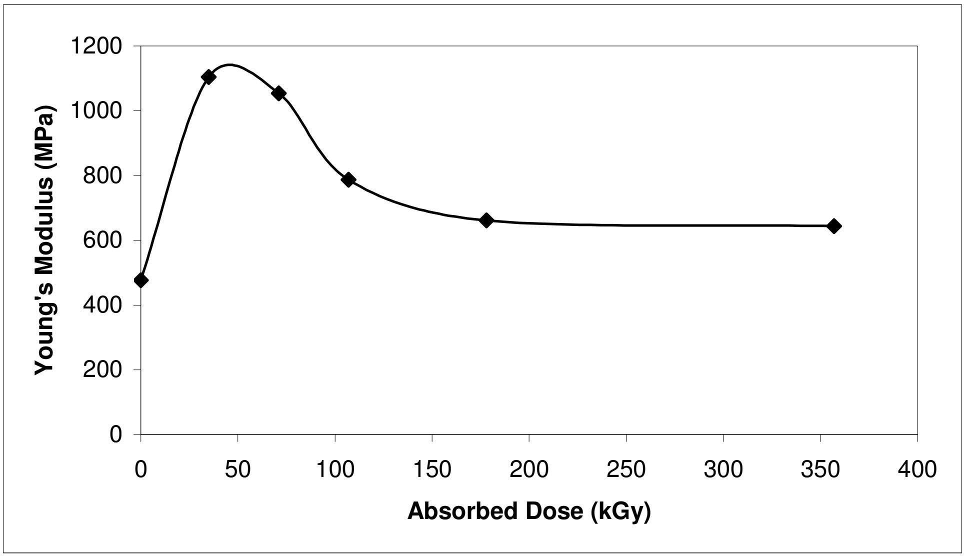

Figure 34. Change of PMMA's Young's modulus with abs. dose

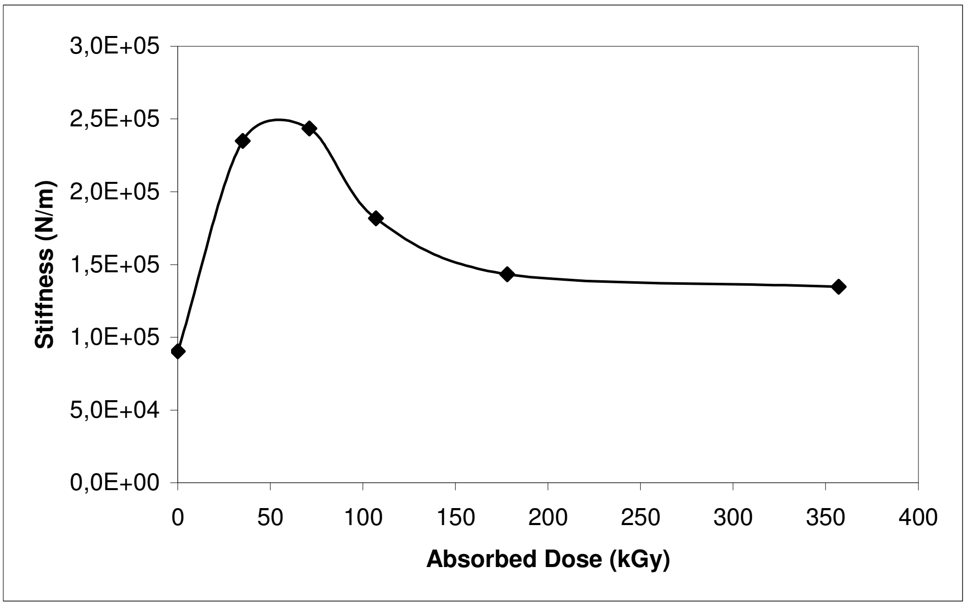

Figure 35. Change of PMMA's stiffness with abs. dose

3.2. LOW DOSE RATE EXPERIMENTAL RESULTS

3.2.1. PCU

Tensile tests have been made for the PCU irradiated with 35, 71, 107, 143, 178 and 357 kGy and tensile test results are given in Table 10. Comparison of the relative change of the mechanical properties with dose rate is given in the section 3.3.1.1.

Table 10. PCU mechanical test results-LDR

Absorbed Dose (kGy)	0	35	71	107	143	178	357
Stiffness (N/m)	$1.1\text{x}10^4$	$1.2\text{x}10^4$	$1.1\text{x}10^4$	$1.5\ \text{x}10^4$	$1.6\ \text{x}10^4$	$1.4\ \text{x}10^4$	
Young's Modulus (MPa)	65.0	82.8	75.4	89.7	87.5	91.8	
Ultimate Tensile Strength (MPa)	49.6	59.3	59.8	54.7	45.5	51.7	33.1
Load at Break	264.6	269.0	265.5	235.4	250.7	269.2	190.3
Extension at Break	75.8	83.7	86.2	81.0	69.8	81.7	
Stress at Break	49.6	59.3	59.8	54.7	45.5	51.7	33.1
Strain at Break	2.446	2.70	2.78	2.61	2.30	2.63	1.49
Work to Break	10.2	11.4	11.5	9.9	9.5	11.5	

3.2.2. PBEH

Tensile tests have been made for the PBEH irradiated with 35, 71, 107, 143, 178 and 357 kGy and tensile test results are given in Table 11. Comparison of the relative change of the mechanical properties with dose rate is given in the section 3.3.1.2.

Table 11. PBEH Mechanical tests results -LDR

Absorbed Dose (kGy)	0	35	71	143	178	357
Stiffness (N/m)	$1.2 x 10^5$	$1.6 x 10^5$	$1.3 x 10^5$	$1.9 x 10^5$	$1.3 x 10^5$	$1.6 x 10^5$
Young's Modulus (MPa)	686.7	952.2	922.1	952.0	802.7	870.9
Load at yield (N)	233.6	245.5	235.4	266.3	227.1	255.0
Extension at yield (mm)	2.6	2.4	2.2	2.2	2.2	1.9
Tensile Strength at yield (MPa)	48.7	49.6	53.3	47.1	46.6	51.5
Work to yield (J)	0.3	0.3	0.3	0.3	0.2	0.2
Load at Break (N)	188.6	126.2	160.9	120.8	158.3	249.6
Extension at Break (mm)	10.2	4.0	4.2	2.8	2.7	2.0
Stress at Break (MPa)	39.2	25.3	36.5	21.4	32.6	50.4
Strain at Break	0.38	0.137	0.136	0.098	0.089	0.074
Work to Break (J)	1.78	0.55	0.62	0.37	0.34	0.2

3.2.3. PMMA

Tensile tests have been made for the PMMA irradiated with 35, 71, 107 and 178 kGy and tensile test results are given in Table 12. Comparision of the relative change of the mechanical properties with dose rate is given in the section 3.3.1.3.

Table 12. PMMA mechanical test results-LDR

Absorbed Dose (kGy)	0	35	71	107	178
Stiffness (N/m)	9.0×10^5	2.2×10^5	3.1×10^5	2.8×10^5	1.0×10^5
Young's Modulus (MPa)	476.7	882.5	1015.0	1191.1	661.0
Extension at yield	2.3	1.9	1.6	1.5	1.3
Ultimate Tensile Strength (MPa)	28.2	33.9	32.1	30.1	18.5
Work to Maximum	0.2	0.2	0.2	0.1	0.1
Load at Break	161.8	259.8	292.1	215.1	86.1
Extension at Break	2.3	1.9	1.6	1.5	1.3
Stress at Break	28.2	33.9	32.1	30.1	18.5
Strain at Break	0.74	0.61	0.53	0.47	0.41
Work to Break	0.18	0.19	0.18	0.12	0.05

3.3. COMPARISONS OF IRRADIATION RESULTS

3.3.1. Comparisons of Mechanical Tests

Comparisons of the relative results of mechanical tests of high dose rate (1485 Gy/h) and low dose rate (81.9 Gy/h) irradiations are given in the following sections.

3.3.1.1. PCU

Comparisons of the relative results of mechanical tests of high dose rate (1485 Gy/h) and low dose rate (81.9 Gy/h) irradiations are given in Figures 36-39. Comparison of the relative data obtained from the two different dose rate irradiations with same total absorbed dose does not result with the exactly same changes in the mechanical properties of the PCU. Although, ultimate tensile strength and strain at break data for low and high dose rate irradiations have comparable data up to 178 kGy absorbed dose, there was a big difference them at absorbed dose of 357 kGy. The half values of the non irradiated PCU's ultimate tensile strength and strain at break values are shown as dotted lines in Figures 36-37 respectively. HVD (tensile strength) was found as 436 kGy from Figure 36 and HVD (elongation) was found as 400 kGy from Figure 37 for the irradiation rate of 81.9 Gy/h.

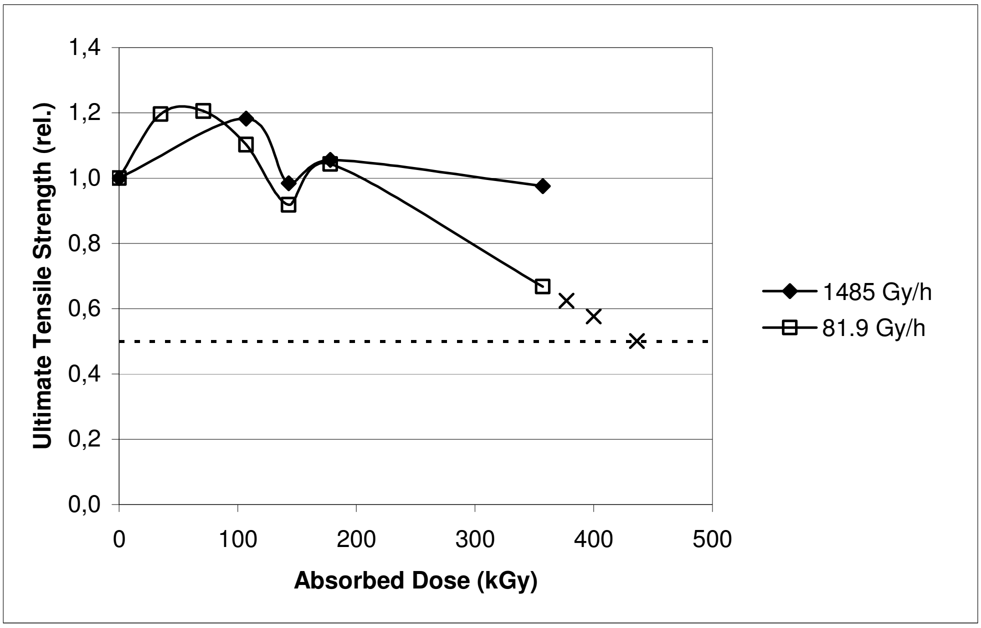

Figure 36. Comparison of PCU ultimate tensile strength (relative)

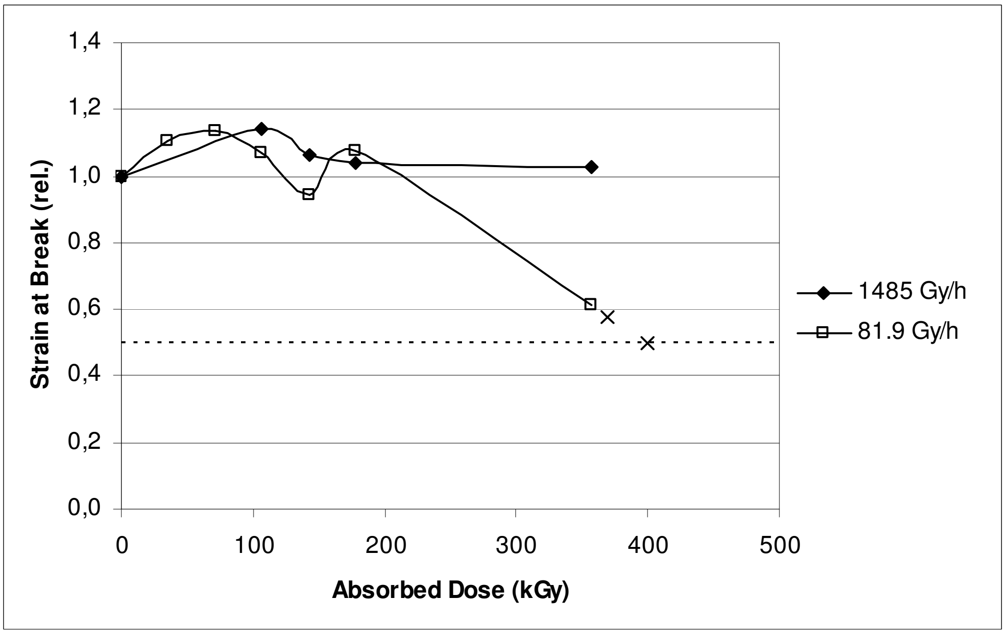

Figure 37. Comparison of PCU strain at break (relative)

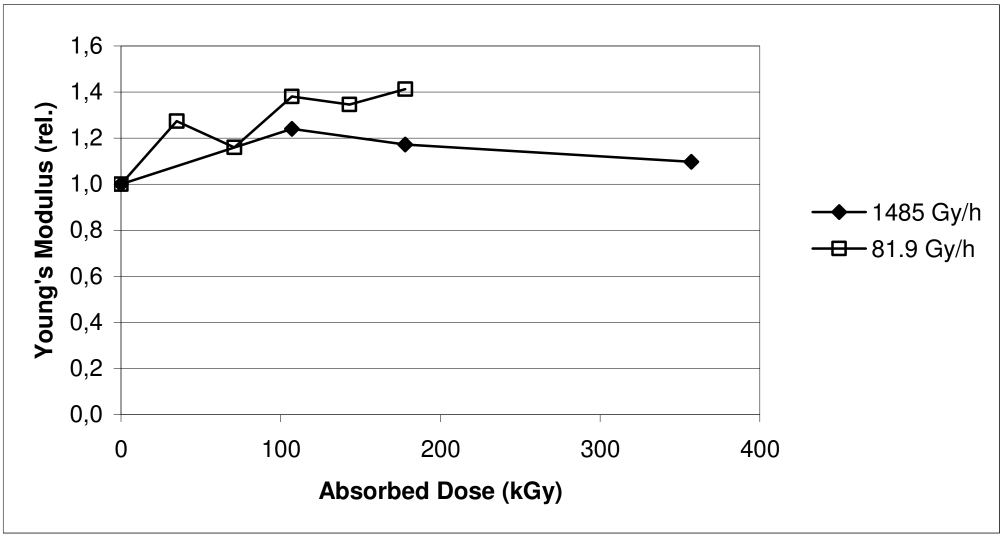

Figure 38. Comparison of PCU Young's Modulus (relative)

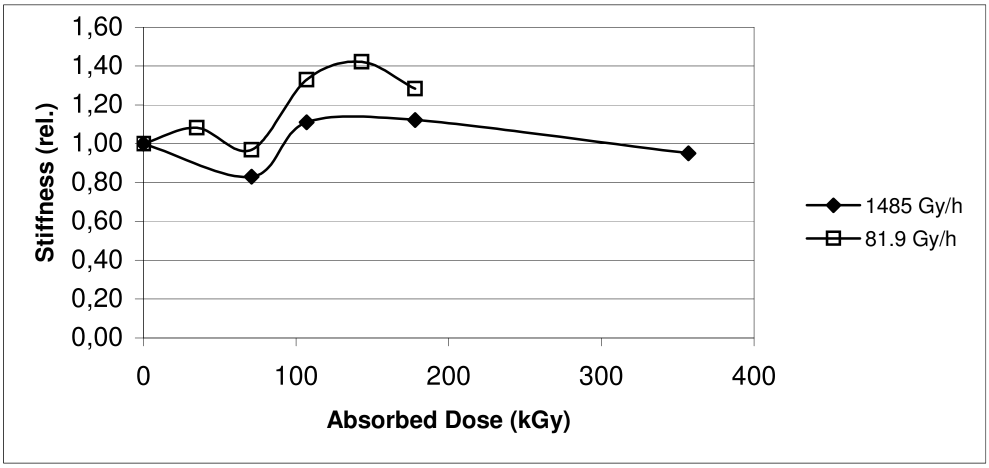

Figure 39. Comparison of stiffness (relative)

3.3.1.2. PBEH

Comparisons of the relative results of mechanical tests of high dose rate (1485 Gy/h) and low dose rate (81.9 Gy/h) irradiations are given in Figures 40-42. Comparison of the relative data obtained from the two different dose rate irradiations with same total absorbed dose does not result with the exactly same changes in the mechanical properties of the PBEH. However, it is worth to mention the tensile strength at yield data at

357 kGy absorbed dose was not deviated from both irradiation rates, and it was not the case for PCU.

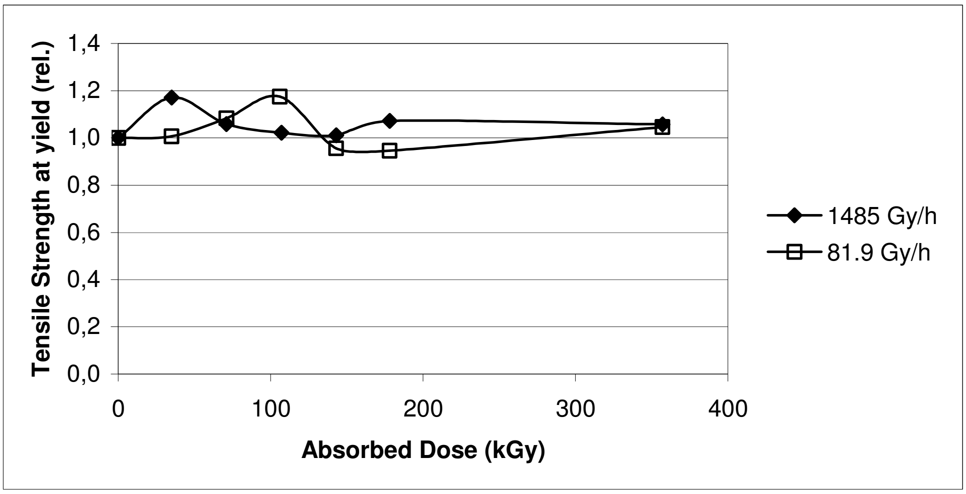

Figure 40. Comparison of PBEH Tensile Strength at yield (relative)

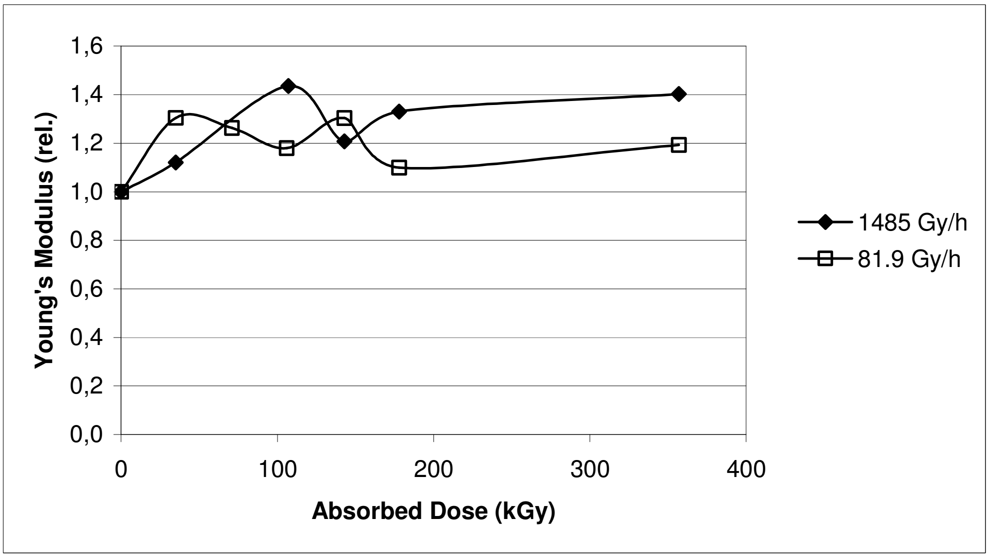

Figure 41. Comparison of PBEH Young’s Modulus (relative)

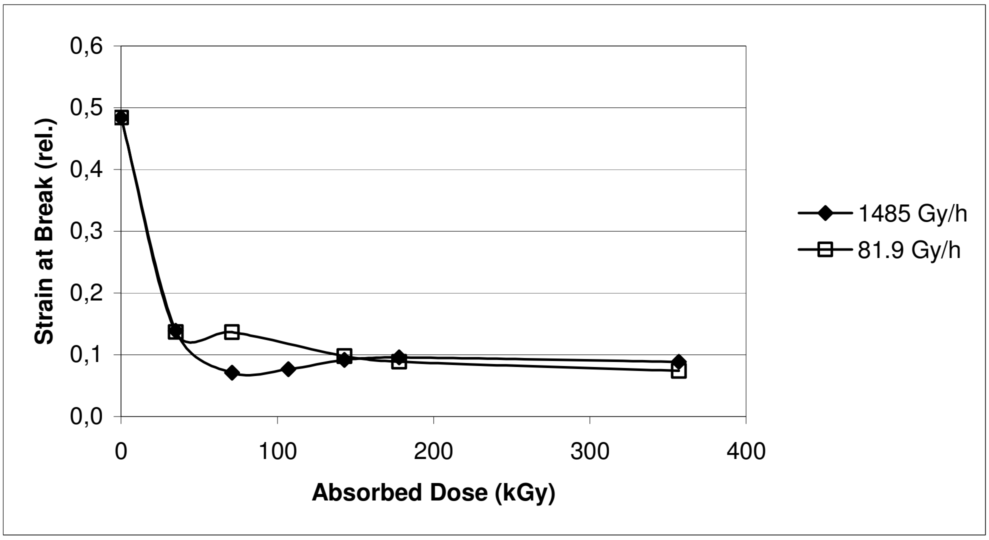

Figure 42. Comparison of PBEH strain at break (relative)

3.3.1.3. PMMA

Comparisons of the relative results of mechanical tests of high dose rate (1485 Gy/h) and low dose rate (81.9 Gy/h) irradiations are given in Figures 43-46. Low and high dose irradiations have not resulted with the same changes in the mechanical properties. However, both of the irradiations followed the parallel patterns for the change of PMMA samples' ultimate tensile strength, which had a peak point in the initial part of the irradiation then started to decrease with the increase of the absorbed dose as shown in Figure 43.

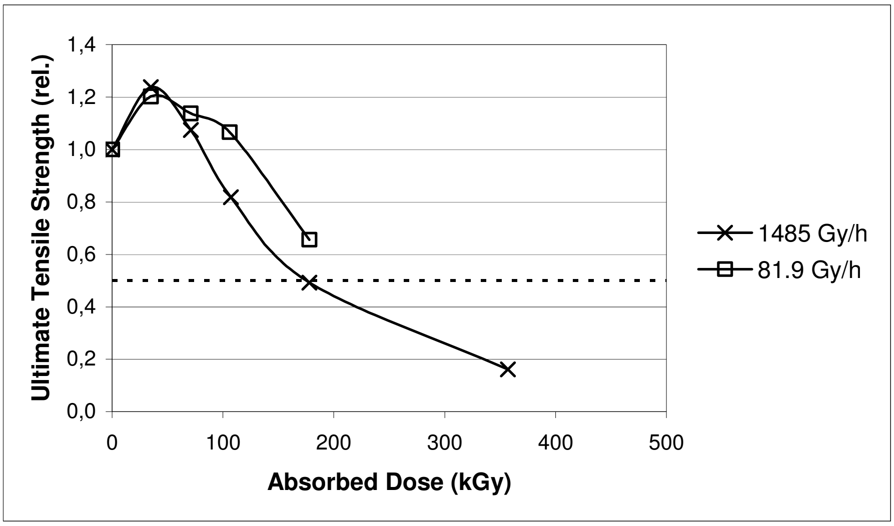

Figure 43. Comparison of PMMA ultimate tensile strength (relative)

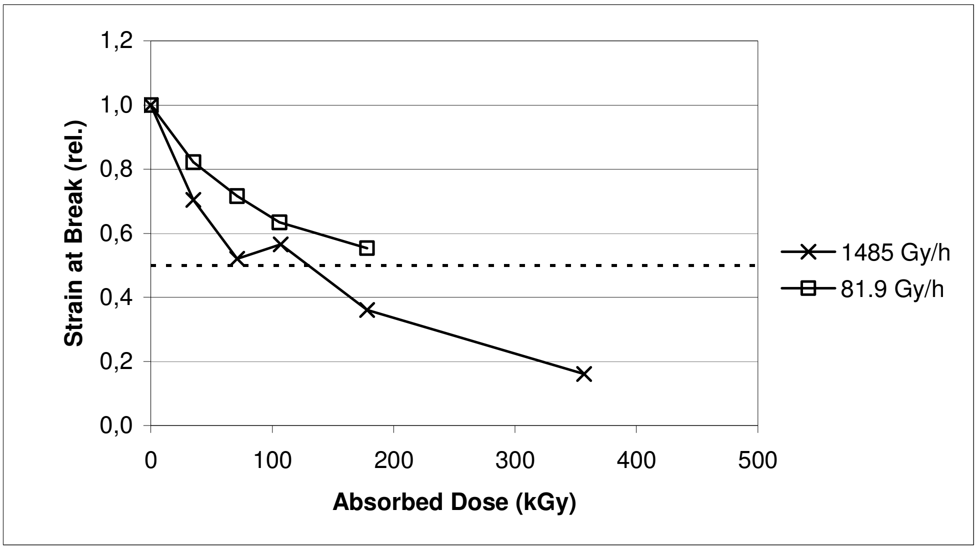

Figure 44. Comparison of PMMA strain at break (relative)

Although neither of the irradiations have resulted in same changes of the mechanical properties, they followed the parallel patterns for the change of Young's Modulus and stiffness, which in both high and low dose rate irradiations had a peak point in the initial part of the irradiation then started to decrease as shown in Figures 45-46.

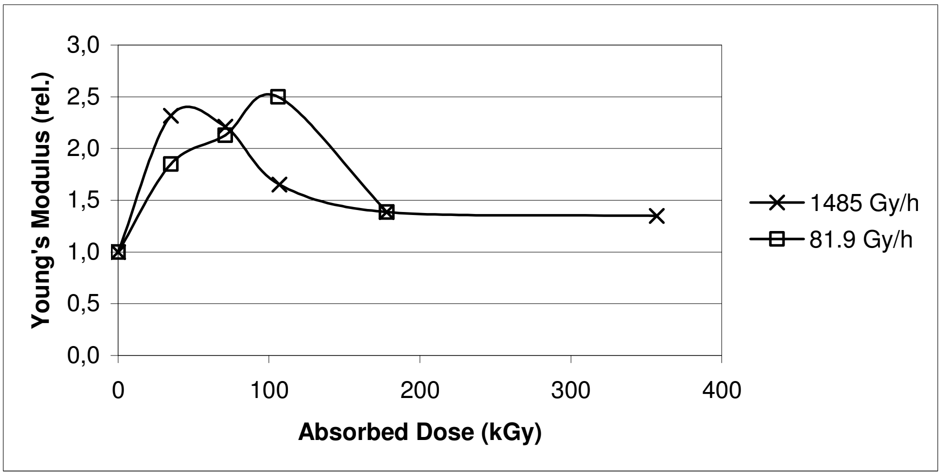

Figure 45. Comparison of PMMA Young's Modulus (relative)

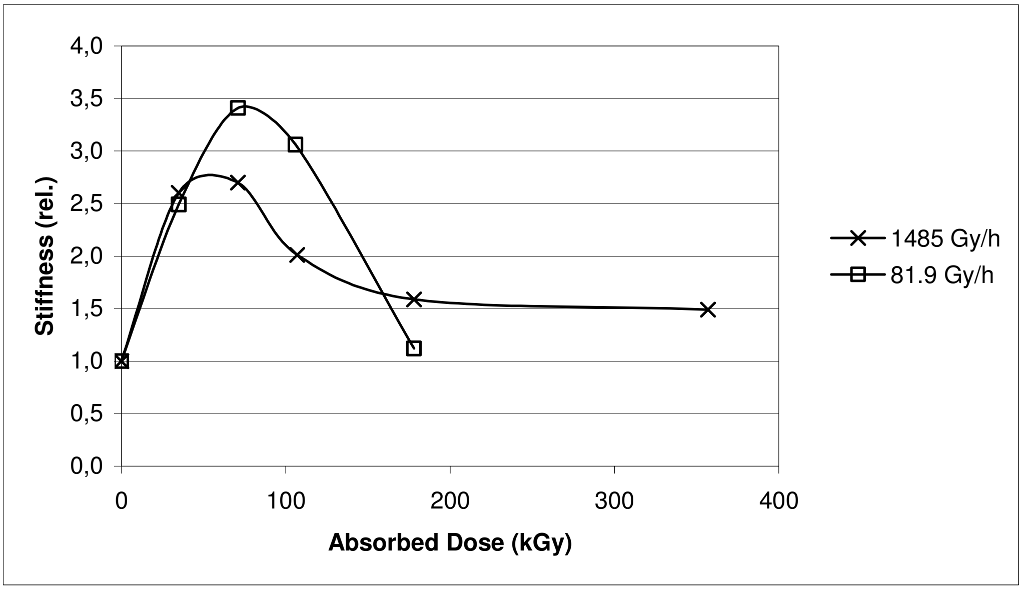

Figure 46. Comparison of PMMA stiffness

3.3.2. Comparisons of TGA Thermograms

3.3.2.1. PCU

Comparisons of TGA thermograms of the PCU with different absorbed doses are given in Figure 47 where it is seen that there is sudden loss of the % weight in a short temperature range for non-irradiated and 107 kGy irradiated PCU. Non-irradiated sample start to degrade at about 266 °C and 107 kGy irradiated sample start to degrade at about 250 °C. The 4590 kGy irradiated sample starts to degrade at about 200 °C.

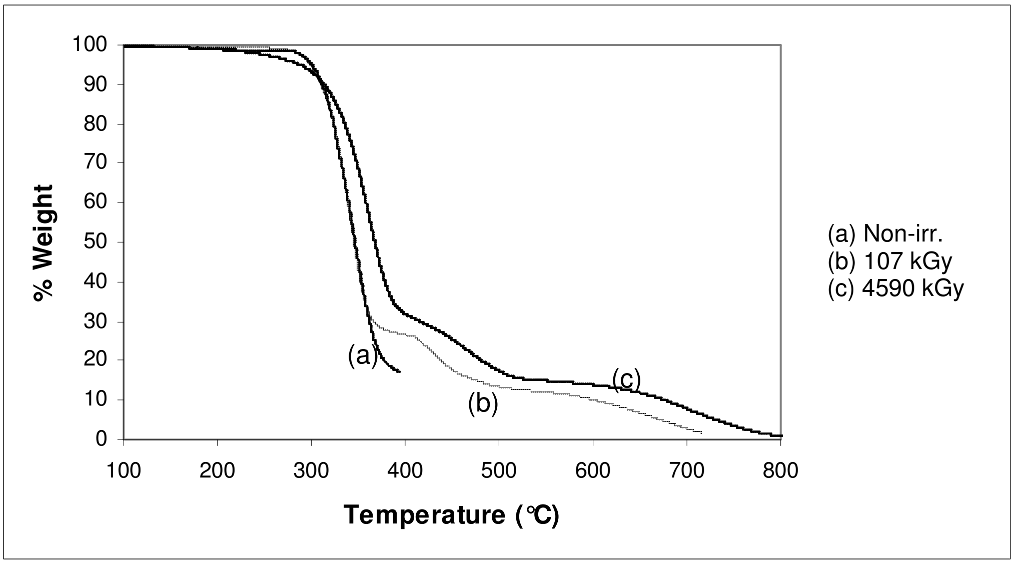

Figure 47. Comparisons of TGA thermograms of PCU

3.3.2.2. PBEH

Comparisons of TGA thermograms of the studied polymers with different absorbed doses are given in Figure 48, where it is seen that non-irradiated PBEH starts to degrade at about 375 °C and 2150 kGy irradiated PBEH starts to degrade at about 325 °C.

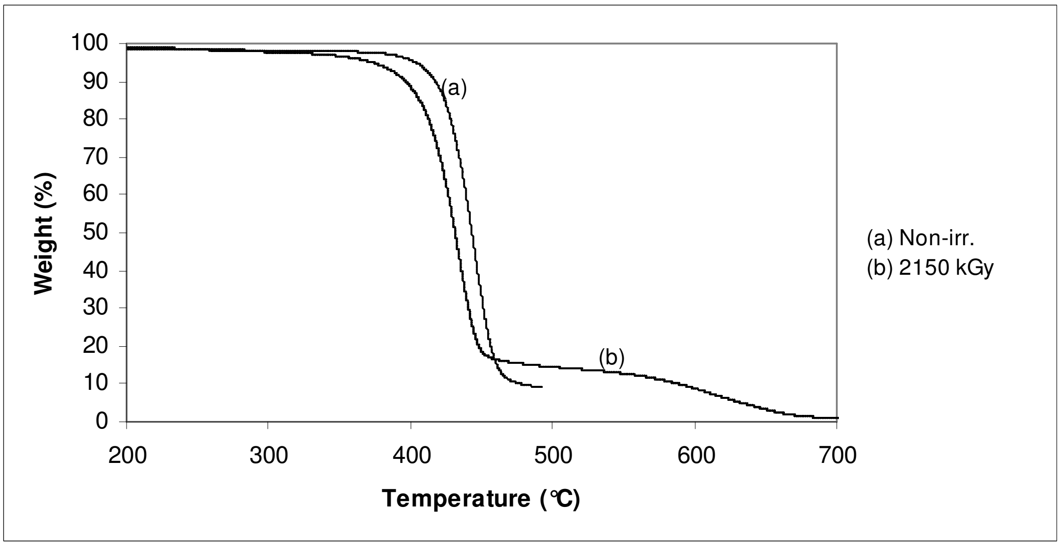

Figure 48. Comparisons of TGA thermograms of PBEH

3.3.2.3. PMMA

Comparisons of TGA thermograms of the studied polymers with different absorbed doses are given in Figure 49 , where it is seen that non-irradiated PMMA starts to degrade at about 215 °C and 107 and 357 kGy irradiated PCU start to degrade at about 205 °C.

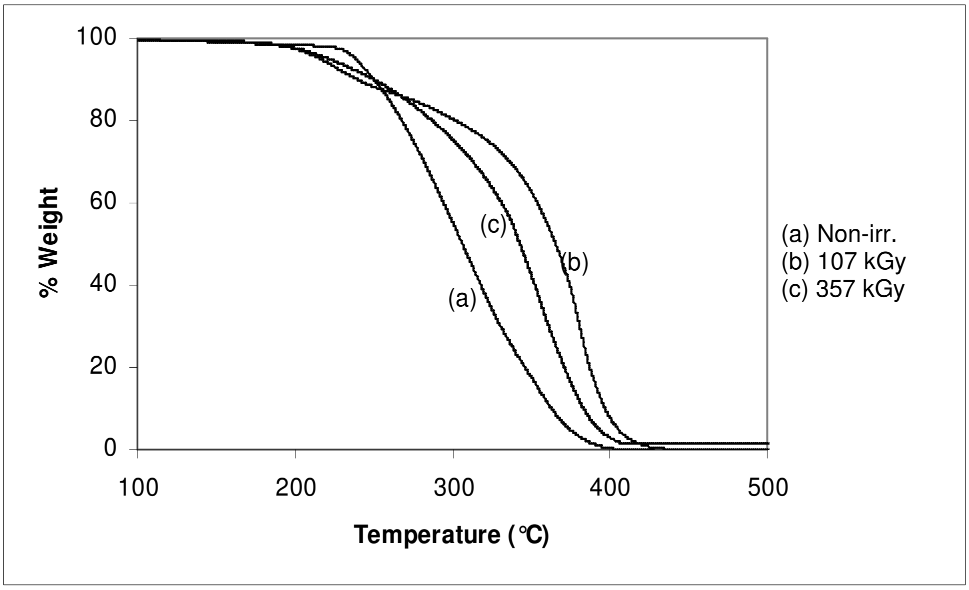

Figure 49. Comparisons of TGA thermograms of PMMA

3.3.3. Comparisons of DSC Thermograms

3.3.3.1. PCU

DSC thermograms for PCU irradiated with different absorbed doses are given in Figure 50.

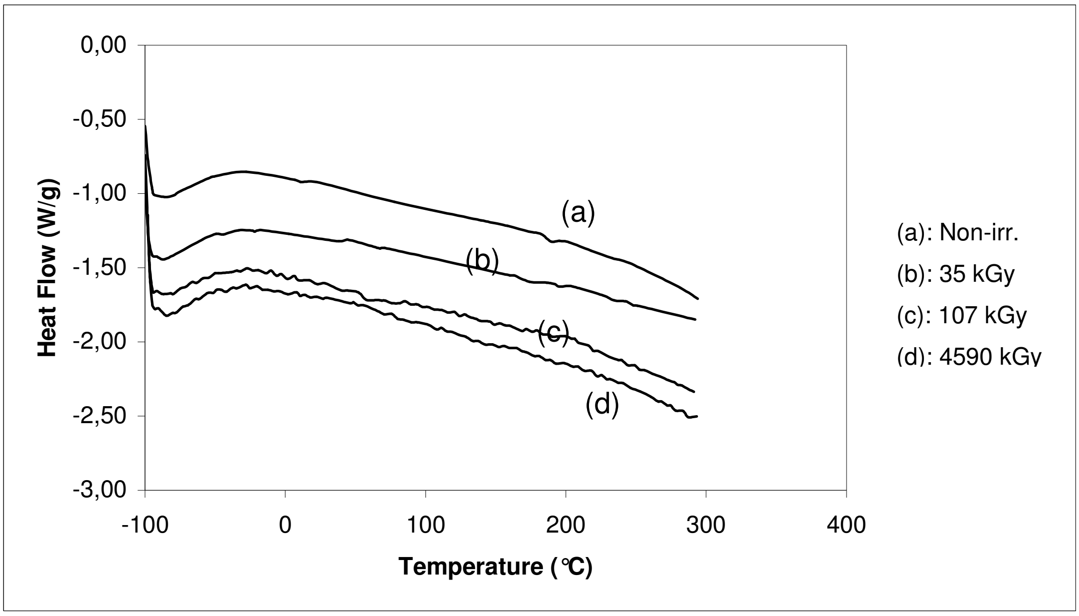

Figure 50. Comparison of DSC thermograms for PCU

3.3.3.2. PBEH

DSC thermograms for PBEH irradiated with different absorbed doses are given in Figure 51.

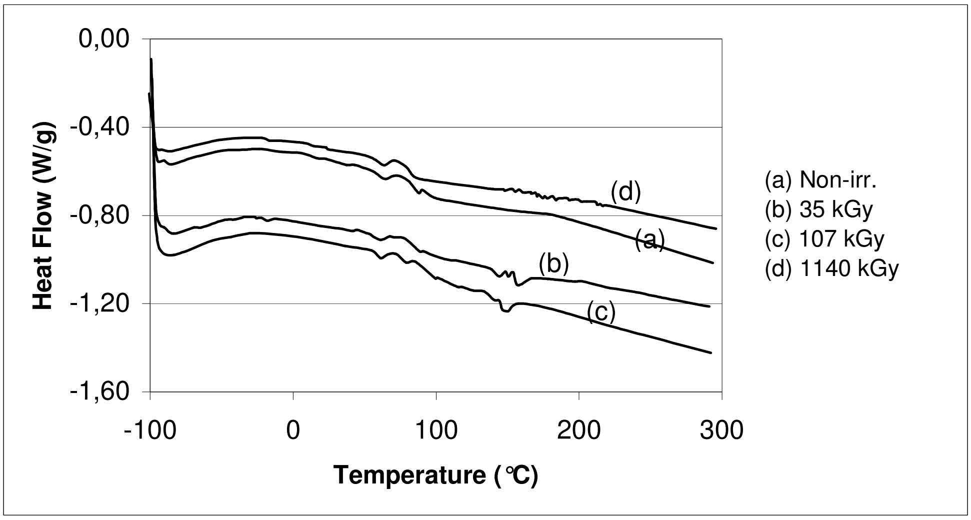

Figure 51. Comparison of DSC thermograms for PBEH

3.3.3.3. PMMA

DSC thermograms for PCU irradiated with different absorbed doses are given in Figure 52.

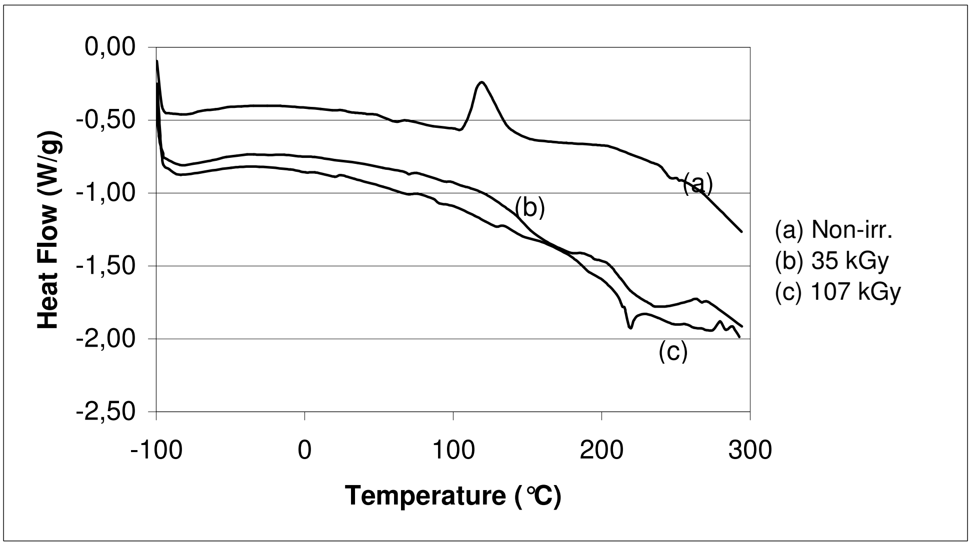

Figure 52. Comparison of DSC thermograms for PMMA

3.3.4. Comparisons of DMA Diagrams

3.3.4.1. PCU

Storage and loss modulus and damping factor are given in the Figures 53-55. The storage modulus (Figure 53) showed considerable change with absorbed dose. The curve for non irradiated sample had maximum storage modulus value at 1.45 GPa at about 20 °C, then decreased slightly to 1.0 GPa up to 78 °C. The rate of decrease was high reaching to zero at 98 °C. When the sample was irradiated, curve shape changed to one stage changes with rate of decrease in storage modulus value increased with total dose.

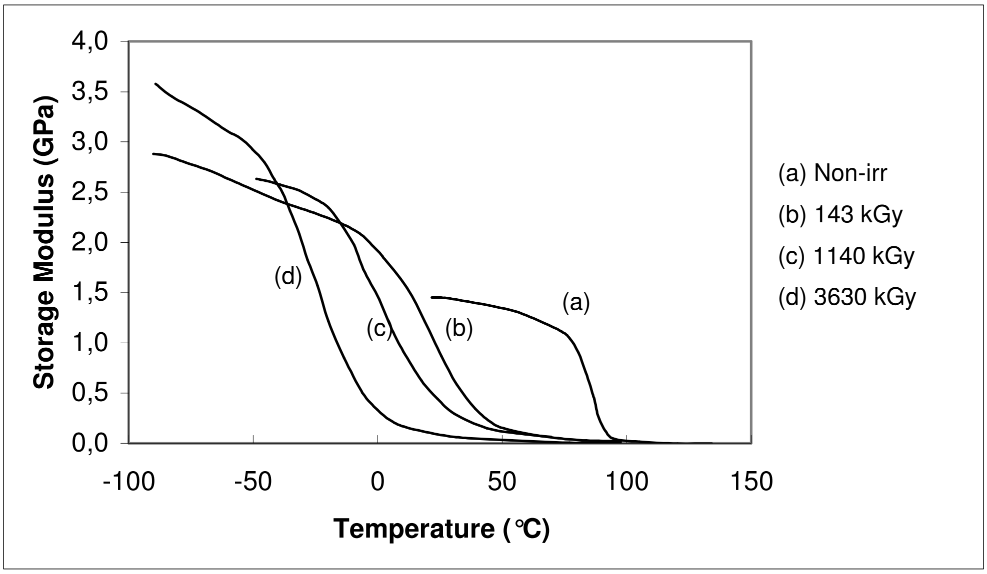

Figure 53. Storage modulus for PCU for HDR irradiations

Peak temperature of loss modulus decreases with irradiation and irradiated samples have loss modulus lower than that of non-irradiated PCU, the loss modulus data are given in Figure 54. Widening of the loss modulus peaks for the irradiated cases showed the change in molecular weight distribution in irradiated cases.

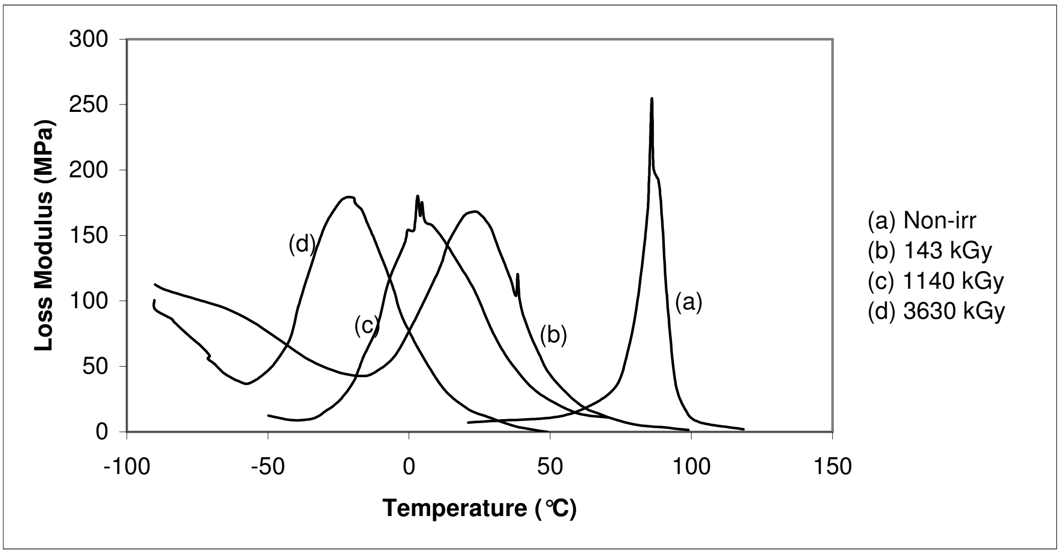

Figure 54. Loss modulus for PCU for HDR irradiations

Peak temperature of damping factor and Tg decreases with irradiation and irradiated samples have damping factor lower than that of non-irradiated, the damping factor data are given in Figure 55.

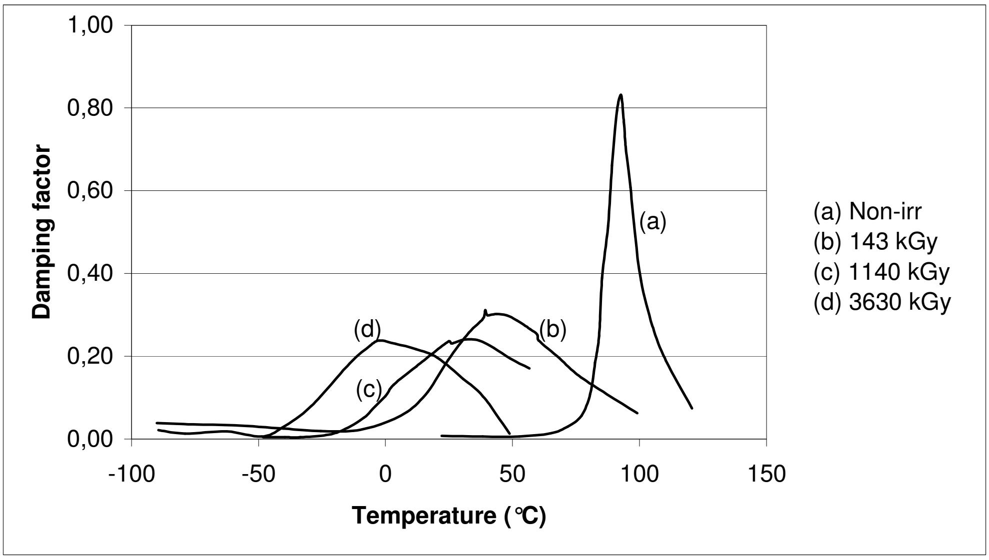

Figure 55. Damping factor for PCU for HDR irradiations

3.3.4.2. PBEH

Storage and loss modulus and damping factor for both low and high dose rate irradiations are given in the Figures 56-58. Storage modulus and loss modulus decreased when irradiated with 1690 kGy dose. Loss modulus peak widened for the case of high dose irradiation showing increase of molecular weight distribution.

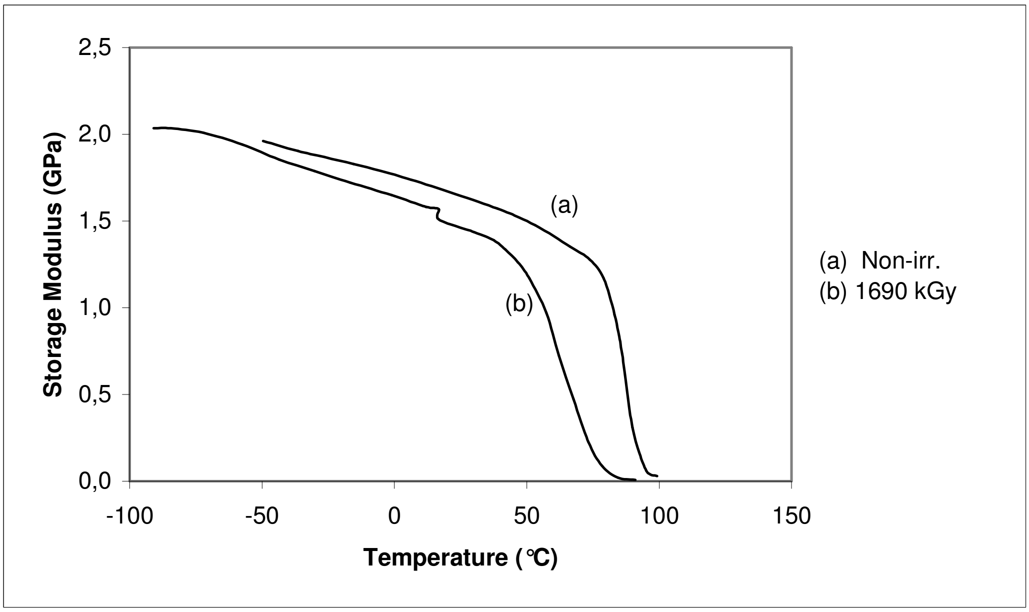

Figure 56. Storage modulus for PBEH for HDR irradiations

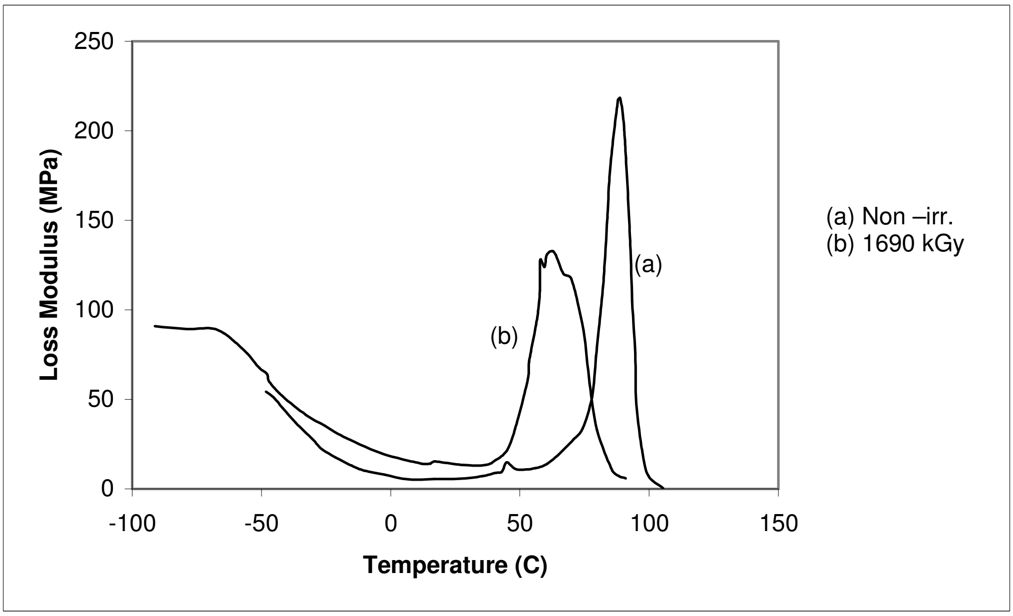

Figure 57. Loss modulus for PBEH

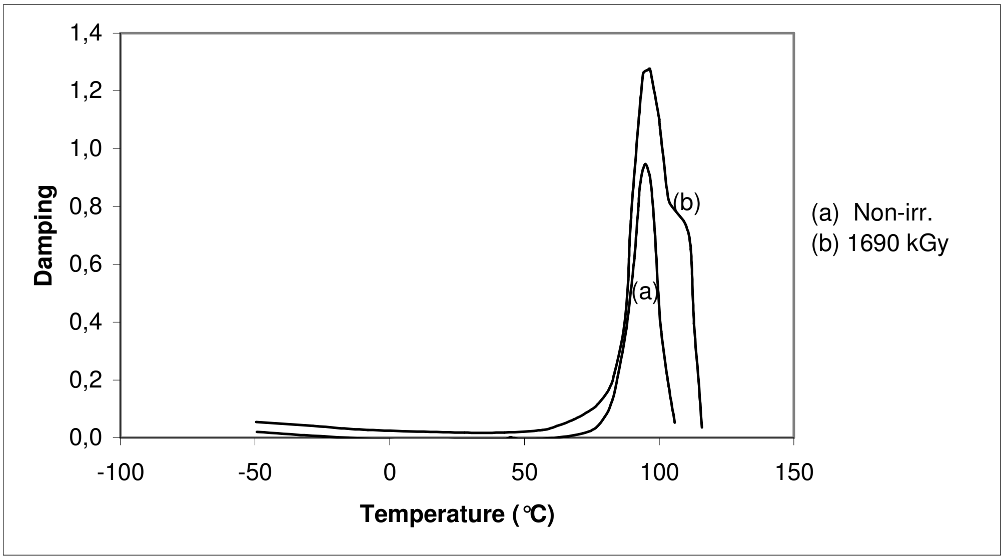

Figure 58. Damping factor for PBEH

3.3.4.3. PMMA

Storage and loss modulus and damping factor for irradiations at different doses are given in Figures 59-61. Storage modulus increases in the initial part of the irradiation and then decreases with the increase of the absorbed dose. Loss modulus decreases with the increase of the absorbed dose as shown in Figure 60. Damping factor decreased with 357 kGy irradiation.

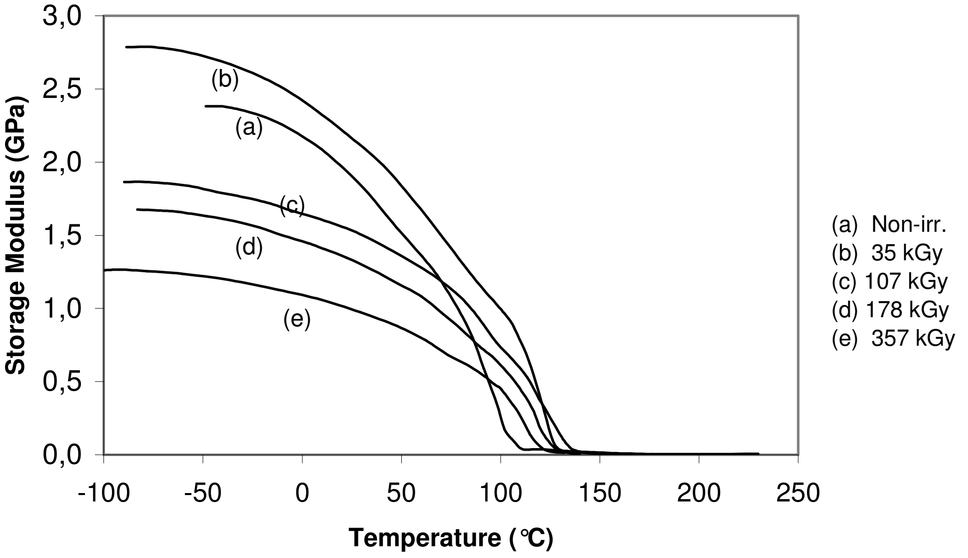

Figure 59. Storage modulus for PMMA

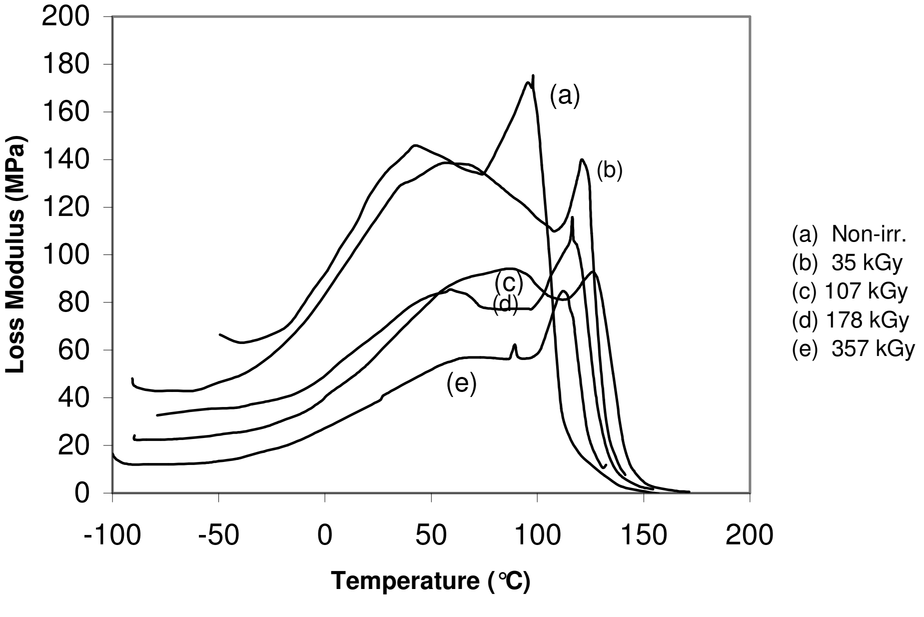

Figure 60. Loss modulus for PMMA

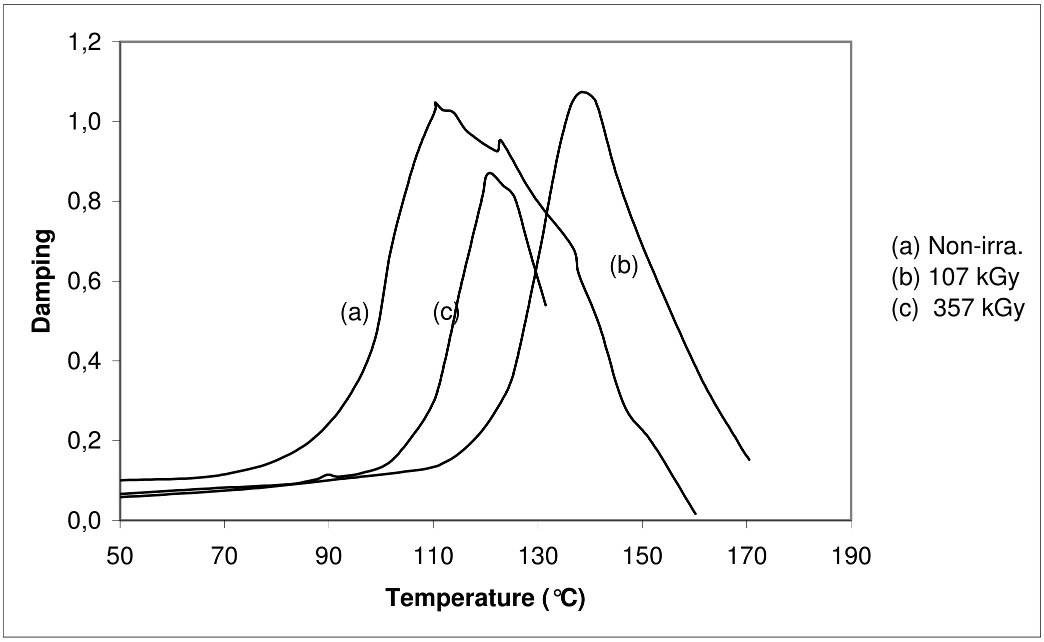

Figure 61. Damping factor for PMMA

3.3.5. Comparisons of ATR-FTIR Spectrums

3.3.5.1. PCU

Comparison of the ATR-FTIR spectrums for the non-irradiated, 107 kGy and 4590 kGy irradiated PCU samples are given in Figure 62. From the ATR-FTIR spectra, it is seen that the same functional groups exist in the non-irradiated and 107 kGy irradiated samples. However, there are three new peaks observed in case of 4590 kGy irradiated sample. These new peaks have the bands of 930 cm^{-1}, 1173 cm^{-1} and 1651 cm^{-1} shown as points A, B and C respectively in Figure 62. The peak at the band of 930 cm^{-1} was assigned to γ(C-H) functional group. The peak at the band of 1173 cm^{-1} was assigned to branched ether, showing the crosslinking in the soft segment. The peak at the band of 1651 cm^{-1} was assigned to free aromatic amine showing the hard segment degradation [38-39].

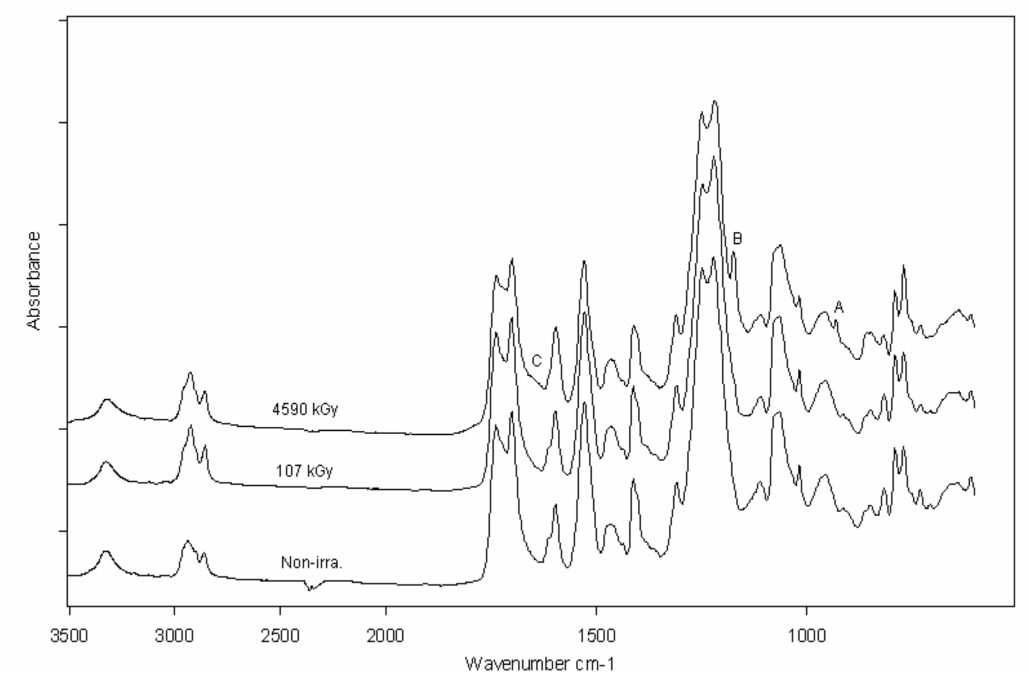

Figure 62. Comparisons of ATR-FTIR spectrums for PCU

FTIR spectrum of gas effluents from the TGA sample of PCU with absorbed dose of 107 kGy (90.8 wt % remained) at 311 °C is given in Figure 63 and FTIR spectrum of gas effluents from the TGA sample of PCU with absorbed dose of 4590 kGy (86.6 wt % remained) at 312.4 °C is given in Figure 64. From the comparison of the Figure 63 and Figure 64, it is observed that same functional groups (CH_2, phenyl, CO and CO_2, carbonyl, -C-O-C- groups) exist in the gas effluents of the 107 kGy and 4590 kGy irradiated samples. However, these FTIR spectrums for the gas effluents of the 107 and 4590 kGy irradiated samples from the TGA-FTIR analyses are different from the that of the same sample irradiated with 107 kGy and 4590 kGy respectively. This may be due to that the irradiation degradation type is not a depolymerization type.

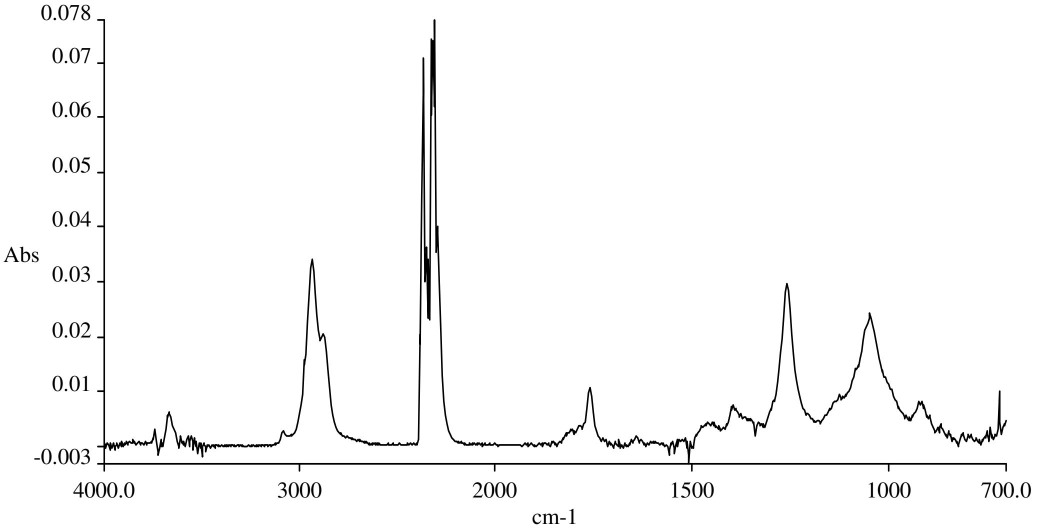

Figure 63. FTIR of PCU gas effluents at 311 °C with 107 kGy dose

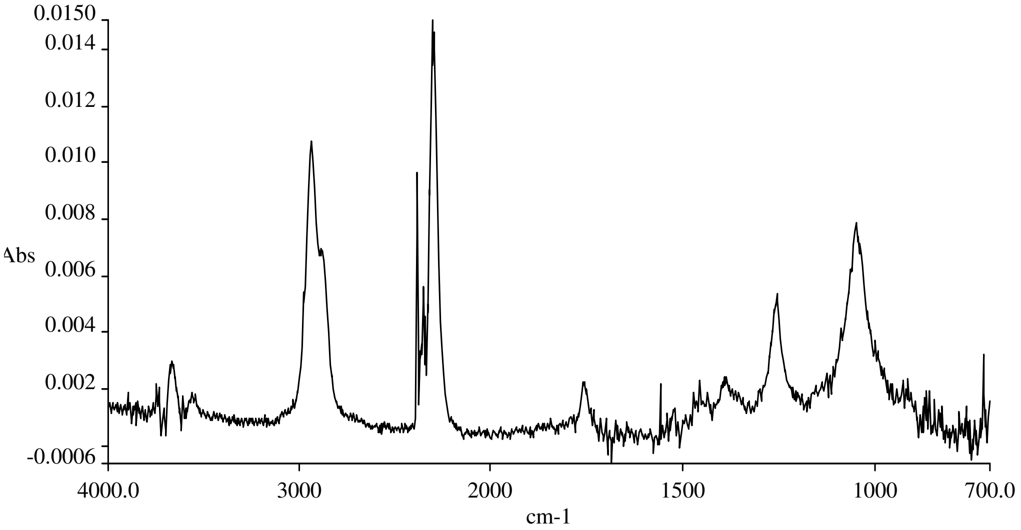

Figure 64. FTIR of PCU gas effluents at 312.4 °C with 4590 kGy dose

FTIR spectrum of gas effluents from the TGA sample of PCU with absorbed dose of 4590 kGy (40.6 wt % remained) at 377 °C is given in Figure 65. The comparison of the two FTIR spectra of the same polymer sample with about 65 °C difference in temperature and 46% weight loss difference(86.6 - 40.6 wt %) indicates that have same functional groups.

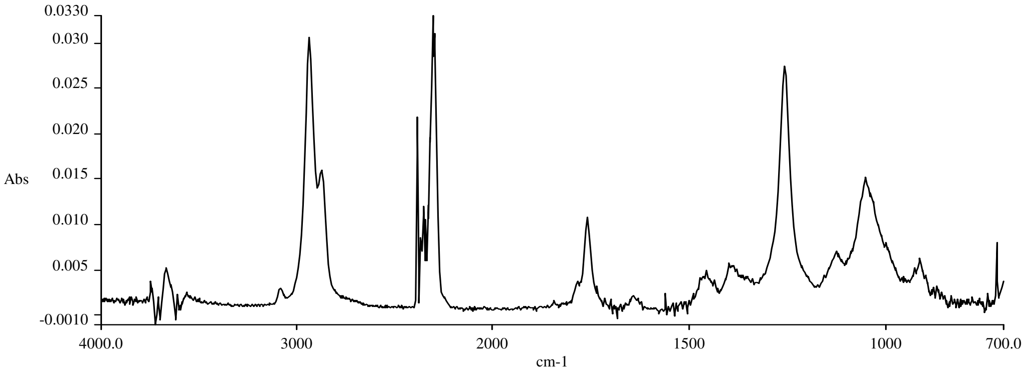

Figure 65. FTIR of PCU gas effluents at 377 °C with 4590 kGy dose

3.3.5.2. PBEH

Comparisons of the ATR-FTIR spectrums for the non-irradiated and 2150 kGy irradiated samples are given in Figure 66. A new peak having the band of 1660 cm^{-1} was observed in case of 2150 kGy irradiated sample and this peak indicates oxidation reactions [20].

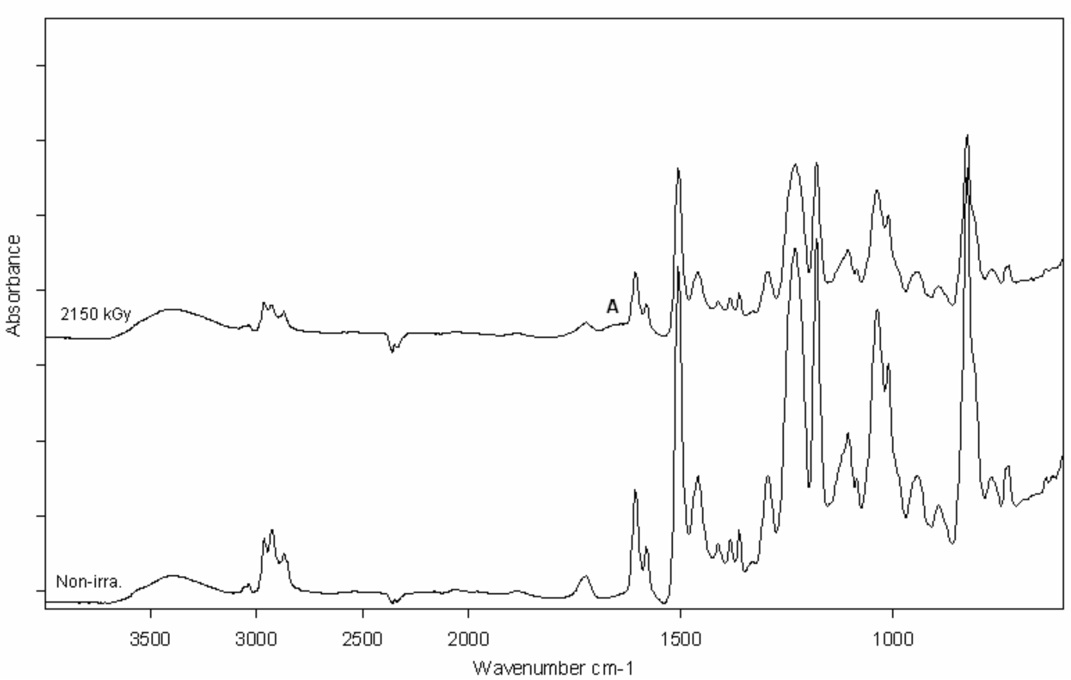

Figure 66. Comparisons of ATR-FTIR spectrums for PBEH

FTIR spectrum of gas effluents from the TGA sample of PBEH with absorbed dose of 2150 kGy (92.5 wt % remained) at 388 °C is given in Figure 67 and that of at 424 °C (64.6 wt % remained) is given in Figure 68. The comparison of the two FTIR spectra of the same polymer sample with 36 °C difference in temperature and about 28% weight loss difference (92.5 - 64.6 wt %) indicates that they have same functional groups. However, the FTIR spectrum for gas effluents of the 2150 kGy irradiated sample from the TGA-FTIR analysis is different from the FTIR spectra of the same sample which is shown in Figure 66. This may be due to that the irradiation degradation type is not a depolymerization type for PBEH.

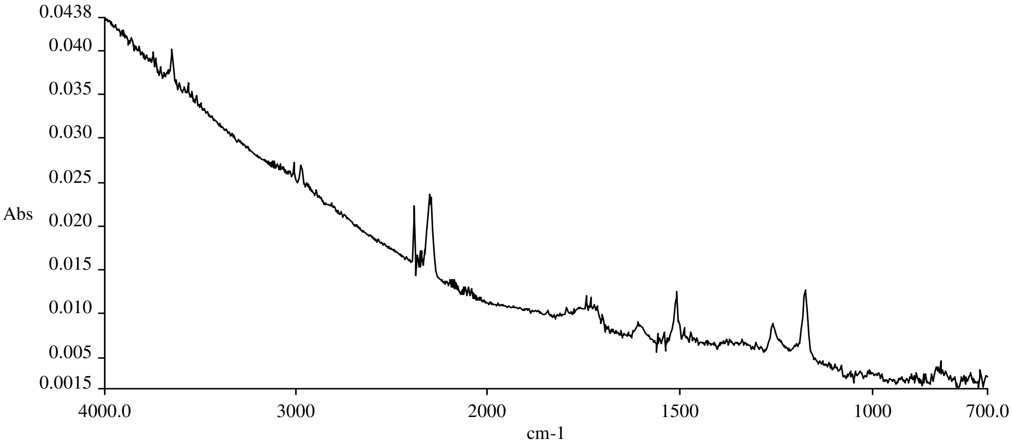

Figure 67. FTIR of PBEH gas effluents at 388 °C with 2150 kGy dose

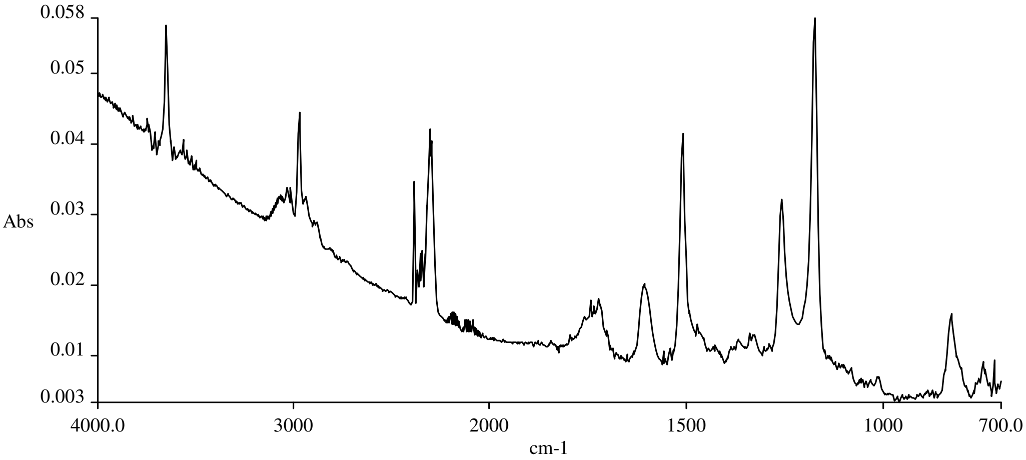

Figure 68. FTIR of PBEH gas effluents at 424 °C with 2150 kGy dose

3.3.5.3. PMMA

Comparison of the ATR-FTIR spectrums for the non-irradiated and 357 kGy irradiated PMMA samples are given in Figure 69. Typical IR spectral bands of C-O stretching (1732 cm^{-1}), CH_2 deformation (1436 cm^{-1}), CH_3 symmetrical deformation (1386 cm^{-1}), C-C(C=O)-O and O-C-C-CH_3 in -CH_2-CH(CH_3)-CH_2-(1242 and 1271 cm^{-1}) for PMMA were observed [40]. Moreover, peaks with bands of 987 and 966 cm^{-1} assigned to vinyl and t-vinyldiene functional groups exist in the ATR-FTIR spectra, existence of these two peaks indicates main chain scission.

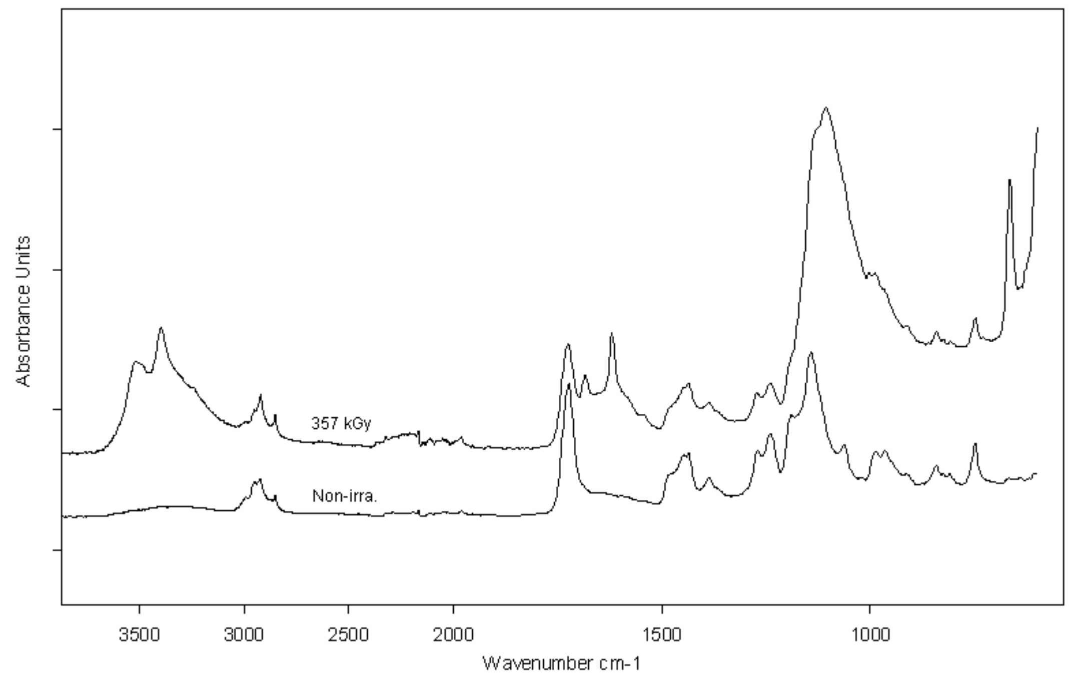

Figure 69. Comparisons of ATR spectrums for PMMA

FTIR spectrum for PMMA gas effluents at 233 °C with absorbed dose of 357 kGy (93 wt% remained) is given in the Figure 70 where typical IR spectra of methyl methacrylate and IR bands of CO and CO_2 groups are seen, indicating that a depolymerization type of degradation.

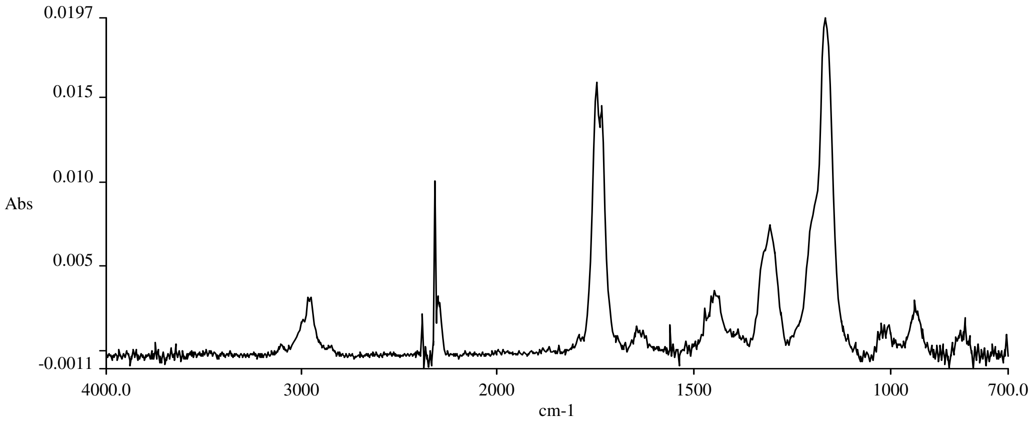

Figure 70. FTIR of PMMA gas effluents at 233 °C with 357 kGy dose

CHAPTER IV

DISCUSSIONS

Selected polymers have been investigated based on the radiation stability criteria and their possible use in the radioactive waste immobilization process was studied. The important criteria for the selection of the media for final disposal of radioactive waste are listed below.

- Effective immobilization
- Effective radiation stability
- Good leaching characteristics
- Good mechanical properties after irradiation
- Not any biodegradation after disposal

In this study, gamma irradiation degradation has been considered only, although radioactive waste would be emitting other types of ionizing radiations depending on the waste characteristics. However, in this study mainly low and intermediate–short-lived waste category has been considered and this type of waste category has limited amount of alpha emitting radionuclides.

Decrease of mechanical properties of selected polymers in high dose irradiations shows that the degradation mechanism is mainly chain scission. All of the polymers irradiated, showed an increase in tensile strength in the initial part of irradiation after which they degraded. In the initial part of irradiation, polymers have a more packed structure due to the chain scission. However, as the irradiations continued the scission lead the continuous degradation of polymer chains where the mechanical properties are deteriorated. Molecular weight affects the mechanical properties strongly and decrease of the mechanical properties in high dose irradiation clearly shows the loss in the molecular weight of the polymers due to chain scission.

Irradiation of the selected polymers caused the change in the dynamic mechanical properties of the polymers. Storage modulus decreases at high dose irradiations due to the degradation of polymer chains via chain scission. Loss modulus peaks were widened for the cases of PCU and PBEH due to change in both molecular weight and molecular weight distribution during chain scission. Tg was decreased in the high dose irradiations for PCU. However, since the PMMA have not been irradiated in very high dose region, the change of Tg of PMMA could not be observed effectively in high dose irradiations.

In the TGA analyses, it was observed that the irradiated samples start to degrade at lower temperatures compared with the non-irradiated ones due to degradation.

Dose rate along with thickness of polymer is an important parameter, when studying the degradation of polymers under ionizing radiation with/without oxygen.

From the ATR-FTIR studies, it was seen that there is no oxidation effect in the high dose rate irradiation of PCU. Same functional groups were seen in the spectra in addition with some degradation products showing that the diffusion induced oxidation is not the potential mode of degradation. However, the low dose rate irradiated PCU showed very earlier degradation and the possible reason could be the diffusion induced oxidation caused homogeneous radiation oxidation of PCU in low dose rate irradiation case. One of the important parameter for the homogeneous radiation oxidation is the thickness of the polymer being irradiated and thickness of PCU samples allowed homogeneous oxidation in the case of low dose rate irradiation.

Radiation resistance of PBEH has been decreased due to the non-usage of solidifying agent (hardener) the radiation resistance reported in the literature is 10 MGy for the hardener mixed case [22].

The PBEH showed comparable change in the mechanical properties with the high and low dose rate short term irradiations, this might be due to the heterogeneous oxidation on the surface of the samples and very low diffusion of oxygen into polymer. However, in the long term high dose irradiated PBEH case, the tensile strength shows relatively small change in up to 622 kGy where it is starts to decrease. This may possibly be due to the increased rate of oxygen diffusion. PMMA showed comparable change in the mechanical properties with the high and low dose rate short term irradiations, this might be due to the heterogeneous oxidation on the surface of the samples and very low diffusion of oxygen into polymer.

In radioactive waste management, active institutional control period is set as 300 years for low and intermediate-short lived radioactive waste category' disposal facilities [41]. Total dose to be absorbed by the waste matrix for 300 years can be calculated from the following equation, where TD is Total Dose (kGy), DR_o is initial dose rate (kGy/year), t is time period (year) and k is decay constant [ln(2)/(half-life of the radionuclide)],

$$TD = \int_0^T DR_o \times e^{-kt} dt \tag{4.1}$$

Integration of the equation (4.1) gives,

$$TD = \frac{DR_o}{k} \times (1 - e^{-kT}) \tag{4.2}$$

Dose rate of low and intermediate level radioactive waste varies from 1 to 31000 mGy/h and most of them are between 100-1000 mGy/h [42]. It was experimentally observed that PBEH can resist up to 1100 kGy. Since HVD (elongation) is more sensitive measure of the degradation than that of tensile strength [16], elongation data were extrapolated. Extrapolation of elongation data of the experimental results showed that the PCU can resist up to about 7500 kGy (Figure 12), and PMMA can resist up to about 450 kGy (Figure 32).

Assuming the half-life of the radioactive waste is 30 years (the maximum half-life of low and intermediate–short lived waste category) initial dose rate that would lead a total dose of 7500 kGy to PCU during 300 years period can be calculated from Equation (4.2) as 19.8 Gy/h theoretically. Based on this data a decay graph, in log-log scale, of the initial dose rate of 19.8 Gy/h over 300 years can be constructed as given in Figure 71 and the cumulative dose is also shown on the line. Since PCU is a biostable material, it meets the criteria of biostability of the waste matrix.

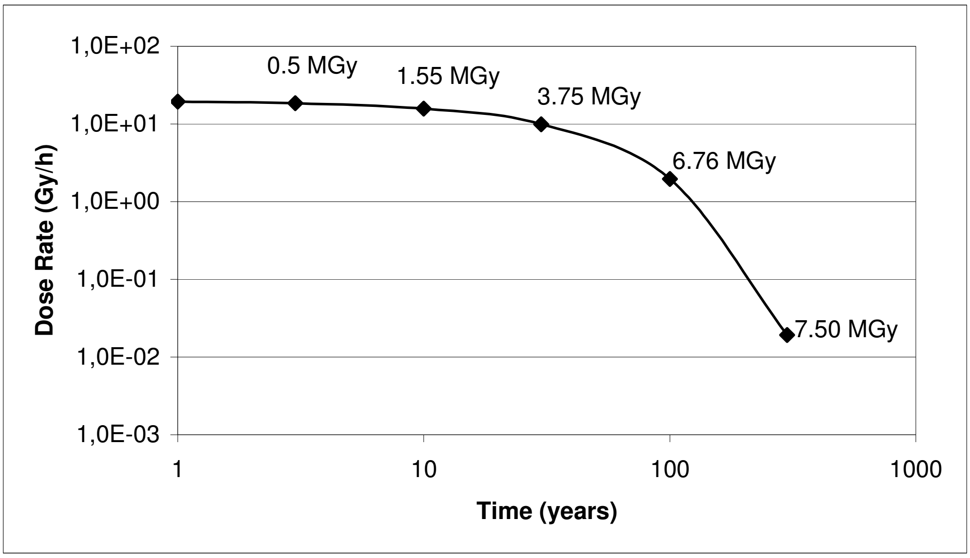

Figure 71. Dose rate and cumulated dose to the PCU over 300 years

Based on same assumptions, initial dose rate that would lead total dose of 1100 kGy to PBEH during 300 years period can be calculated from equation (4.2) as 2.9 Gy/h theoretically. A decay graph of the initial dose rate of 2.9 Gy/h over 300 years can be constructed as given in Figure 72 and the cumulative dose is also shown on the line.

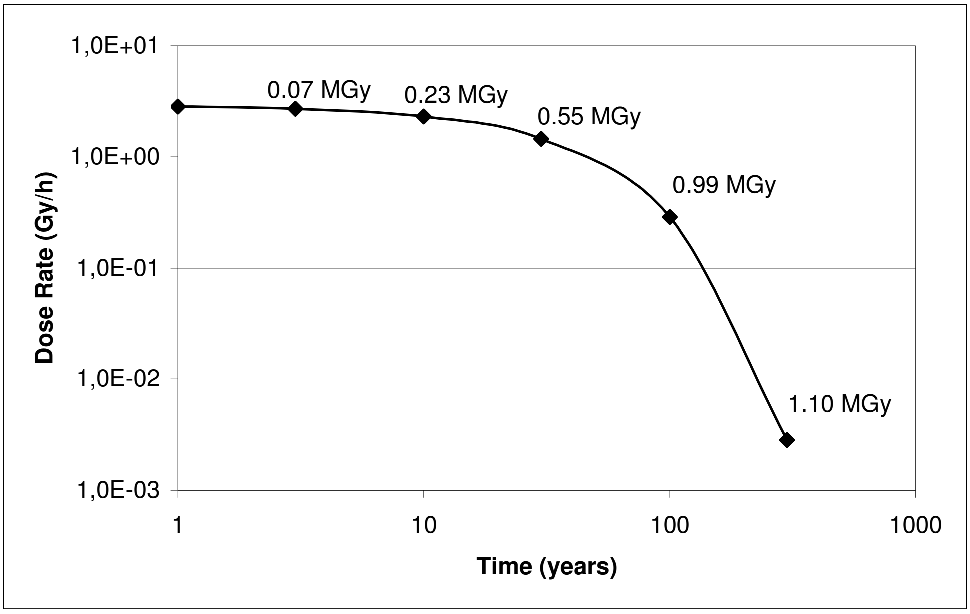

Figure 72. Dose rate and cumulated dose to the PBEH over 300 years

Based on same assumptions, initial dose rate that would lead total dose of 450 kGy to PMMA during 300 years period can be calculated from equation (4.2) as 1.3 Gy/h theoretically. A decay graph of the initial dose rate of 1.3 Gy/h over 300 years can be constructed as given in Figure 73 and the cumulative dose is also shown on the line.

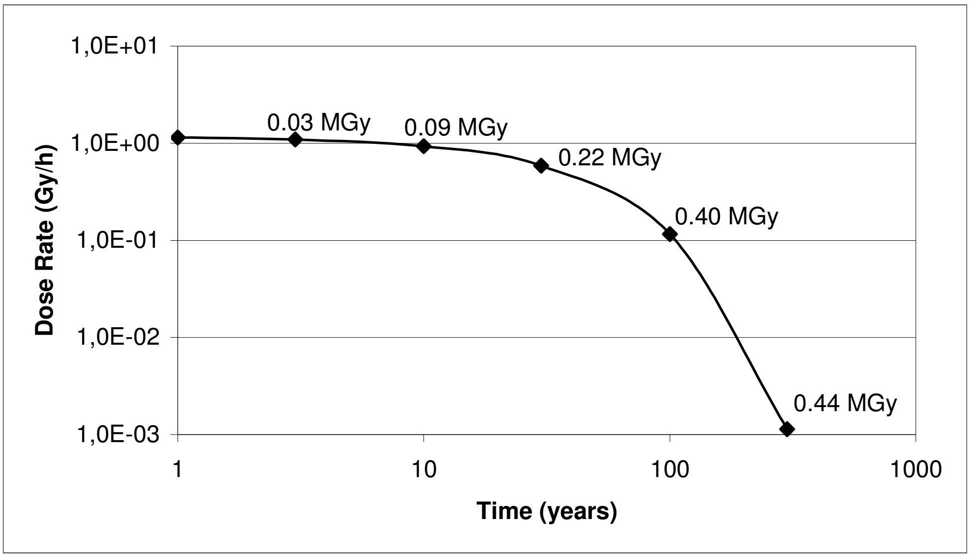

Figure 73. Dose rate and cumulated dose to the PMMA over 300 years

PMMA does not have high radiation stability rather it is moderate; however IPN's of PCU and PMMA may also be investigated for possible use in radioactive waste management, since Frisch et. al. [43] concluded that the full IPN's of PCU and PMMA exhibits a maximum tensile strength at a certain composition, and superior solvent and heat resistance compared to pseudo IPN's, linear blends and the pure crosslinked PCU and PMMA. Moreover, PMMA can also be used for the conditioning of the low level radioactive waste.

CHAPTER V

CONCLUSIONS

Polymers having wide range of applications can also be used in the radioactive waste management. PCU and PBEH can possibly be used in the radioactive waste management, as they are radiation stable polymers. PMMA has moderate resistance to the irradiation and cannot be used effectively for intermediate level radioactive waste embedding. However, it can be used for the conditioning of low level radioactive waste.

Irradiation rate is an important parameter and it is well known that the irradiation rate lead different effects for the same polymer with equal amount of total absorbed dose. If the irradiations are made open to the atmosphere, the diffusion limited oxidation became a critical factor for the radiation-induced effects on the polymers.

The following conclusions can be made for each of the polymer studied.

Biostability of the PCU make it a good option for being used as a media for waste immobilization. Random chain scission is the possible degradation mechanism at very high irradiation doses. Storage modulus, Tg and α relaxation temperature decreases with higher absorbed dose. Tensile strength and toughness had a peak point with irradiation, after which they decreased with higher absorbed doses. High and low dose rate irradiations, with same total absorbed dose delivered to the samples, have not resulted with the same relative change in the mechanical properties. HVD (tensile strength) of 6010 kGy and HVD (elongation) of 4010 kGy (at dose rate of 1.54 kGy/h) were found from the interpolation of the experimental results. However, HVD (elongation) was found as 400 kGy and HVD (tensile strength) was found as 436 kGy for the irradiation rate of 81.9 Gy/h.

Non-irradiated sample start to degrade at about 266 °C and 107 kGy irradiated sample start to degrade at about 250 °C. The 4590 kGy irradiated sample start to degrade at about 200 °C. Tangent loss decreases and the PCU become more stiff and rigid via irradiation and this result is in agreement with the mechanical test results. Change of PCU's color from transparent to brown was observed.

PBEH is a radiation resistant material. Random chain scission is the possible degradation mechanism in high dose irradiated samples. High and low dose rate irradiations, resulting same total absorbed dose to the samples, have not resulted with the same relative change in the mechanical properties. Tensile strength had a peak point with irradiation after which it has decreased with higher absorbed dose delivered and toughness decreased continuously via irradiation. HVD (elongation) of 29 kGy and HVD (tensile strength) of 885 kGy were found from the interpolation of the experimental results of the high dose rate irradiation at 1485 Gy/h. HVD elongation is low compared to HVD tensile strength this is due to the sudden decrease in the elongation at break in the irradiated case. However, interpolation results for the HVD (elongation) of both low and high dose rate irradiations were same. From TGA, it was seen that the non–irradiated PBEH starts to degrade at 375 °C, but the 2150 kGy irradiated PBEH starts tp degrade at about 325 °C. This data show clearly the radiation degradation. In the non-irradiated and at relatively low dose irradiations case neck formation was observed and samples showed ductile properties, however for the case of samples irradiated with 1.1 MGy gamma dose, there were no neck formation and the samples became brittle. Change of PBEH's color from transparent to yellow was observed via irradiation.

PMMA have moderate radiation resistance. Degradation follows a depolymerization mechanism. High and low dose rate irradiations resulting same total absorbed dose to the samples have not resulted with the same relative change in the mechanical properties. Tensile strength decreased with high irradiation dose. Moreover, storage modulus was decreased with the increase of the absorbed dose for the irradiated PMMA. HVD (elongation) of 148 kGy and HVD (tensile strength) of 178 kGy were found from the experimental results of high dose rate irradiations with dose rate of 1485 Gy/h. From the TGA curve, it was seen that the non–irradiated PMMA starts to degrade at 215 °C, but the 107 and 357 kGy irradiated PMMA start to degrade at about 175 °C.

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NOMENCLATURE

abs. dose	:	Absorbed dose
ATR	:	Attenuated total reflectance
DMA	:	Dynamic mechanical analysis
DSC	:	Differential scanning calorimetry
HDR	:	High dose rate
LDR	:	Low dose rate
per.	:	Percentage
PBEH	:	Poly(bisphenol-a-epichlorohydrin)
PCU	:	Poly(carbonate urethane)
PMMA	:	Poly(methyl methacrylate)
TS	:	Tensile strength
TGA	:	Thermal gravimetric analysis

APPENDIX A

DOSE RATE OF HIGH DOSE IRRADIATION SOURCE

Change in the dose rate of high dose irradiation source is given in Table 13.

Table 13. Dose rate of high dose irradiation source

Period	Dose rate (kGy/h)
1-15 January 2005	1.63
16-31 January 2005	1.62
1-15 February 2005	1.61
16-28 February 2005	1.60
1-15 March 2005	1.60
16-31 March 2005	1.59
1-15 April 2005	1.58
16-30 April 2005	1.57
1-15 May 2005	1.56
16-31 May 2005	1.55
1-15 June 2005	1.54
16-30 June 2005	1.54
1-15 July 2005	1.53
16-31 July 2005	1.52
1-15 August 2005	1.51
16-31 August 2005	1.50
1-15 September 2005	1.49
16-30 September 2005	1.49
1-15 October 2005	1.48
16-31 October 2005	1.47
1-15 November 2005	1.46
16-30 November 2005	1.45
1-15 December 2005	1.45
16-31 December 2005	1.44

APPENDIX B

CURRICULUM VITAE

PERSONAL INFORMATION

Surname, Name: Özdemir, Tonguç

Nationality: Turkish (TC)

Date and Place of Birth: 30 August 1975, Malatya

Marital Status: Married

e-mail: tonguc.ozdemir@taek.gov.tr

EDUCATION

Degree	**Institution**	**Year of Graduation**
MS	METU Chemical Engineering	1999
BS	METU Chemical Engineering	1996
High School	Malatya High School	1991

WORK EXPERIENCE

Year	Place	Enrollment
1999-Present	Turkish Atomic Energy Authority	Engineer
1996-1999	METU Department of Chemical Engineering	Research Assistant

FOREIGN LANGUAGES

English

PUBLICATIONS

1) Özdemir T.,Öztin C., Kıncal N. S., Treatment of Waste Pickling Liquors: Process Synthesis and Economic Analysis, Chem. Eng. Comm., 193:548–563, 2006