DEGRADATION OF EPDM VIA GAMMA IRRADIATION AND POSSIBLE USE OF EPDM IN RADIOACTIVE WASTE MANAGEMENT

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ABSTRACT

DEGRADATION OF EPDM VIA GAMMA IRRADIATION AND POSSIBLE USE OF EPDM IN RADIOACTIVE WASTE MANAGEMENT

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In this study, degradation of ethylene propylene diene terpolymer (EPDM) via gamma radiation and possible use of EPDM in radioactive waste management were investigated. In estimation of radiation stability and possible use of EPDM in radioactive waste management, dose rate (both high and low), irradiation environment (in water and in air), additives (carbon black, zinc oxide, plasticizer) used in formulation, peroxide type (either aliphatic or aromatic) and content were parameters which were analyzed.

Three EPDM samples having different peroxides were irradiated in water and in air with two different dose rates (993 Gy/h, 54 Gy/h) to 2163 kGy (for high dose rate) and 1178 kGy (for low dose rate). Irradiation periods for low dose rate were 2.5 years (last sample) which have not been observed in literature. Characterization of irradiated EPDM samples were done by mechanical (tensile, hardness, compression), dynamic mechanical (DMA), thermal (TGA-FTIR) and morphological (ATR-FTIR, XRD, SEM) tests. High dose rate irradiations were done in predicting how far EPDM resist to radiation and which dose rate emitted waste can be immobilized and stored in EPDM for 300 years. Low dose rate irradiations were carried out in determining

morphological changes in structure, thermal stability, oxygen effect and types of reactions (crosslinking, chain scisson) which were dominant in irradiated samples.

According to the test results, improvement in thermal properties and decrease in elasticity on EPDM via radiation were recorded from thermal and mechanical tests respectively. Moreover, structural changes were monitored from ATR-FTIR, SEM and XRD analysis. Mechanical tests showed that irradiated EPDM samples, which were differentiated with respect to peroxide type (aliphatic, aromatic), could resist up to total absorbed doses of 3750 kGy and 3955 kGy respectively. Up to 1178 kGy in low dose irradiation, there were not much structural changes, which were observed in ATR-FTIR analysis, in EPDM chain.

It was concluded that EPDM rubber used in this study were radiation stable polymer so that they could possibly be used in conditioning of radioactive waste.

Keywords: EPDM, Radioactive waste management, Radiation Stability, Degradation

ÖZ

EPDM TER-POLİMERİNİN GAMA RADYASYONU İLE BOZUNMASI VE EPDM TER-POLİMERİNİN RADYOAKTİF ATIK YÖNETİMİNDE OLASI KULLANIMI

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Bu çalışmada EPDM ter-polimerinin gama ışınımı ile bozunması ve EPDM ter-polimerinin radyoaktif atık yönetiminde olası kullanımı araştırılmıştır. EPDM ter-polimerinin radyasyon kararlılığı ve radyoaktif atık yönetiminde olası kullanımının belirlenmesinde; doz hızı (yüksek ve düşük), ışınlanma ortamı (suda ve havada) ve formülasyonda kullanılan katkı maddelerinin etkileri (karbon siyahı, proses yağı, çarpraz bağlayıcı) analiz edilen parametrelerdi.

Farklı oranlarda ve çeşitlerde çarpraz bağlayıcı içeren 3 farklı EPDM örneği iki değişik doz hızında (993 Gy/s, 54 Gy/s) suda-susuz ortamda 2163 kGy (yüksek doz) ve 1178 kGy (düşük doz)'e kadar ışınlanmıştır. Düşük doz ışınlamalarda, son örnek 2,5 yıl ışınlanmıştır ki bu süreye EPDM elastomerinin radyasyon ile bozunması konusunu içeren çalışmalarda bugüne kadar rastlanmamıştır. Işınlanan EPDM örneklerinin karakterizasyonu mekanik (gerilme, sertlik, sıkıştırma), dinamik mekanik (DMA), termal (TGA-FTIR) ve yapısal (ATR-FTIR, SEM, XRD) testler ile yapılmıştır. EPDM ter-polimerinin radyasyona ne kadar dayanabildiğinin ve hangi doz hızındaki radyoaktif atıkların 300 yıl süre ile EPDM polimerinde sabitlenmesinin

tahmini için yüksek doz ışınlamalar, EPDM ter-polimerininin gama ışınımı ile oluşan yapısal değişikliklerinin, termal kararlılığının, oksijen etkisinin ve hangi reaksiyon türünün (çarpraz bağlanma, zincir kırılması) ışınlanan örneklerde baskın olarak gerçekleştiğinin belirlenmesi için ise düşük doz ışınlamalar gerçekleştirilmiştir.

Yapılan çalışmaların sonuçlarına göre, EPDM polimerinin termal özelliklerinde iyileşme, elastik özelliklerinde ise gerileme kaydedilmiştir. Buna ek olarak, yapısal değişiklikler, ATR-FTIR, SEM ve XRD analizlerinde görüntülenmiştir. Mekanik testler, alifatik ve aromatik çarpraz bağlayıcı içeren EPDM örneklerinin 3750 ve 3955 kGy'e kadar dayanabileceğini göstermiştir. 1178 kGy (düşük doz)'e kadar, gama ışınımının, EPDM ter-polimerinin yapısında çok büyük miktarlarda değişikliklere uğratmadığı ATR-FTIR analizlerinde gözlemlenmiştir.

Bu çalışmada kullanılan EPDM ter-polimer örneklerinin gama ışınımına karşı dayanıklı oldukları ve bundan dolayı radyoaktif atıkların şartlandırılmasında kullanımlarının olası olduğu anlaşılmıştır.

Anahtar Sözcükler: EPDM, Radyoaktif atık yönetimi, Radyasyon kararlılığı, Bozunma

To My Family and Şerife Özdemir…

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LIST OF ABBREVIATIONS

EPDM:	Ethylene propylene diene ter-polymer
ENB:	Ethylidene norbornene
NBR:	Acrylonitrile butadiene rubber
BBPIB:	Bis(t-butylperoxy isopropyl)benzene
DMBPHa:	2,5-Dimethyl-2,5-di(t-butylperoxy)hexane
TAC/S:	Triallylcyanurate
TMPTMA:	Trimethylolpropane trimethacrylate
Phr:	Parts per hundred parts of resin
Gy:	Gray
kGy:	Kilogray
k:	Decay constant
t:	Irradiation period
E:	Elastic modulus
T:	Temperature at which measurements are carried out
R:	Gas constant
η:	Crosslink density
TD:	Total dose
Dr_i:	Initial dose rate
CS:	Compression Set
DMA:	Dynamic Mechanical Analysis
TGA-FTIR:	Thermogravimetric Analysis
ATR-FTIR:	Attenuated Total Reflection Fourier Transform Infrared Spectroscopy
XRD:	X-Ray Diffraction Analysis
SEM:	Scanning Electron Microscopy

CHAPTER 1

INTRODUCTION

1.1. EPDM

Ethylene Propylene elastomers (EPM) are man-made (synthetic) non-polar hydrocarbon based elastomers including ethylene and propylene units in the main chain. The first commercial ethylene propylene elastomers were synthesized by using the technique of random copolymerization (in solution) in the presence of a catalyst referred to as Ziggler-Natta [1]. Ethylene propylene copolymers have a fully saturated main chain so they are highly resistant to environmental effects, such as ozone, oxidation, weathering and radiation [2].

In addition, curing for ethylene propylene polymers is required because raw ethylene propylene copolymers are devoid of crystallinity. They are lack of sulfur and peroxide curing. For this reason, unsaturation of the ethylene propylene copolymer is required. Unsaturation is performed by the copolymerization of the ethylene propylene comonomer with a non-conjugated diene so that interchain sulfur cross-linking is made possible [1,2]. Non-conjugated diene supply its double bond for the vulcanization process. After unsaturation occurred, the new polymer is referred to as ethylene propylene diene terpolymer (EPDM).

Raw EPDM rubbers are not suitable for industrial application. They need to be improved in order to be used commercially. Improvement of EPDM can be achieved by adding fillers, antioxidants, plasticizer, reinforcement and curing agents [3].

Additives not only improve the mechanical, the electrical properties and the processability of polymers, but also decrease and dissipate undesirable properties. In some cases, additives are used in order to reduce the cost [3,4]. Types and functions of additives are given in Table 1.1.

Table 1.1 Types, examples and functions of additives [3,4]

Type	Examples	Functions
Fillers and Reinforcements	Calcium Carbonate, Talc (Magnesium Silicate Hydroxide)	Enhance stiffness and surface hardness of polymer
Fiber Reinforcements	Aramid, carbon, glass, natural fibers	Enhance mechanical properties
Colorants	Pigments, liquid colours, colour pastes, dyestuffs,	Makes easier mixing, used in replacement of heavy metals
Black and white pigments	Carbon black, titanium dioxide	Supply UV resistivity, enhance electrical conductivity (carbon black)
Heat and radiation resistance	Antioxidants and stabilizers	Prevent and postpone the oxidation of polymer under heat and radiation
UV resistance	UV stabilizers	Prevent and postpone oxidation of polymer under sunlight
Flame retardants	Halogenated (Potassium Perfluorobutane Sulfonate) Flame Retardants	Prevent and delay combustion of polymers, prevent
Antistatics, conductives	Stainless Steel Fiber, Carbon Fiber	Enhance electrical conductivity and inhibit electrostatic discharge.
Curing systems for thermosets	Accelerators (Alkylphenol disulfide) curing agents (sulphur), and catalysts	Trigger, accelerate and control the cure of polymers

Table 1.1 continue		
Type	**Examples**	**Functions**
Cross-linking, coupling, compatibilizing	Peroxides	Generate cross-links between polymer, additives and other molecules
Plasticizers	Phthalates, Tricresyl phosphate, citric acid esters	Enhance processibility and flexibility of polymers. Generally utilized in PVC
Process modifiers, processing aids	Lubricants and plasticizers	Enhance blending and mixing, control the viscosity
Blowing agents	Inert gas or gas-forming chemicals	Produce foam and expand the polymer, replace chlorofluorocarbons
Lubricants	Calcium stearate, lead stearate, zinc laurate	Enhance the process, delay gelation, prevent friction, lower melt viscosity
Other types	Barrier properties, shrinkage, acoustics, surfactants, antimicrobials	Supply specific properties
Recycling additives	Impact modifiers, stabilizers	Utilized in order to enhance and conserve properties of polymers while recycling.

Ethylidene norbornene is the most commonly used diene in the unsaturation of EPDM rubber. It has advantages that polymerization occurs quickly, the curing rate is faster and the formation of excessive gel is prevented [2]. Figure 1.1 and 1.2 show structures of EPDM and ethylidene norbornene respectively.

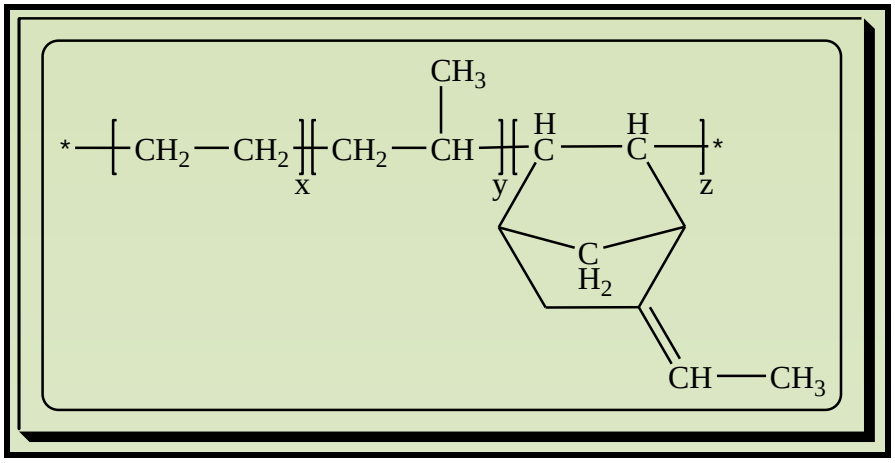

Figure 1.1 Structure of EPDM

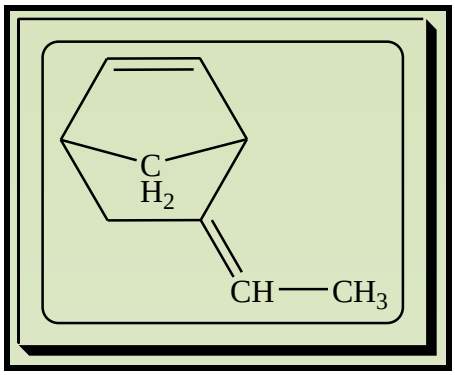

Fig.1.2 Structure of ethylidene norbornene (ENB)

EPDM rubbers are used in the automobile industry, cable insulation, nuclear power plants (as cable covers), plastic modification, weather protection, tire sidewalls, roof system applications and the electrical industry (connector) [2]. EPDM rubbers have good heat resistance since their application temperature can rise to 148-176 ^{o}C. Also, at very low temperatures such as minus 50 and minus 56 ^{o}C, EPDM rubbers can be processed. With respect to mechanical properties, EPDM rubber has good resistance to impact and abrasion [2]. Table 1.2 shows the representational physical and mechanical properties of EPDM rubbers, which contain medium amounts of the ethylene repeating unit.

Table 1.2 Physical and mechanical properties of EPDM [1-5]

Physical and mechanical properties	**Values**
Specific gravity	0.85-0.88
Specific heat, cal/g	0.56
Brittle point	-68 ^{o}C
Elasticity, % (at room temperature)	77
Insulation resistance (megohms/1000 ft)	25500
Tensile strength (MPa)	6.5-8.8
Elongation at break, %	550-640
Hardness, Shore A	30-90
Abrasion resistance	Good-Excellent
Useful Temperature Range, ^{o}C	-50 ^{o}C-148 ^{o}C
Resistance to sunlight	Superb
Compression set, % (at 70 ^{o}C) **(at 100 ^{o}C)**	8-10 12-26
Resistance to heat and radiation	Superb
Modulus at 100 % elongation (MPa)	1.9-3.6
Modulus at 300 % elongation (MPa)	4.7-6.8

Values, in Table 1.2, vary according to the compounding. The properties of EPDM rubbers change with respect to the ethylene/propylene ratio, the types/amounts of additives and the dienes. EPDM rubbers, having low or medium ethylene content, are generally amorphous and more elastic. Amorphous or low crystalline EPDM rubbers have excellent low temperature flexibility and low glass transition temperatures at approximately minus 60 ^{o}C [4]. On the other hand, EPDM rubbers, which include higher ethylene content, are semi-crystalline or crystalline. The physical and mechanical properties of EPDM rubbers, having high ethylene content, are superior. However, there are disadvantages when using high ethylene contents in EPDM rubbers because high ethylene content gives lower thermal properties and complicate the processability [4,5]. Generally, commercial EPDM rubbers include ethylene between 50 - 75 wt% and diene between 1.5 % - 10 wt% [6].

In addition, effects of compounding, which were varied according to peroxide, diene content, plasticizer and carbon black content, on mechanical and rheological properties of EPDM were studied by Çavdar [7]. Compounded EPDM samples were characterized by mechanical, dynamic mechanical and thermogravimetric tests. According to the results, increase in the amount of carbon black content increased the vulcanization rate constant, hardness and viscosity, while it decreased elongation at break values. Increase in peroxide content affected hardness, elongation and vulcanization rate in an irregular way. Relative crosslink density was found maximum for EPDM containing 5 phr peroxide in all EPDM samples including 2.5, 7.5 and 10 phr peroxide. Plasticizers decreased viscosity, strength, and increased elongation of EPDM. On the other hand, the vulcanization rates were not affected by plasticizer. Increases in the diene content did not improve EPDM's mechanical properties. Relative crosslink densities were at a maximum for EPDM containing 5.6 wt% ENB in all EPDM having 5 wt%, 7.5 wt% and 8.9 wt% ENB.

1.2. RADIATION CHEMISTRY OF POLYMERS

Irradiation (gamma (γ) rays, X-rays, accelerated electrons) of polymers causes the formation of highly reactive intermediates and free radicals. Formed free radicals and reactive intermediates lead to reactions in the polymer. As a result of these reactions, disproportionation, chain scission (degradation), decrease in molecular weight, hydrogen abstraction, crosslinking and formation of new bonds can occur in polymer structure [8]. The degree of these modifications depends on the structure of polymer, additives, temperature and conditions of irradiation (high or low dose rate, presence of oxygen).

The field of radiation chemistry of polymers is generally divided into three parts [9]:

- Radiation induced polymerization: Synthesizing of polymers via ionizing radiation of monomers.

- Chemical changes in polymer systems via irradiation including;

    - Radiation-induced graft co-polymerization: Modifying polymers and synthesizing polymers via grafting monomers.
    - Formation of cross-linking by radiation: Synthesizing three-dimensional cross-linked systems from linear or branched polymers.
    - Chain scission and degradation of polymers via irradiation.

- Polymers' radiation resistivity and ways of polymer protection against ionizing radiation.

In general, main reactions occurring in the polymer due to irradiation are classified as crosslinking, chain scission and oxidation [8]. Crosslinking by irradiation has various advantages over the polymers' properties. It enhances the stability of the polymer and provides high strength, functional properties at high temperature, high impact and chemical resistance to the polymer. Crosslinked polymers preserve their

shapes at high temperatures. Moreover, crosslinking due to irradiation can result in molecular weight increase in the polymer [8-10]. Degradation of the polymer by irradiation results in chain scission, oxidation (free radicals react with oxygen and form unstable peroxide radicals or hydroperoxides), hydrogen gas abstraction and molecular weight decrease. The mechanical and the chemical properties of polymers are diminished by degradation [8-10].

1.3. EFFECTS OF IONIZING RADIATION ON POLYMERS

Ionizing radiation can affect the polymers' structure both positively and negatively depending on the dose rate, the presence of oxygen, the structure and the compounding of polymers. Polymers are organic molecules containing C-C, C-H, C-O bonds and these bonds are susceptible to radiation [11]. Ionizing radiation excites these bonds. Excited bonds result in bond cleavage and radicals formation. Formed radicals cause reactions in polymer matrix. As a result of these reactions, the polymer chain is affected by virtue of the ionizing radiation. These effects are classified as constructive (crosslinking) and destructive (degradation) [12]. Reactions caused by ionizing radiation on polymers are classified in to six parts [11,12]:

- **Recombination Reactions:** Not observed any significant effects in the polymers' structural and mechanical properties

- **Cross-linking:** Results in increase in strength, molecular weight, glass transition temperature and decrease in elongation. Classified as constructive.

- **Chain Scission:** Results in decrease in strength, elongation, glass transition temperature and molecular weight. Classified as destructive.

- **Formation of volatile products:** Mainly hydrogen gas evolution or side-chain deterioration. Classified as destructive.

- **Formation of peroxy radicals in presence of oxygen:** Classified as destructive.

- **Unsaturation production or deterioration:** Classified as both constructive and destructive.

Crosslinking and chain scission occur in the structure of the polymers at the same time via radiation. These reactions are classified as primary reactions [8,11]. On the other hand, one of these reactions dominates numerically in the structure and this domination designates whether or not the polymer is crosslinkable or degradable under ionizing radiation [8,11]. Table 1.3 shows some polymers which are classified as crosslinking or degradable under radiation.

Table 1.3 Classification of polymers' behaviour under ionizing radiation [3,8,11,13]

Crosslinkable Polymers	**Degradable Polymer**
Polyethylene	Polyisobutylene
Polystyrene	Poly(∝-methylstyrene)
Polyacrylates	Polymethacrylates
Polyacrylamide	Polymethacrylamide
Polyvinyl chloride	Poly(vinylidiene chloride)
Poly(ethylene-vinyl acetate)	Cellulose
Polyamides	Polytetrafluoroethylene
Polyesters	Polytrifluorochloroethylene
Polysiloxanes	Polypropylene
Polyvinyl alcohol	Polybutene
Ethylene Propylene Diene Terpolymers	Polyether
Ethylene Propylene Copolymers	
Conjugated diene butyl rubber	

In crosslinkable polymers, scission reactions occur often as crosslinking reactions in the main chain. However, these scission reactions take place in the C-H bonds. Hydrogens in C-H bonds are ruptured by the effect of radiation [14]. After rupturing, newly formed radicals are connected to each other at their radicalic sites. On the

other hand, in degradable polymers, scission reactions take place not only in the C-H bonds but also in the main chain (i.e. C-C bond cleavage). Therefore, in degradable polymers, molecular weight decreases and depletion in the mechanical and the chemical properties are observed [14]. Additionally, there are several effects apart from crosslinking and chain scission in the polymer structure by virtue of radiation. These effects are called secondary effects [11]. These secondary effects result in the formation of gas and peroxy radicals in the presence of oxygen. Moreover, ionizing radiation decreases crystallinity to some extent in crystalline polymers [15].

In addition to Table 1.3, to predict whether a polymer is crosslinkable or degradable under ionizing radiation, it is important to know the structure and the compounding of the polymer, the substituents in the main chain, the bond types and bond energies. The types of additives and their quantity are important in the radiation stability of polymer. Some additives like antioxidants, reinforcement agents, and peroxides show a protective influence against ionizing radiation to some extent [16]. The presence of π bonds in the main chain and the existence of a substituent in the structure are important parameters in predicting the polymers' behavior under radiation. Including π bonds in the main chain causes the polymer to degrade. This is due to the difference in the values of bond dissociation energies. In π bonds, less overlapping is observed between the component p-orbitals due to their parallel orientation. Less overlapping results in weakness in the π bonds. For this reason, the dissociation energy value of π bonds is smaller than σ bonds [17]. Therefore, the minimum required dose to excite the π bonds becomes smaller. Formation of unstable radicals is accelerated in polymers containing π bonds in the main chain. As a result, polymers including π bonds in the main chain are classified as degradable. Moreover, if a polymer's main chain includes substituted groups, the polymer's resistivity to radiation decreases as substituted groups in polymer chain increase. Polymers which have querternary carbon atom, have low resistance to ionizing radiation. Querternary carbons do not have C-H bonds due to the tetra substitution; C-C bonds are ruptured by virtue of the radiation [18]. Therefore, cleavage of C-C bonds causes degradation of the polymers [14]. Figure 1.3 shows the monomer types which are classified as crosslinkable or degradable under ionizing radiation.

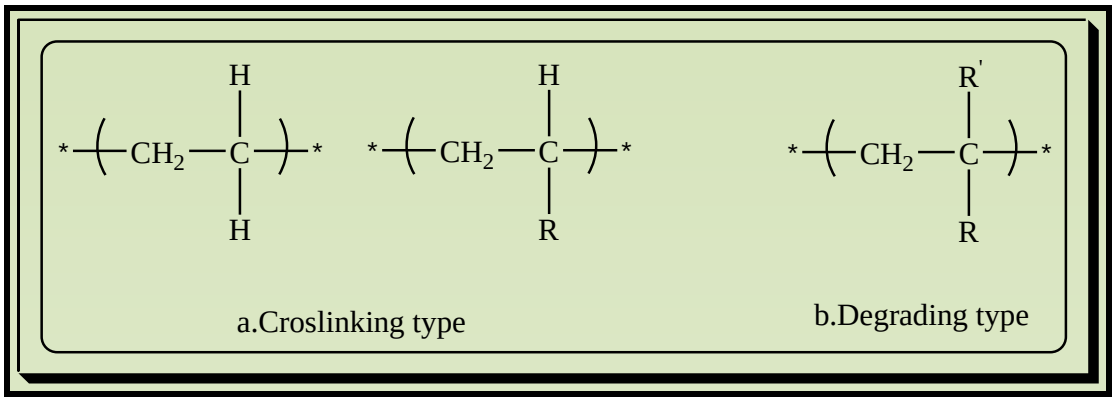

Fig. 1.3 Degrading and crosslinking type of monomers

1.4. RADIATION EFFECTS ON EPDM

Various types of EPDM rubbers are preferable for use in hard radiation areas such as cover material for electrical cables because of their higher resistance to environmental effects when compared to other types of rubbers (Natural rubber, Teflon) [19]. Therefore, it is crucial to predict EPDM rubbers' long term stability under ionizing radiation. Using EPDM rubber in a concentrated hard radiation environment makes it one of the most analyzed and studied polymers in the area of polymer degradation. EPDM rubber is classified as radiation resistant, because the structure of the EPDM includes fully saturated bonds in the main chain and having no tetra substituted carbon atoms [13,18]. Bonds in the main chain are σ bonds, which have higher bond energies than π bonds. Therefore they can absorb more energy without any chain scission. These properties make EPDM rubber as crosslinkable polymers under ionizing radiation [13].

Apart from the crosslinking and the chain scission reactions, additional and more complex reactions such as formation of oxidized species in the presence of oxygen, reactions due to additives, changes in the morphology of the polymer, formation of cracking on the surface and hydrogen gas evolution were observed in EPDM structure via irradiation [14].

1.5. RADIOACTIVE WASTE MANAGEMENT

Any material including or contaminated with radionuclides is referred to as radioactive waste [20]. Radioactive wastes cannot be exterminated by any chemical or physical methods. The only way for radioactive waste destruction to occur is decay of the wastes to stable elements. Therefore, radioactive waste management includes the controlling and the diminishing of radioactive wastes to allowable levels, condensation and concentration of wastes (especially liquid wastes) in order to constitute an appropriate form for storage and the disposal of these wastes [20]. Radioactive wastes can be in solid, liquid or gaseous form. Diffusion of radioactivity into the environment generally occurs through the liquid and the gaseous effluents generated in nuclear power plants. Therefore, removal of radioactive particles from effluents is important.

Classification of wastes, conditioning for radioactive wastes, and regulations for waste disposal are essential parameters which should be considered in radioactive waste management.

Radioactive wastes could be classified in various ways and the classification could be done nationally or internationally. Most widely accepted classification internationally is the classification done by International Atomic Energy Agency (IAEA). According to classification scheme of IAEA [21,22,29], radioactive wastes are categorized into three parts:

- Exempt wastes
- Low and intermediate level wastes
- High level wastes

Low and intermediate level radioactive wastes are divided into two groups, namely short lived and long lived. In long lived wastes, the amount of radionuclides emitting alpha rays is higher than in short lived radioactive wastes [20,23].

Nuclear industry produces extensive amounts of radioactive waste, and these wastes must be properly disposed. In waste disposal, wastes are treated in order to be condensated. The solidification process is applied to condense radioactive particles from effluents. This process includes evaporation, precipitation, ion exchange and adsorption methods. In the solidification process, obtaining stable forms is crucial to prevent radioactivity release into the environment [24]. After the solidification process, wastes are immobilized into cement, polymer or bitumen.

Cementation is a common method for disposal of radioactive waste, however it has been claimed that via radiation, emitted from wastes, cement and radioactive waste are forming complexes that are water soluble, and these water soluble complexes lead to the migration of radionuclides [26].

Moreover, immobilization of radioactive organic species into cement is not as successful as in the immobilization of heavy metals. Radiation originating from organic species can damage the matrix of the cement binders and the organic species. Therefore, the cement binders' efficiency can decrease in the immobilization of radioactive organic wastes [27].

In radioactive waste management, polymers can be utilized in the conditioning and the packaging of wastes. For example, polyethylene is heated and mixed with powdered radioactive waste and the mixtures are transferred into a dumping container [28].

1.6. LITERATURE REVIEW

Various studies related to the gamma irradiation of EPDM are available in literature. Some of these studies focused on radiation induced crosslinking and vulcanization; some of these focused on the stability and the degradation of EPDM. These studies differed from each other by irradiation periods/conditions and EPDM formulation. Some researchs related with degradation of EPDM via radiation are summarized below:

- Radiation effects on the properties of carbon black filled NBR/EPDM rubber blends were investigated by Zeid [30]. Rubber blends with different amount of carbon black were irradiated up to 250 kGy by high dose rate (7.6 kGy/h). Irradiated EPDM rubbers contained 60 wt% ethylene, 32 wt% propylene and 8 % diene. Samples were characterized by mechanical and thermal tests. According to results; tensile strength, modulus at 100 % elongation, hardness, thermal stabilities of blends were increased, on the other hand, elongation at break values were decreased with increase in the total dose and the carbon black content.

- Ito [19] studied degradation of ten different EPDM rubbers via radiation and heat in order to analyze whether or not compounding for heat resistant is durable against irradiation. Irradiations of samples were carried out at 70 ^{o}C, dose rate and total dose were 5.0 kGy/h and 0.9 MGy respectively. Elongation at break values were taken for the evaluation of the radiation stability. As a result of the study; it was observed that formulas improving the thermal stability did not bring radiation stability to samples.

- The radiation resistance of EPDM (vulcanized by sulfur) without a filler was investigated by Nakase and co-workers [31]. Four EPDM samples (72.5 mol% of ethylene) with different sulfur content were irradiated at three different dose rate in order to determine the dose rate and the sulfur effect on the degradation of EPDM. After irradiation, gel fraction, mechanical and hardness tests were carried out. According to the results; at the beginning of irradiation, increase in gel fraction and

hardness values were observed. On the other hand, further irradiation caused a decrease in hardness and gel fraction values. It was stated that EPDM having more sulfur content showed better results. Additionally, low dose rate caused more deterioration in the structure of EPDM because of more oxidation.

- Basfar et al. [32] investigated antioxidant efficiency on accelerated aging of EPDM rubber via radiation. Samples were irradiated up to 200 kGy. Characterizations of irradiated samples were carried out by mechanical tests. According to results; up to 100 kGy, antioxidant addition increased the radiation stability of EPDM.

- Placek et al. [33] performed a study to determine the EPDM rubbers life time in nuclear power plants. EPDM rubbers having two different thicknesses were irradiated up to 90 kGy which was the total dose simulating 10 years service for the initial dose rate of 1 Gy/h. After irradiation, mechanical, gas leakage and compression set (CS) tests were carried out. In the determination of service time, compression set were used as reference. CS endpoint criterion was set for the tested samples at 85%. According to the results; compression set of 85 % was reached for 7 mm thick EPDM at simulation equivalent to 2 years service. On the other hand, CS of 85 % was not reached for EPDM with a 14 mm thickness equivalent to 4 years of service.

- Effects of the dose rate, peroxide and ENB content on the radiation degradation of the vulcanized EPDM were analyzed by Özdemir [34]. EPDM samples were irradiated under low dose rates (64.6 Gy/h) and high dose rates (1280 Gy/h) up to 31, 45, 95, 130 and 184 kGy. In compounding of two different EPDM samples, they differentiated from each other by ENB content and peroxide types (aliphatic, aromatic) with varying in content (3-5 and 5-7 %). Mechanical, ATR-FTIR, dynamic mechanical, thermogravicemetric (TG) analysis were carried out in order to determine the degradation of EPDM. In mechanical tests, maximum stress at break, elongation at break, elastic modulus, hardness and compression set values of high dose rate and low dose rate irradiated EPDM samples were compared.

Mechanical test results indicated that high dose rate irradiation degraded the EPDM samples faster than the low dose rate irradiation to 184 kGy. Up to the total absorbed dose of 31 kGy, the dominant mechanism was chain scission, further irradiation to 184 kGy made crosslinking as the dominant mechanism in the structure of EPDM. The highest rate of crosslink via irradiation was found in EPDM containing 3 phr of aliphatic peroxide. Higher ENB content resulted in higher elastic modulus and this was because of the higher relative rate of crosslinking reaction in the EPDM having higher ENB content. Intensity increase in the hydroxyl and hydroperoxides group absorption region (showing degradation of EPDM) and intensity decrease in dienic double bond group absorption region were observed in the ATR-FTIR spectra. The relative degree of crosslinking with irradiation was confirmed by the DMA results in which the damping factor peak temperature increased via irradiation. In thermal analysis, according to differential thermogravimetric (DTG) curves, decreases in the rate of weight loss via irradiation were observed. As a result of that study; it was concluded that dose rate, change in ENB and peroxide content affected the extent of the modification/degradation of the EPDM's properties.

- Sixteen different EPDM rubbers were compounded by Çavdar et al. [35]. EPDM rubbers containing different ENB content and ethylene contents were vulcanized and were differentiated from each other by types and compositions of peroxide (aromatic, aliphatic) and coagents (allylic, acrylic). After synthesizing the EPDM rubbers, the characterizations of the rubbers were studied in order to determine the optimum formulation of EPDM for a better application in the automotive industry. Vulcametry, tensile, compression and thermal tests were carried out in characterization of specimens. As a result of that study; the thermal, vulcametric and the mechanical properties of EPDM samples were affected by type/composition of peroxide, EPDM grade and coagent. Aromatic peroxide and allylic coagent increases thermal stability. The cure time of the aromatic type peroxide and the allylic type coagent included EPDM were higher than EPDM containing the aliphatic type peroxide and acrylic type coagent. This was thought to be probably due to the slower reaction in the allylic type of coagent compared to the acrylic type of coagent.

1.7. AIM OF THIS STUDY

In this study, the degradation of EPDM rubbers which are generally used in nuclear power plants as insulation materials for electrical wires via ionizing radiation (with gamma source) were studied by applying mechanical, morphological and thermal tests. The gamma irradiation of EPDM rubbers was analyzed in order to understand the radiation stability and determine possible use of EPDM in radioactive waste management. During the study, three different EPDM samples were irradiated. The content of the EPDM samples differentiated from each other in terms of peroxide type and amount used in vulcanization. Irradiations were carried out with high dose rate (993 Gy/h) and low dose rate (54 Gy/h) gamma sources. Irradiations were also carried out in aquatic environment. During the studying of radiation stability of EPDM, dose rate (both high and low), irradiation environment (in water and in open to air), additives (carbon black, zinc oxide and plasticizer) used in formulation, peroxide type (either aliphatic or aromatic) and content were parameters which were analyzed. Irradiated samples were characterized by applying mechanical (tensile, hardness, compression set), dynamic mechanical (DMA), thermal (TGA-FTIR) and morphological (ATR-FTIR, SEM, XRD) tests. High dose rate irradiations were performed to see the total dose that EPDM can resist and to estimate the initial dose rate of radioactive waste that could be embedded into polymer matrix for 300 years storage. Low dose rate irradiations were carried out to see the morphological changes in structure, changes in thermal stability, oxygen effect and to determine which types of reactions (crosslinking, chain scisson) were dominant in the structure during irradiation. Moreover, effects of irradiation environments (in water and air) were analyzed in order to estimate how water and air affected the EPDM's mechanical, thermal and morphological properties during irradiation. The peroxides and the additives' effects on EPDM via irradiation were attempted to be determined by using mechanical tests results. As mentioned in review part, there are various studies concerned with the degradation of EPDM. In those studies, formulations of EPDM were differentiated from each other and in general ethylene contents were chosen between 60-70 %. Parameters that make this study specific and differentiate from other studies were carbon black and ethylene content, peroxide and coagent types,

irradiation environment, irradiation period and the dose rates. In this study, 90 phr carbon black, whose amount was close to amount of EPDM (100 phr), was used in formulation. This large amount of carbon black content in EPDM compounding has not been encountered in literature dealing with EPDM degradation via radiation. In addition, the most distinctive property that differentiates this study from other studies was the irradiation period during which EPDM samples were irradiated in low dose rate up to 2.5 years which have not been seen in literature.

CHAPTER 2

EXPERIMENTAL

2.1. MATERIALS

2.1.1. EPDM and Ingredients Used in Compounding

Trade names, compositions and functions of EPDM and its' constituents are given in Table 2.1 and Table 2.2.

Table 2.1 Trade names, ethylene and diene contents of EPDM used in this study

Trade names	Ethylene Content (%)	Diene (ENB) Content (%)
KELTAN 27	50.8	5.0
BUNA EP G 6850	52.9	7.5

Table 2.2 Trade names, composition and functions of ingredients used in this study

Trade names	Composition	Function
PERKADOX 14/40 MB-gr	40% Bis(t-butylperoxy isopropyl)benzene (BBPIB) in whiting and silica	Vulcanizing agent (aromatic)
LUPEROX 101XL45	45% 2,5-Dimethyl-2,5-di(t-butylperoxy)hexane (DMBPHa) in carrier system	Vulcanizing agent (aliphatic)
STEARIC ACID 101	Stearic acid	Activator
ZnO	Zinc Oxide (min 99.7%)	Activator
FEF N 550	Carbon Black (Surface area 42 m^2/g)	Filler
RHENOFIT TAC/S	70% Triallylcyanurate (TAC/S), 30% Silica	Coagent (allylic,aromatic)
SARTOMER SR 350	Trimethylolpropane trimethacrylate (TMPTMA)	Coagent (acrylic)
TUDALEN 3909	High refined saturated mineral oil	Plasticizer

Compounding of three different EPDM samples which are irradiated is given in Table 2.3.

Table 2.3 Compounding of EPDM samples which were irradiated

Constituent	Amount		
	EPDM-1	**EPDM-2**	**EPDM-3**
Ethylene (phr)	50.8	52.9	52.9
Propylene (phr)	44.2	39.6	39.6
ENB (phr)	5.0	7.5	7.5
DMBPHa (phr) (aliphatic)	3	5	-
TMPTMA (phr) (acrylic)	2.5	2.5	-
BBPIB (phr) (aromatic)	-	-	5
TAC/S (phr) (aromatic)	-	-	2.5
Carbon Black (phr)	90	90	90
Plasticizer (phr)	30	30	30
Zinc Oxide (phr)	5	5	5
Stearic Acid (phr)	1	1	1

2.2. IRRADIATIONS

EPDM samples were irradiated by two gamma sources, the first source supplied low dose rate, and second one supplied comparatively high dose rate radition. High dose rate irradiations were performed in a Tenex Issledovatel model Co-60 (half life is 5.26 years source having an activity of 2516 Ci (in 2005) and a dose rate of 993 Gy/h, on the other hand, low dose irradiations were performed in Gammacell 220 model including Co-60 source, having an initial activity of 12400 Ci (in 1968) and a dose rate of 54 Gy/h. Dose rates of low dose rate and high dose rate irradiation sources are given in Appendix A. Irradiations were carried out in the presence of oxygen or water. The dose rate ratio of the high dose irradiation source to the low dose irradiation source was about 18. Total doses and periods for irradiation are given in Table 2.4.

Table 2.4 Irradiation periods (days) and absorbed dose (kGy) values for irradiated samples

	Total Doses (kGy) for Low Dose Rate Ir.							**Total Doses (kGy) for High Dose Rate Ir.**		
Days →	**84**	**125**	**308**	**345**	**527**	**747**	**912**	**28**	**42**	**92**
EPDM-1	108	160	383	426	727	992	1178	-	-	-
EPDM-2	108	160	383	426	-	-	-	663	993	2157
EPDM-3	108	160	383	426	-	-	-	663	993	2157

Irradiations in water were carried out for only EPDM-1 samples up to 160, 383 and 426 kGy. Total absorbed doses were calculated using the Equation 1 [36].

$$TD = \int DR_i \times e^{-kt}\, dt \quad \Rightarrow \quad TD = \frac{DR_i}{k} \times (1 - e^{-kt}) \qquad (1)$$

Where **TD** is total dose, $\mathbf{DR_0}$ is initial dose rate, **t** is period and **k** is decay constant.

2.3. CHARACTERIZATION OF IRRADIATED EPDM

2.3.1. Tensile Tests

Hounsfield Tensometer with a crosshead displacement rate of 500 mm/min was used for tensile tests. Tests were carried out in accordance with ASTM D412. Maximum stress at break, elastic modulus and elongation at break results were noted from the machine readings.

2.3.2. Compression Set

E Type Universal Testing Machine Zwick Roell E Type Universal Testing machine was used to determine the Load Deflection of EPDM samples.

2.3.3. Hardness

Zwick Roell Type A Durometer was used to determine the Shore A Hardness of irradiated EPDM samples.

2.3.4. Dynamic Mechanical Analysis (DMA)

DMA curves of irradiated samples were taken by using the 983 Dynamic Mechanical Analyzer Dupont Series. DMA studies were carried out under N_2 atmosphere with the heating rate of 10 ^{o}C/min. The temperature range for the DMA analysis was -100 and 300 ^{o}C.

2.3.5. Thermogravimetric Analysis (TGA-FTIR)

The thermogravimetric analysis (TGA) was carried out on Perkin Elmer Pyris 1 TGA which was connected to Perkin Elmer Spectrum 1 FTIR Spectrometer. TGA studies were carried out under N_2 atmosphere with the heating rate of 10 ^{o}C/min. Samples were analyzed from room temperature to 800 °C.

2.3.6. Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR)

Attenuated total reflection Fourier Transform Infrared (ATR-FTIR) spectra of irradiated EPDM samples were noted at 25 ^{o}C on a Bruker Vertex 70 Fourier Transform Infrared Spectrophotometer. Samples were scanned from 4000 cm^{-1} to 600 cm^{-1} with a resolution of 16 cm^{-1}.

2.3.7. X-Ray Diffraction Analysis (XRD)

Powder X-ray diffraction (XRD) patterns of irradiated EPDM samples were recorded with a MAC Science MXP 3TZ diffractometer using Cu Kα radiation (wavelength 1.5406 Å, 40 kV, 55 mA).

2.3.8. Scanning Electron Microscopy (SEM)

EPDM samples were monitored at magnification between 100 and 400K. Scanning electron microscope (SEM) images were analyzed by using a JEOL JSM-5310LV at 15 kV and 33 Pa in a low-vacuum mode with golden coating.

CHAPTER 3

RESULTS AND DISCUSSIONS

3.1. MECHANICAL TESTS

After completion of irradiations, the mechanical tests were carried out and the results were obtained. Results for the compression set, elongation at break, hardness, elastic modulus and maximum stress at break are given below.

3.1.1. Compression Set

Compression set (CS) test quantify the permanent deformation of a material after it is loaded to compressive forces for a determined time period [33]. In this study, compression set analysis was carried out in order to assess whether EPDM keeps its' elastic properties via irradiation. Radioactive wastes including low or medium level of radioactivity are stored or immobilized in containers made of polymers and later they are buried underground. Containers storing wastes are exposed to a constant compressive force which affects the structure of the containers and decreases the service time. In order to predict the optimum service time of irradiated EPDM samples used in radiated areas and in radioactive waste management, the compression set testing assessment is useful and important [37].

According to the compression set, the higher value of the compression set, the lesser recovery of sample to its initial position [33]. For elastomers used in nuclear power plants as seals, compression set values which specify the life time, are between 75 – 90 % [21]. According to the compression set results of irradiated EPDM-1 samples, relative compression set (CS) values showed a decrease in the early stage of

irradiation to total dose of 160 kGy in air and 383 kGy in water. After 160 kGy in open to air conditions, CS values increased with a rise in a total dose to 992 kGy. On the other hand, in water conditions, after 383 kGy, CS values of EPDM increased with the rise in the total absorbed dose up to 426 kGy. Compression set values could give information about brittleness and stiffness which are one of the most important properties which should be discussed on the topic of irradiation of polymers. Increase in compression set results in increase in stiffness and brittleness in the structure via irradiation [33,38]. According to the CS values of the irradiated EPDM samples in air, to 160 kGy, irradiation affected the elastomeric properties of the EPDM positively. At high doses CS values indicated that irradiation after 160 kGy increased the stiffness of EPDM which became harder. Elastomeric properties of EPDM decreased via further irradiation. Tables 3.1, 3.2 and Figure 3.1 show compression set results of EPDM-1 samples irradiated in air and in water at low dose rate.

Table 3.1 Compression set values of EPDM-1 samples irradiated in air

Total Dose	Compression Set (%)	Compression set (rel.)
0	24.00	1.00
160 kGy	13.00	0.54
383 kGy	20.91	0.87
426 kGy	21.00	0.88
727 kGy	33.00	1.38
992 kGy	40.76	1.70

Table 3.2 Compression set values of EPDM-1 samples irradiated in water

Total Dose kGy	Compression Set (%)	Compression set (rel)
0 kGy	24.00	1.00
160 kGy	10.10	0.87
383 kGy	8.67	0.36
426 kGy	11.00	0.46

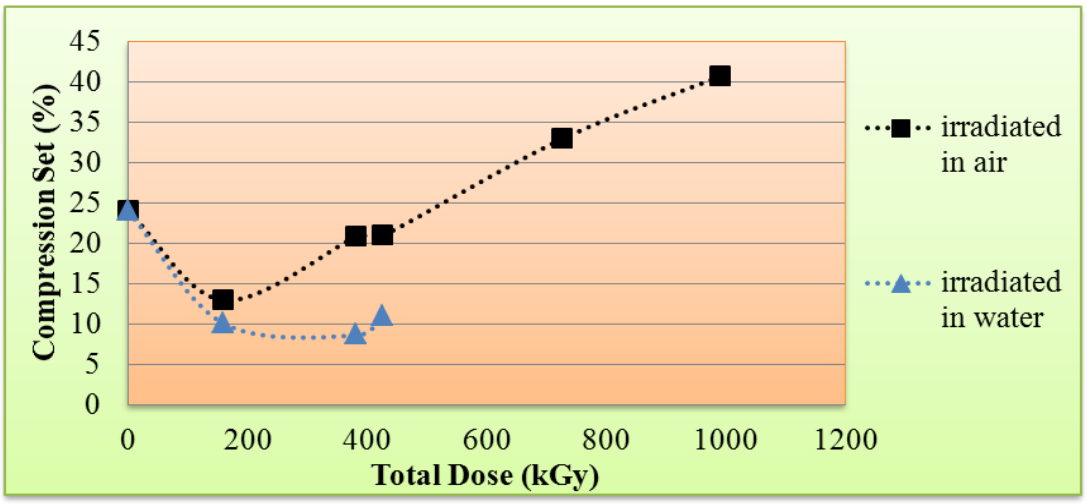

Fig 3.1 Compression set values of EPDM-1 samples which were irradiated in water and in air

Absorbed doses of 487 kGy, 516 kGy, 2286 kGy and 2729 kGy which were calculated using the equation in the Figure 3.2, CS values of EPDM reached 24 % (which belongs to non-irradiated EPDM), 25 %, 85 % and 100 % respectively. It was concluded from the graph that the optimum dose for EPDM is 516 kGy that can be absorbed considering the possible use of EPDM in radiated areas in accordance with compression set measurements [22,33]. The life time of EPDM in radiated areas is

set to a time at which total absorbed dose is 2286 kGy corresponding to 85 % [22,33]. When observing the possible use of EPDM in radioactive waste management as a container or an immobilized polymer for wastes, the polymer should store wastes for 300 years. At the end of 300 years, radioactive wastes become exempt. Therefore, change and decomposition in the structure of EPDM is not important at the end of 300 years [36]. As a result, the life time of EPDM used as radioactive waste container could be set to a time at which CS value is higher than 100 % corresponding to 2729 kGy. Moreover, non-irradiated and 487 kGy irradiated EPDM samples have the same values of CS. This can be explained by the fact that in the total dose of 478 kGy, as determined from the graph, amounts of destructive reactions such as chain scission, oxidation, and constructive reactions or modifications such as crosslinking and chain entanglement (physical crosslinking) occurred by scission were approximately the same. Figure 3.2 illustrates linear change in irradiated samples' compression set values.

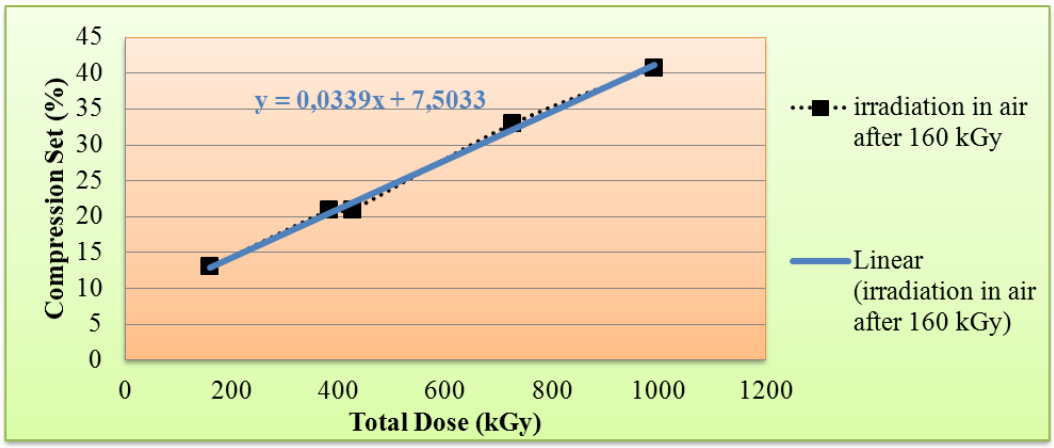

Fig 3.2 Linear change in compression set values of EPDM-1 after 160 kGy

Moreover, it is important to see the behavior of the material to be burried in the aquatic environment, because water could migrate to the disposal site, thus the performance of material becomes very critical to assess the stability of the material in

which the radioactive waste would be embedded. In order to estimate the water effect on EPDM, compression set values of the samples irradiated in air and water conditions were compared. According to the results, at the beginning of irradiation, CS values of both in air and in water condition decreased to a total dose of 160 kGy. On the other hand, only in water conditions, the CS values for 383 kGy irradiation decreased. CS values of EPDM samples (in water) for 160 kGy, 383 kGy and 426 kGy irradiation were more preferable and suitable; i.e. the amounts of destructive reactions were less in water condition. These results indicate that water shielded the radiation to some extent, therefore real dose absorbed by EPDM reduced in water condition as compared to air condition. Absorbing radiation by water made EPDM's mechanical properties better. In other words, water had a self shielding property and to 383 kGy, water prevented undesired effects of radiation partially. After 383 kGy compression set values increased in water condition. These increases can be explained by the fact that EPDM has hydrophobic properties and it does not intend to absorb water, hydrophobic properties of EPDM probably decreased with high doses.

3.1.2. Elongation at Break

As mentioned it was attempted to estimate which peroxide is more suitable for EPDM's radiation stability. Peroxides used in the formulation were 2,5-Di(t-butylperoxy)-2,5-dimethylhexane (DMBPHa) and Di(tert-butylperoxyisopropyl) benzene (BBPIB). The life time of elastomers used in irradiated areas is generally set to a time at which elongation at break value is 50 % (half value dose) of its initial elongation at break value [22,36]. This value is 30 % of its initial elongation for ethylene propylene elastomers [22].

Comparison of elongation at break values gives information about the brittleness, the hardness and the elasticity that these properties assist in deciding service time of EPDM in radiated areas [22].

Tables 3.3, 3.4 and Figures 3.3, 3.4, 3.5 show values and comparisons of elongation at break values that belong to low dose rate irradiated EPDM samples.

Table 3.3 Elongation at break values (rel.) of EPDM samples (low dose rate irradiated samples in air)

	EPDM-2	**EPDM-3**
Total Dose	**Elong. at Break (rel.)**	**Elong. at Break (rel.)**
0	1.00	1.00
108 kGy	0.89	0.93
160 kGy	0.76	0.79
383 kGy	0.51	0.52
426 kGy	0.49	0.46

Table 3.4 Elongation at break values (rel.) of EPDM samples (low dose rate irradiated samples in water)

	EPDM-2	EPDM-3
Total Dose	**Elong. at Break (rel.)**	**Elong. at Break (rel.)**
0	1.00	1.00
383 kGy	0.60	0.60
426 kGy	0.51	0.49

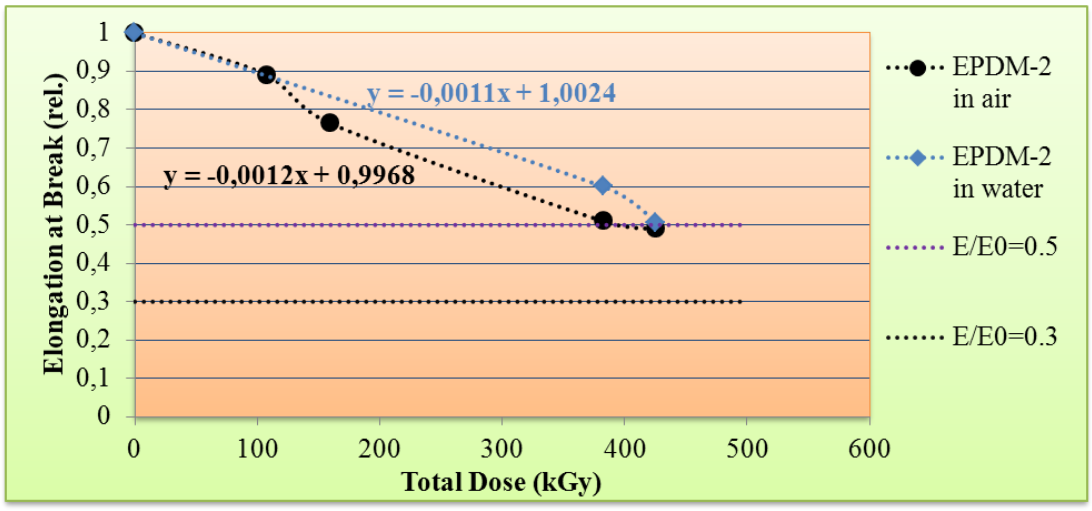

Fig. 3.3 Elongation at break results (rel.) of EPDM-2 for low dose rate radiation

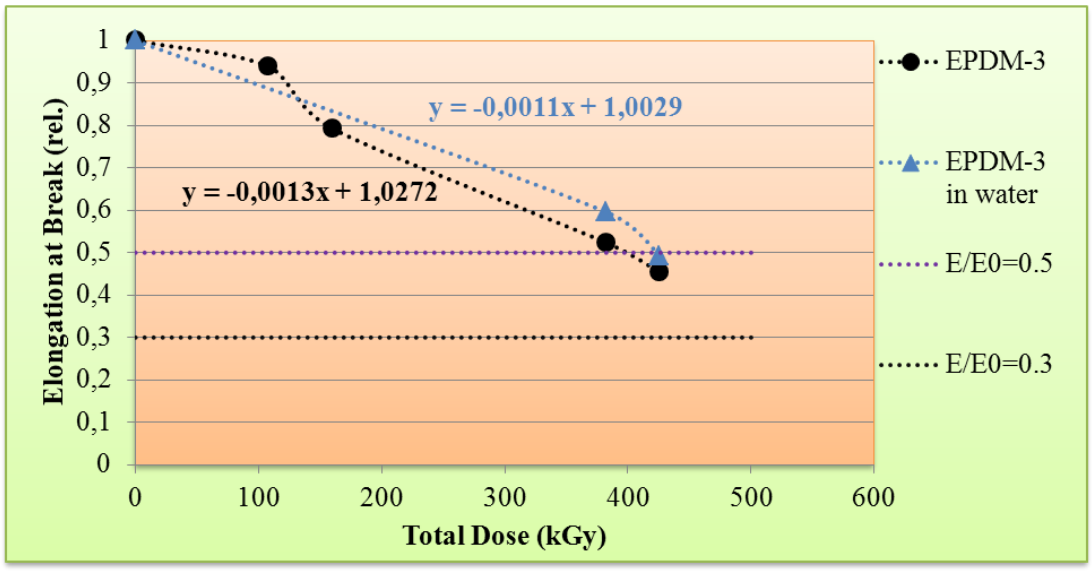

Fig. 3.4 Elongation at break results (rel.) of EPDM-3 for low dose rate radiation

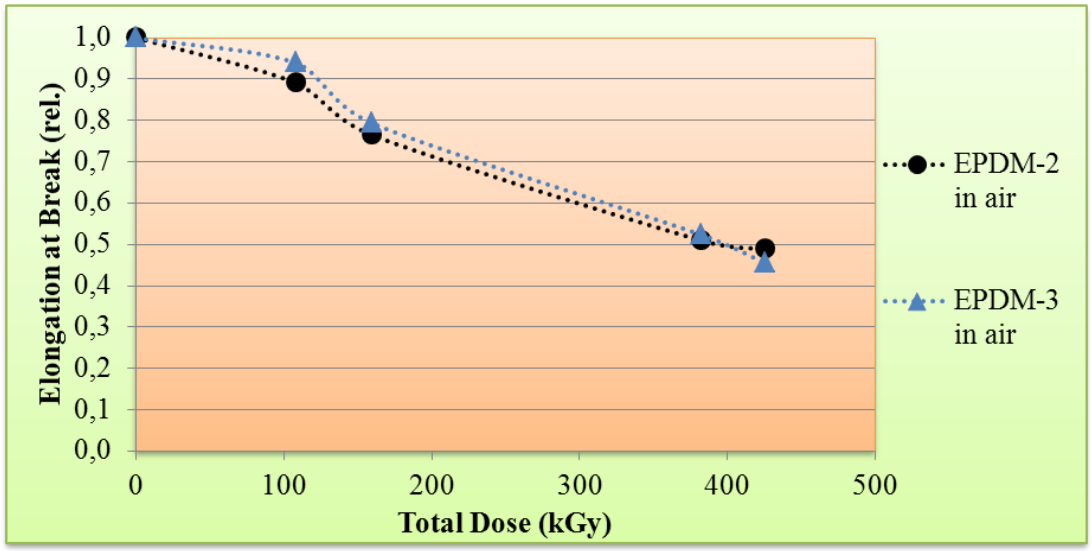

Fig. 3.5 Comparison of elongation at break results (rel.) of EPDM-2 and EPDM-3 samples irradiated in air

According to the test results shown in Figure 3.3, 3.4 and 3.5, increase in the total dose resulted in significant decrease in elongation at break values of the EPDM-2 and the EPDM-3 samples via low dose rate irradiation. These decreases showed linear behaviour. In low dose rate irradiation, radiation penetrated deeply into the structure that caused tracking by virtue of various constructive and destructive reactions not only on the surface but also inside the polymer. Moreover, all external effects such as moisture and oxygen might diffuse deeply resulting in severe damage in the structure of EPDM with irradiation. Decrease in elongation at break values in the EPDM-2 and the EPDM-3 showed an increase in the stiffness of polymer. As a result, elasticity of EPDM was diminished with irradiations showing that EPDM lost its elastomeric behavior.

According to Figure 3.5, elongation at break values of the EPDM-2 and the EPDM-3 samples, which were irradiated in air, were close to each other. In addition, initial elongation at break values of the samples were also similar (267 % and 255 % respectively) to each other. In a way, it could be stated that the equal amounts of 2,5-di-(t-butylperoxy)-2,5-dimethylhexane (DMBPHa) (in EPDM-2) and di-(tert-butylperoxyisopropyl)- benzene (BBPIB) in (EPDM-3) had similar effects on the mechanical properties after vulcanization and ionizing radiation. When elongation at break values of the EPDM samples were compared for radiation stability criteria, both EPDM-2 and EPDM-3, irradiated in water, had higher elongation at break values with respect to irradiation in air. This indicates that water prevented the destructive effects of gamma radiation via self shielding property. Moreover, by using equations in Figures 3.3 and 3.4, it was found that relative elongation at break values of 0.0, 0.3, 0.5 corresponds to 830 kGy, 582 kGy and 414 kGy irradiation for EPDM-2; 790 kGy, 560 kGy and 405 kGy irradiation for EPDM-3. These values were higher for the EPDM samples which were irradiated in water.

Furthermore, the values (rel.) and the comparisons of elongation at break results (rel.) which belong to the high dose rate irradiated EPDM samples, are given in Table 3.5 and shown in Figures 3.6, 3.7 and 3.8.

Table 3.5 Elongation at break values (rel.) of EPDM samples (high dose rate irradiated samples)

	EPDM-2	EPDM-3
Total Dose	**Elong. at Break (rel.)**	**Elong. at Break (rel.)**
0	1.00	1.00
664 kGy	0.31	0.35
993 kGy	0.22	0.24
2157 kGy	0.11	0.15

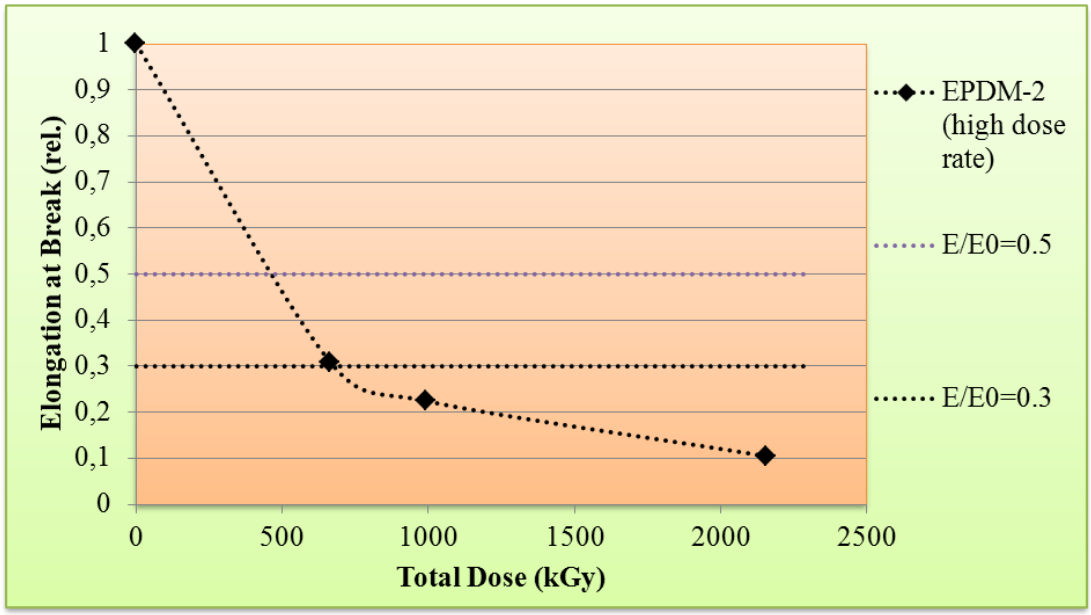

Fig. 3.6 Elongation at break results (rel.) of EPDM-2 for high dose rate radiation

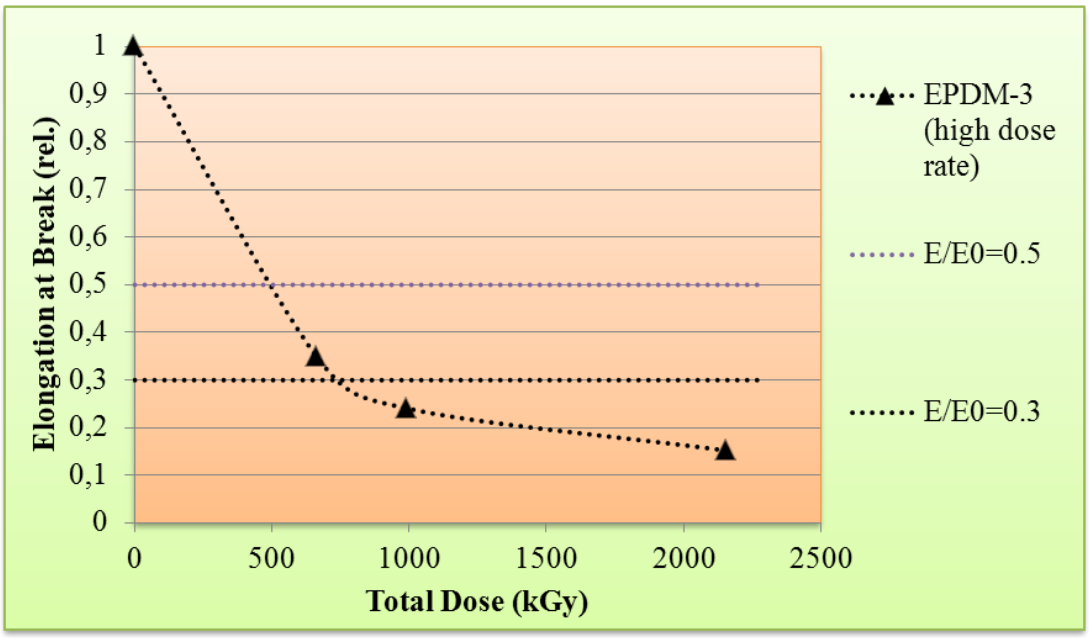

Fig. 3.7 Elongation at break results (rel.) of EPDM-3 for high dose rate radiation

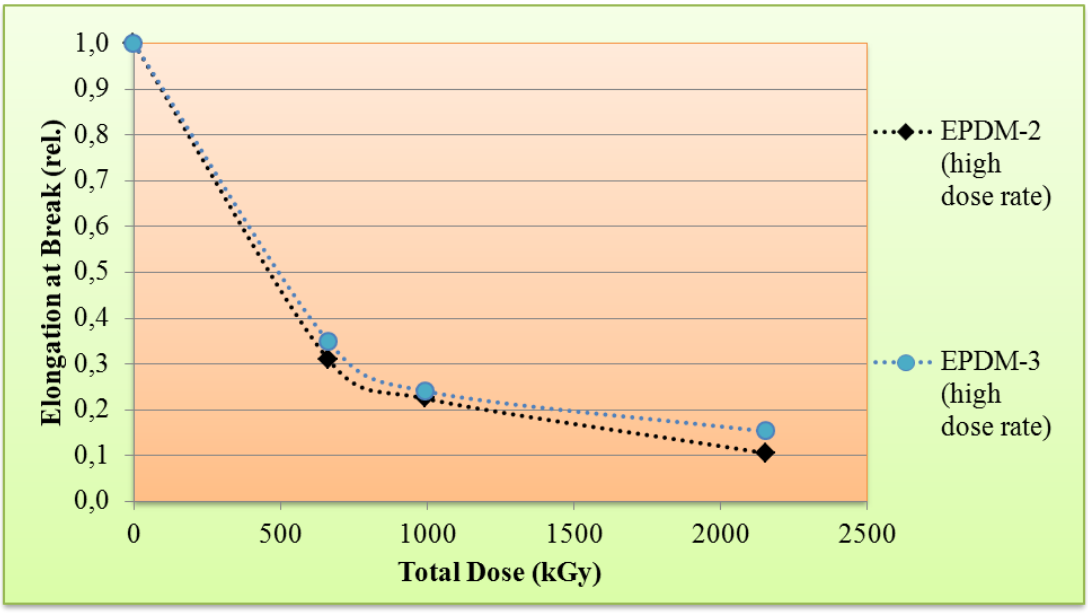

Fig. 3.8 Comparison of elongation at break results (rel.) of EPDM samples for high dose rate radiation

According to high dose rate results, it was concluded that there were sharp decreases in elongation at break values up to 664 kGy. Elastomeric properties of EPDM samples diminished severely as a result of increase in total dose. The reason of sharp decrease up to 664 kGy could be due to the reactions of unreacted peroxides and ENB moieties with each other to form crosslinking in the structure as well as formation of oxidative products and chain scission reactions. Both oxidation and crosslinking reactions might led to a decrease in elongation at break values. After 664 kGy, decrease in elongation at break values showed linear change. According to Figure 3.8, EPDM-3 was slightly more resistant to gamma radiation than EPDM-2. This might probably be due to the peroxide's structure. EPDM-3 included aromatic type peroxide which were relatively more stable because the energy required to excite aromatic type peroxide was higher. Therefore, the peroxide of BBPIB was more resistant to destructive effects of gamma irradiation. In the graph shown in Figure 3.8, after 664 kGy both in EPDM-2 and EPDM-3, decreases in values showed a linear change. Extrapolation of the data would give the theoretical total dose values that EPDM could resist. According to the data extrapolation, it was calculated that EPDM-2 and EPDM-3 could resist total doses of 3751 kGy and 3955 kGy theoretically. When elongation at break values of EPDM samples in air and in water conditions were compared, it could be stated that the radiation stabilities of EPDM under high dose rate radiation was higher. This situation was due to the oxygen diffusion effect. In low dose rate irradiations, oxygen diffused into the structure deeper due to the relatively longer time period of irradiation and relatively low energy of irradiation. Diffusion of oxygen in to the structure deeper caused more oxidative reactions which were destructive [14,39]. Therefore, destructive reactions because of oxygen were higher in low dose irradiations.

3.1.3. Hardness

Hardness is defined as a polymer's resistance to the local deformation [40]. According to the literature, all irradiated samples' hardness values are greater than the hardness values of non-irradiated samples, and the reason for the increase in the hardness values is explained by radiation induced crosslinking reactions [41]. On the other hand, according to the International Atomic Energy Agency reports [22], increase in hardness is a result of radiation induced aging as well. Radiation induced aging consists of constructive and destructive reactions. Radiation induced crosslinking, chemi-crystallization because of the morphological rearrangements of the polymer chains after chain degradation, the formation of oxidative species and the crosslinking of these species, unreacted diene moieties' reactions and chain scission can cause increases in hardness [41,42]. An important point which can be understood from literature is that irradiated EPDM samples' resistivity toward local deformation is higher than for the non-irradiated EPDM samples [41].

Hardness of the EPDM-1 samples (irradiated in air) increased up to 383 kGy as shown in Table 3.6 and Figure 3.9. After 383 kGy, reduction in the hardness was observed up to 426 kGy. After 426 kGy, the hardness of EPDM-1 samples increased up to 1178 kGy which was total dose of irradiation during 2.5 years at low dose rate. Hardness is inversely related with elasticity. Increase in hardness resulted in loss in the elasticity in the polymer structure. Up to 383 kGy, increase in hardness value was probably due to additional crosslinking. After 383 kGy, decrease in hardness was observed. Hardness values at 160 kGy and 426 kGy were the same. This means that between 160 kGy and 426 kGy, constructive (rearrangement of scissed part) and destructive reactions (chain scission) occurred probably to same extent. When compression set and hardness values are combined in order to estimate how radiation affects the EPDM-1 samples, it is concluded that irradiation first improved the mechanical properties of EPDM by radiation induced crosslinking reactions which occurred dominantly than any other reactions to 383 kGy. After 383 kGy to 426 kGy irradiation, degradative reactions might occurred as dominant mechanism. Further irradiation to 1178 kGy brought increases in the hardness values. As a result of

hardness, the elasticity of the EPDM rubbers diminished via irradiation. Hardness increases are tolerated to a certain value for the applications of polymers in the radiation area [22]. A large increase in hardness brings more brittleness which is not desired. In this study, the difference between non-irradiated and the 2.5 year irradiated sample, was 20 %. This increase in hardness could be acceptable for storage of radioactive wastes.

In addition, hardness results of irradiated samples which were kept in water are shown in Table 3.7 and Figure 3.9. According to the results in 383 kGy, hardness value of the sample (irradiated in water) was higher than the hardness value of the sample irradiated in air. For further irradiation up to 426 kGy, the hardness values of samples in air and in water conditions were approximately the same. After point of 383 kGy, the hardness values of EPDM samples irradiated both in water and open to atmosphere conditions were nearly the same. Hardness results of irradiated EPDM samples are given in Tables 3.6, 3.7 and shown in Figure 3.9.

Table 3.6 Hardness (Shore A) values of EPDM-1 samples irradiated in air

Total Dose	Hardness (Shore A)	Hardness (rel.)
0	73	1.00
160 kGy	77	1.05
383 kGy	82	1.12
426 kGy	77	1.05
727 kGy	80	1.10
992 kGy	84	1.15
1178 kGy	87	1.19

Table 3.7 Hardness (Shore A) values of EPDM-1 samples irradiated in water

Total Dose	Hardness (Shore A)	Hardness (rel.)
0	73	1.00
160 kGy	80	1.10
383 kGy	82	1.12
426 kGy	77.5	1.06

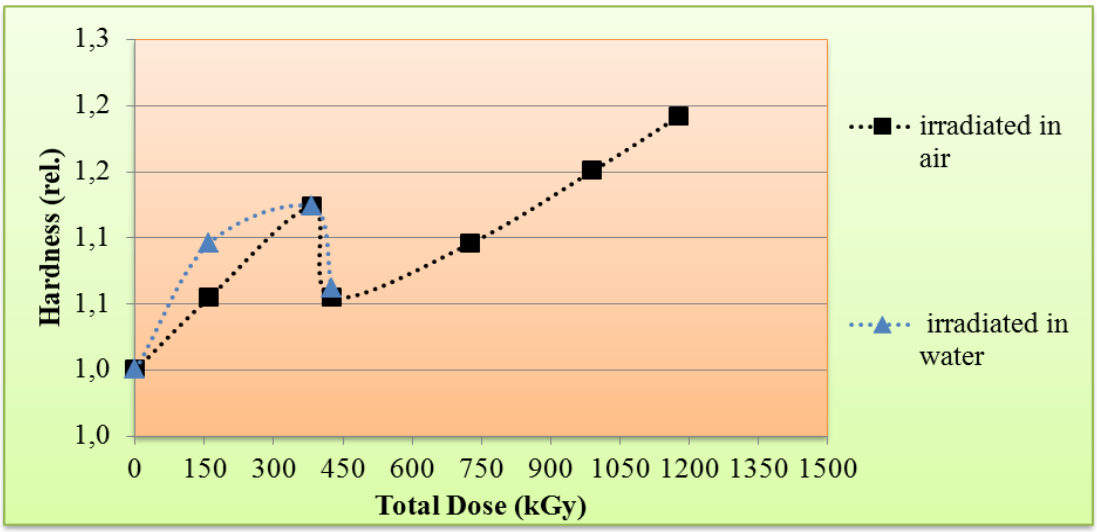

Fig. 3.9 Hardness values (rel.) of EPDM-1 samples irradiated in low dose rate

3.1.4. Elastic Modulus

Elastic Modulus can be calculated by taking the slope of the first linear portion which belongs to stress-strain curve [43]. Elastic modulus gives information about the stiffness of polymers [44]. Moreover, it supplies the opportunity to detect crosslink density by using Equation 2 shown below [45]:

$$E = \eta RT \qquad (2)$$

At which **E** is elastic modulus, **η** is crosslink density, **T** is the temperature at which measurements are carried out and **R** refers to gas constant. Therefore, crosslink density is related to the elastic modulus [45]. Elastic modulus values are given in Tables 3.8, 3.9 and shown in Figures 3.10, 3.11, 3.12.

Table 3.8 Elastic modulus values (rel.) of EPDM samples (low dose rate irradiated in air)

	EPDM-2	**EPDM-3**
Total Dose	**Elastic Modulus (rel.)**	**Elastic Modulus (rel.)**
0	1.00	1.00
108 kGy	1.08	1.16
160 kGy	1.09	1.20
383 kGy	1.58	2.16
426 kGy	1.98	2.46

Table 3.9 Elastic modulus values (rel.) of EPDM samples (low dose rate irradiated in water)

	EPDM-2	EPDM-3
Total Dose	**Elastic Modulus (rel.)**	**Elastic Modulus (rel.)**
0	1.00	1.00
383 kGy	1.49	2.03
426 kGy	1.87	2.52

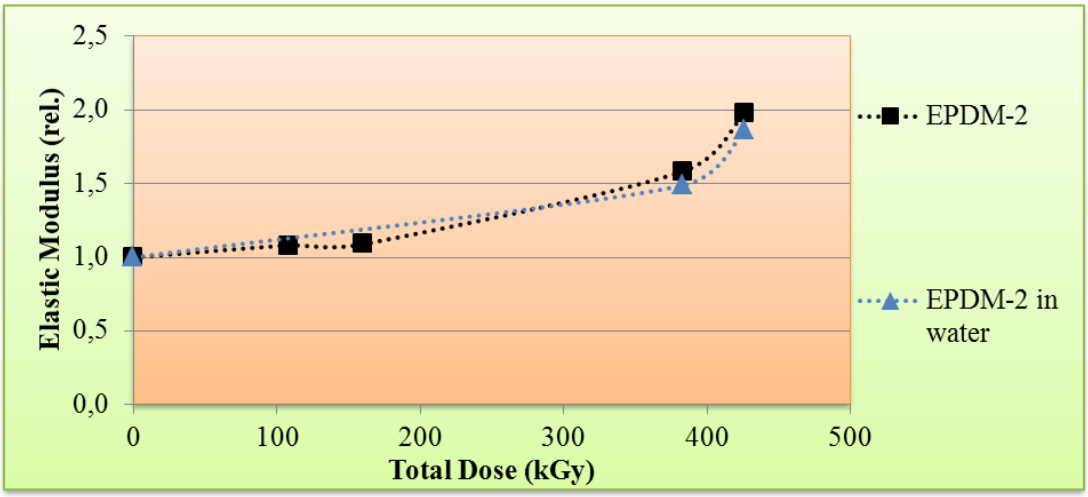

Fig. 3.10 Elastic modulus values (rel.) of EPDM-2 samples irradiated in low dose rate

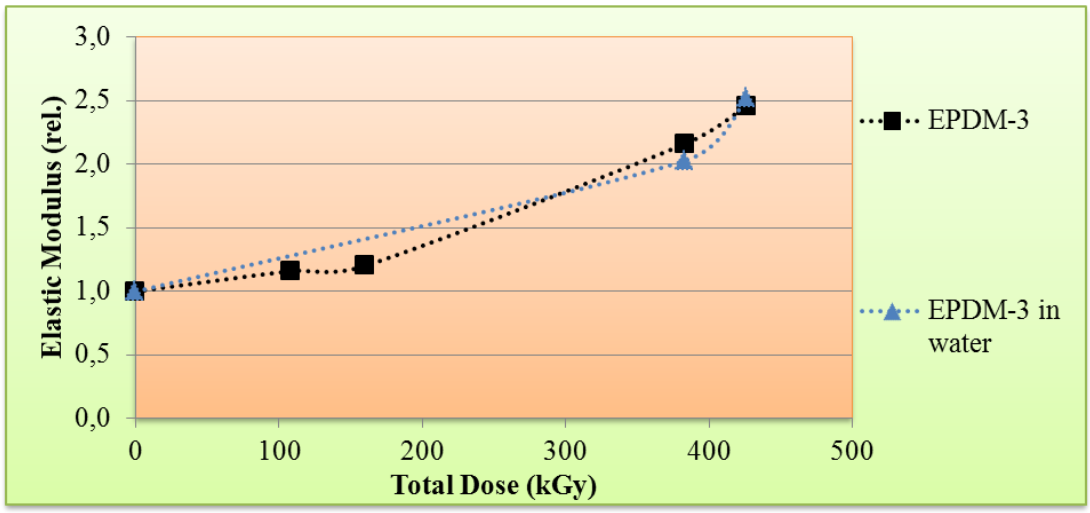

Fig. 3.11 Elastic modulus values (rel.) of EPDM-3 samples irradiated in low dose rate

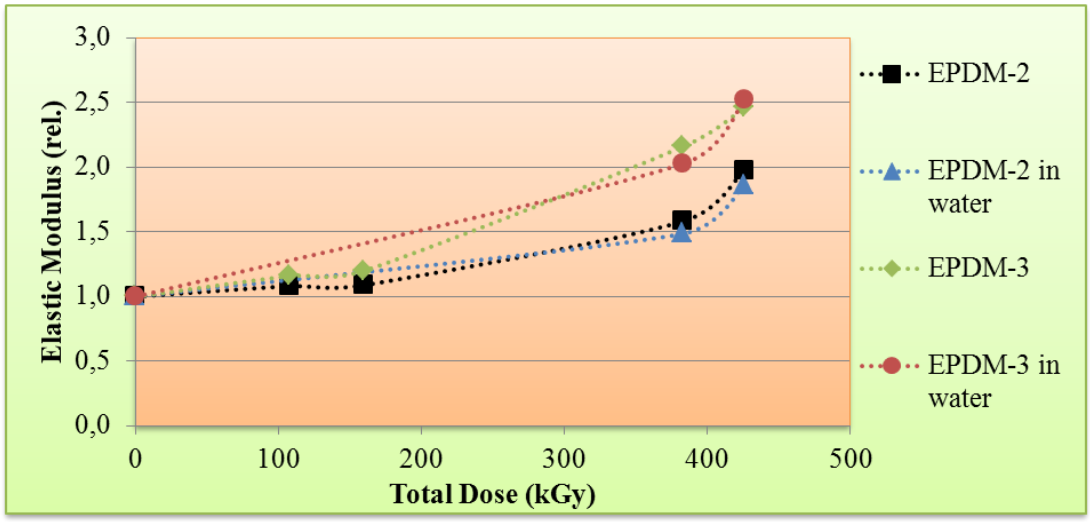

Fig. 3.12 Comparison of elastic modulus (rel.) values of EPDM-2 and EPDM-3 samples irradiated in low dose rate

Decrease in the elastic modulus is described as it is a consequence of chain scission and the increase in elastic modulus is explained as it is a consequence of crosslinking

[46]. According to Table 3.8 and 3.9, elastic modulus values showed increases together with the rise in the total dose. As elastic modulus is related to the crosslink density, increase in the elastic modulus resulted in increment in crosslink density. With reference to results, low dose irradiation to 426 kGy gave rise to more crosslinking reactions in the EPDM's structure. In this study, decrease in elastic modulus was not observed. The reason behind the increase in the elastic modulus values might be that the radiation induced crosslinking due to the presence of non-reacted double bonds, recombination and reticulation of crumbled parts after chain scission or oxidation were probably more prone to occur in the structure of EPDM. When elastic modulus values were compared, relative increases in the elastic modulus values of EPDM-3 were higher than increases in EPDM-2. This situation was probably due to the peroxide effect. EPDM-3 contained aromatic type; on the other hand, EPDM-2 contained aliphatic type of peroxide. During vulcanization, aromatic peroxide produced stronger radicals. During irradiations, ionizing radiation probably initiated reactions between peroxide and EPDM. As a result of these reactions up to 426 kGy, strong peroxide made the EPDM hard. In addition to peroxide effect, water effects on EPDM during irradiations were investigated by comparing elastic modulus values. According to elastic modulus values, water shielded the gamma rays so that at equal doses for EPDM-2 to 426 kGy and for EPDM-3 to 383 kGy, elastic modulus values of samples irradiated in water were lower. On the other hand, for EPDM-3 at 426 kGy, the elastic modulus value of the sample irradiated in water is higher than the sample irradiated in air. It may be infered that after 383 kGy, radiation might disrupt the hydrophobicity of the EPDM-3 so water radicals, which diffused into the EPDM structure, caused additional reactions resulting in increase in hardness.

In addition to the results of the low dose irradiated EPDM samples, high dose irradiated EPDM's results are given in Table 3.10 and shown in Figure 3.13.

Table 3.10 Elastic modulus values (rel.) of EPDM samples (high dose rate irradiated)

	EPDM-2	EPDM-3
Total Dose	**Elastic Modulus (rel.)**	**Elastic Modulus (rel.)**
0	1.00	1.00
664 kGy	2.79	2.70
993 kGy	4.15	6.78
2157 kGy	21.38	14.03

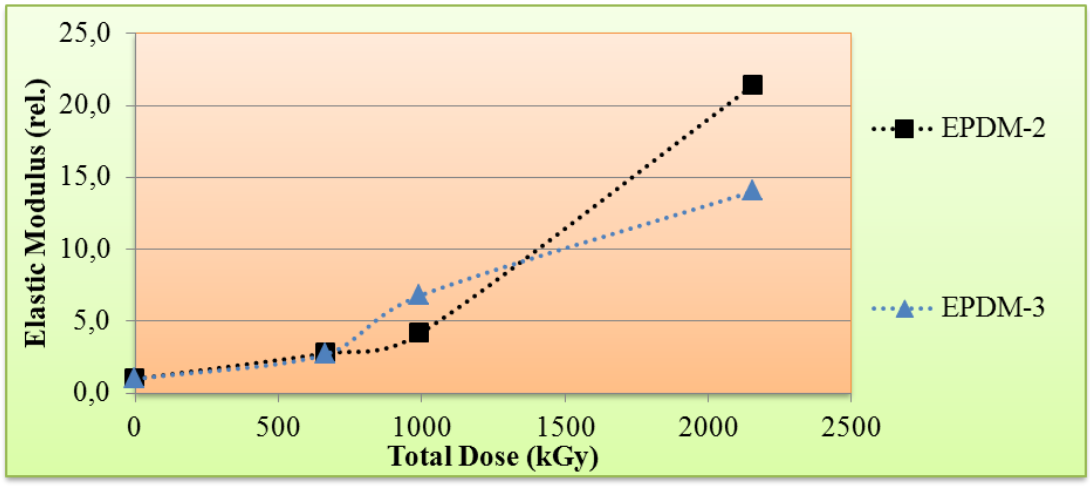

Fig. 3.13 Comparison of elastic modulus values (rel.) of EPDM-2 and EPDM-3 samples irradiated in high dose rate

With regard to the elastic modulus values of the high dose rate irradiated EPDM samples, increase in the total dose resulted in increase in the elastic modulus values. In 664 kGy, the relative elastic modulus values of the EPDM-2 and the EPDM-3 were approximately the same. After 664 kGy to 993 kGy, elastic modulus of the

EPDM-3 was higher; however further irradiation to 2157 kGy made EPDM-2 harder and stiffer than the EPDM-3. The difference between the EPDM-2 and the EPDM-3 might be originated from the peroxide type in that aromatic peroxide retards the radiation effects and prevents the deterioration in the elasticity of the EPDM at higher doses.

3.1.5. Maximum Stress at Break

Maximum stress at break values of irradiated samples help to identify whether or not stiffness and brittleness are increased via irradiation [22]. According to maximum stress at break values of low dose rate irradiated samples shown in Figures 3.14, 3.15, 3.16 and Tables 3.11, 3.12, all maximum stress at break values of irradiated (in air and in water) samples decreased up to 426 kGy. On the other hand, between 383 - 426 kGy for EPDM-2 (in air) and between 160 - 383 kGy for EPDM-3 (in air), there were small increases in maximum stress at break values. Relative maximum stress at break values for the EPDM-2 and the EPDM-3 samples (irradiated in air) were approximately the same. It can be concluded that, low dose rate irradiation diminished the EPDM's elasticity regardless of the peroxide type and the content up to 426 kGy. Stiffness was increased in the EPDM-2 and the EPDM-3 samples via irradiation. Additionally, according to the results, maximum stress at break values (rel.) of EPDM samples (irradiated in water) were higher than in all values of samples which were irradiated in air. This means that in water condition, decrease in elasticity of the EPDM-2 and the EPDM-3 samples was less than the decrease in elasticity in air condition. In EPDM-3 (irradiated in water), containing aromatic type peroxide, change in the maximum stress at break values were lowest in all irradiated samples. The reason for this is that in addition to water, aromatic type peroxide could partially prevent the effects of radiation. [34].

Figures 3.14, 3.15, 3.16 and Tables 3.11, 3.12 show maximum stress at break values of irradiated EPDM-2 and EPDM-3 samples.

Table 3.11 Maximum stress at break values (rel.) of EPDM samples (low dose rate irradiated samples in air)

	EPDM-2	EPDM-3
Total Dose	**Max. Stress at Break (rel.)**	**Max. Stress at Break (rel.)**
0	1.00	1.00
108 kGy	0.96	0.96
160 kGy	0.90	0.85
383 kGy	0.74	0.88
426 kGy	0.83	0.85

Table 3.12 Maximum stress at break values (rel.) of EPDM samples (low dose rate irradiated samples in water)

	EPDM-2	EPDM-3
Total Dose	**Max. Stress at Break (rel.)**	**Max. Stress at Break (rel.)**
0	1.00	1.00
383 kGy	0.86	0.98
426 kGy	0.88	0.94

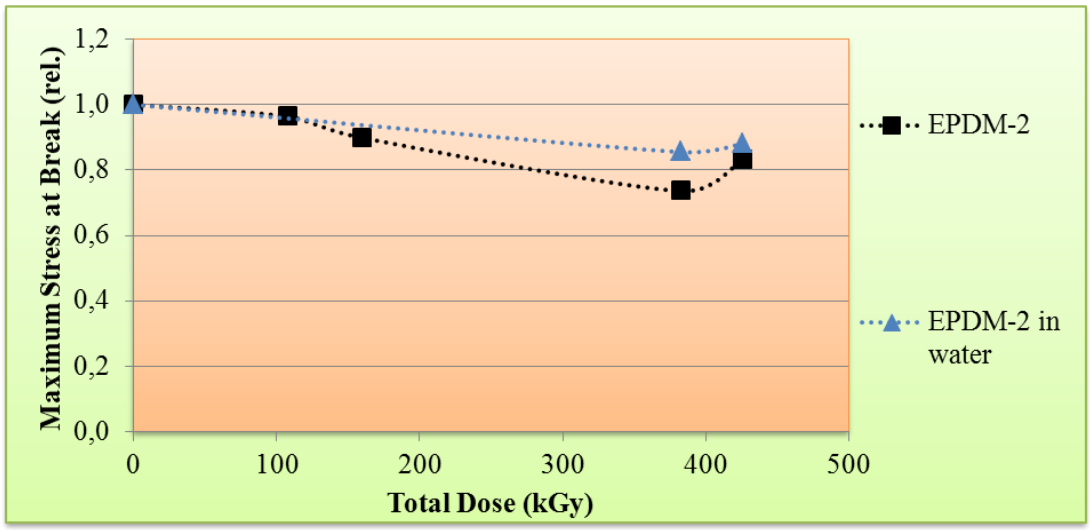

Fig. 3.14 Maximum stress at break values (rel.) of EPDM-2 samples for low dose rate irradiation

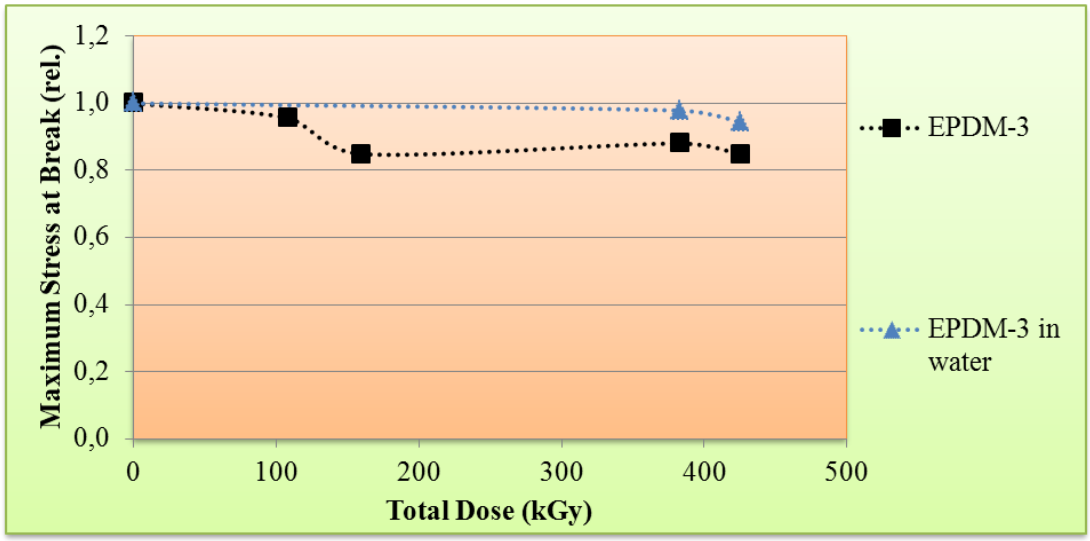

Fig. 3.15 Maximum stress at break values (rel.) of EPDM-3 samples for low dose rate irradiation

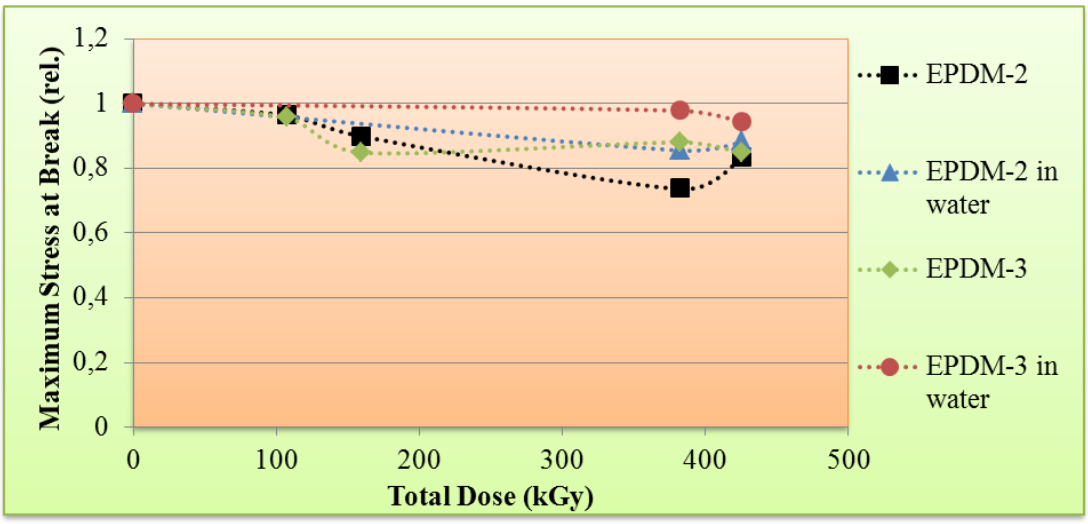

Fig. 3.16 Comparison of maximum stress at break values (rel.) of EPDM-2 and EPDM-3 samples for low dose rate irradiation in air and in water

Maximum stress at break values of the high dose irradiated EPDM samples are given in Table 3.13 and shown in Figure 3.17.

Table 3.13 Maximum stress at break values (rel.) of EPDM samples (high dose rate irradiated samples)

	EPDM-2	EPDM-3
Total Dose	**Max. Stress at Break (rel.)**	**Max. Stress at Break (rel.)**
0	1.00	1.00
664 kGy	0.73	0.76
993 kGy	0.72	0.72
2157 kGy	0.67	0.69

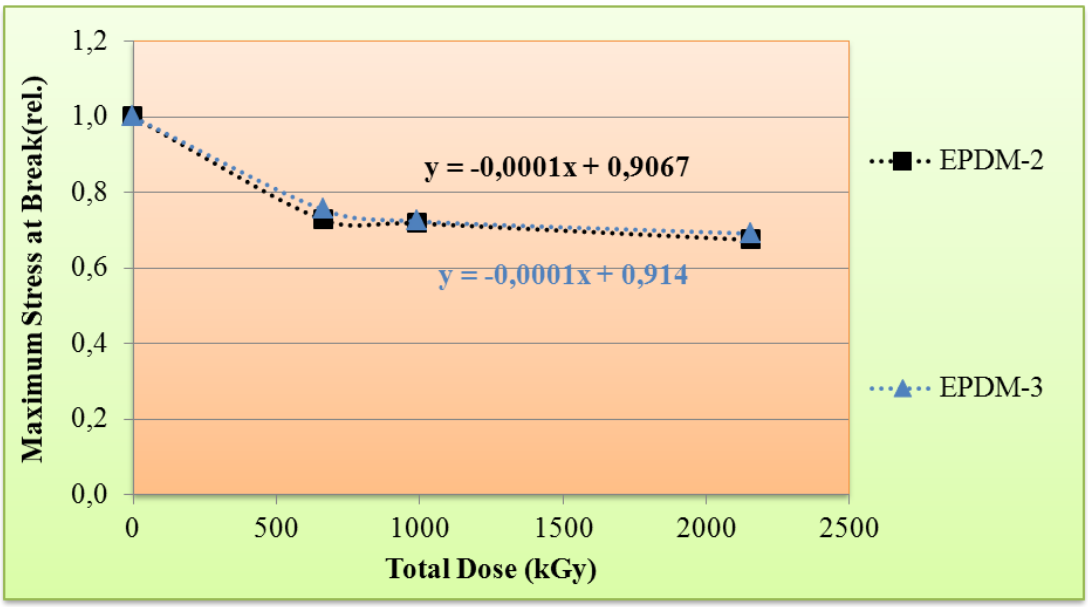

Fig. 3.17 Comparison of maximum stress at break values (rel.) of EPDM-2 and EPDM-3 samples for high dose rate irradiation

According to high dose rate maximum stress at break results, values decreased via irradiation regardless of the peroxide content and the type. Relative values were approximately the same for EPDM-2 and EPDM-3. Irradiation degraded the elasticity of both the EPDM-2 and the EPDM-3 samples. According to the linear change calculated from Figure 3.28, EPDM-2 and EPDM-3 can resist up to 9067 kGy and 9140 kGy respectively regarding radioactive waste storage. On the other hand, it was found 4000 kGy irradiation to which EPDM can resist, from elongation at break results. Elongation at break values are more important and valid in estimating radiation stability, therefore 9000 kGy irradiation could not be resisted by EPDM.

3.2. XRD INVESTIGATION

Four different dose (non-irradiated, 383 kGy, 383 kGy in water, 992 kGy) irradiated EPDM-1 samples were investigated by XRD. The Figure 3.18, belonging to the non-irradiated sample, clearly showed XRD patterns with high intensity. In Figures 3.19 and 3.20, which belong to 383 kGy irradiated in air and in water samples respectively, XRD patterns had relatively less intensity with respect to non-irradiated samples' pattern. It shows that, deformation in the crystallinity started via radiation. On the other hand, XRD patterns of the sample, irradiated to 383 kGy in water, had higher intensities than XRD patterns of the sample, which were irradiated in air. It showed that deformation in the crystallinity was less in the 383 kGy irradiated (in water) sample. The reason behind the lower intensities in water condition can be explained by the fact that water shielded the radiation and this shielding prevents the deformation to some extent. In the last figure which belongs to 992 kGy irradiated EPDM sample, lowest pattern intensities were observed. Figure 3.21 shows that high dose radiation caused high crystallinity deformation and with 992 kGy radiation, the morphology of structure was changed. For this reason, the polymer became amorphous. According to compounding, EPDM-1 samples should be amorphous because of the relatively low ethylene content. However, high intensity patterns most probably came from additives. The possible reason behind the intensity decrease in the XRD patterns could be explained by the decomposition of additives via radiation. This situation can be proved by comparing the results of the mechanical tests, ATR-FTIR with the XRD results. According to previous results, it was stated that oxidation and brittleness occured in the EPDM's structure. Elasticity and oxidation are directly related to the plasticizer and the stearic acid content. Therefore, decrease in the elasticity and the XRD pattern's intensity could be associated with the decrease in the plasticizer and the stearic acid content. Moreover, decreases in peak intensities revealed that chemi-crystallisations via radiation did not occurred [42].

Figures 3.18, 3.19, 3.20, 3.21 and 3.22 demonstrate XRD patterns of non-irradiated and irradiated EPDM-1 samples.

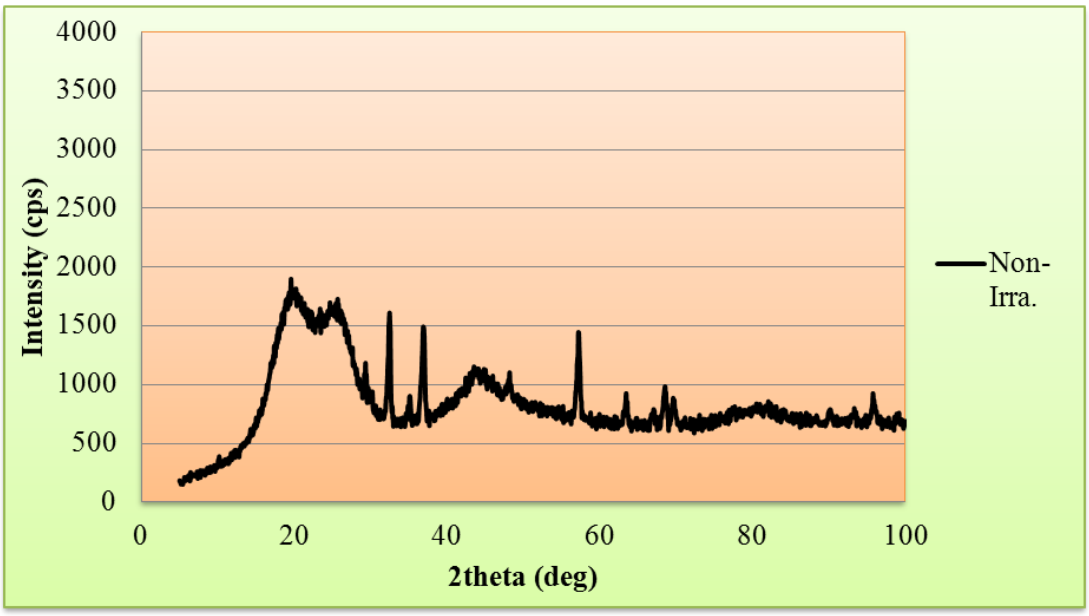

Fig. 3.18 XRD patterns of non-irradiated EPDM-1 samples

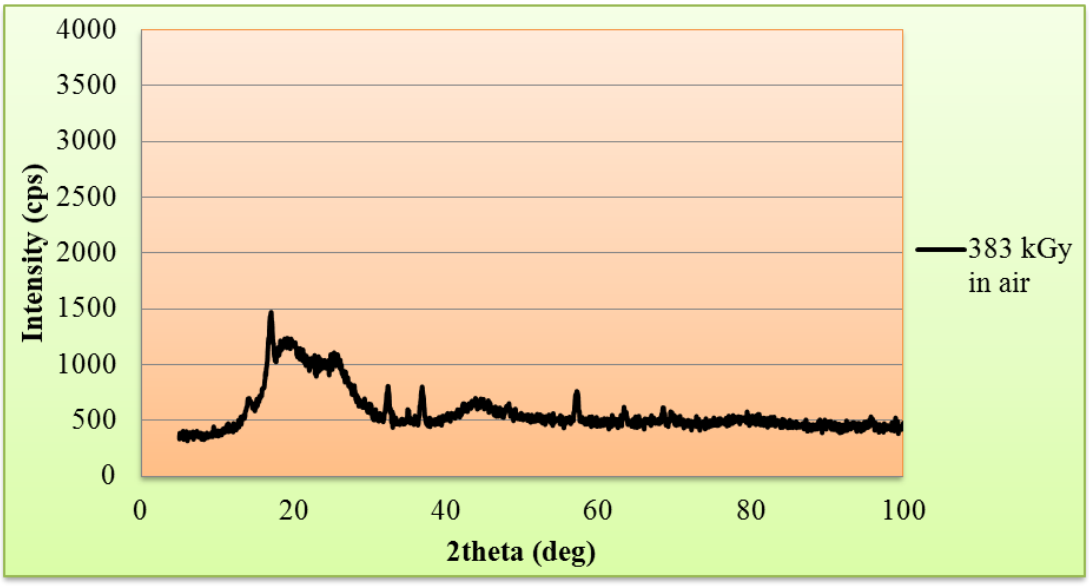

Fig. 3.19 XRD patterns of 383 kGy irradiated (in air) EPDM-1 samples

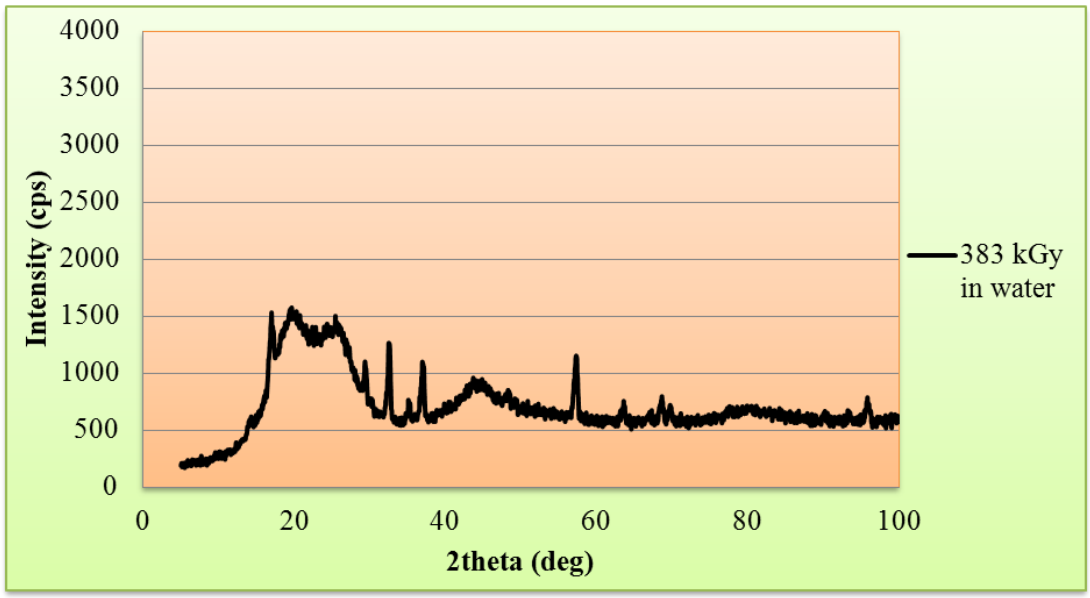

Fig. 3.20 XRD patterns of 383 kGy irradiated (in water) EPDM-1 samples

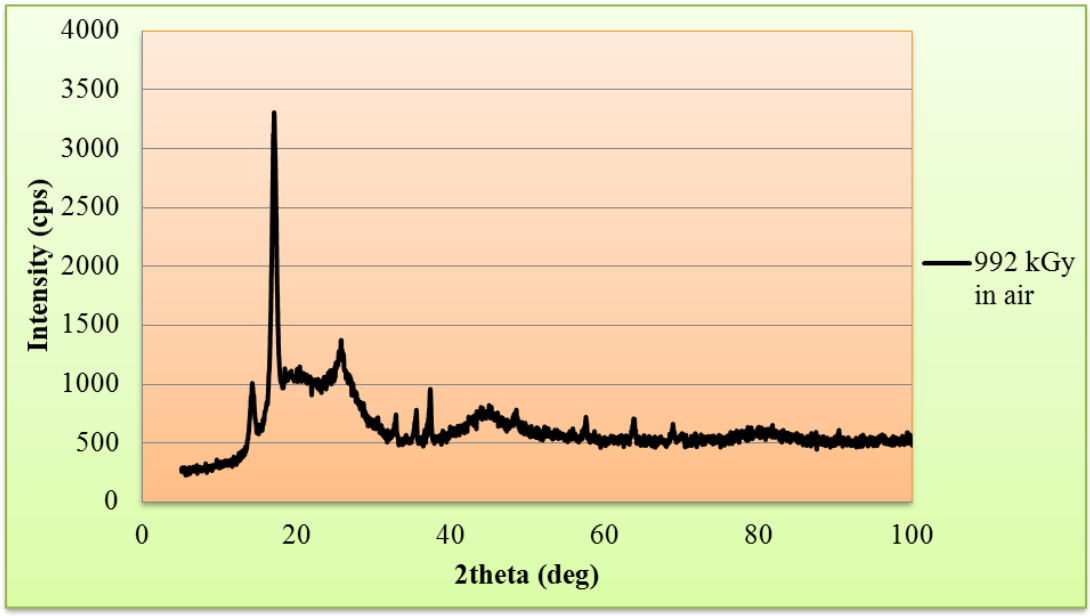

Fig. 3.21 XRD patterns of 992 kGy irradiated EPDM-1 samples

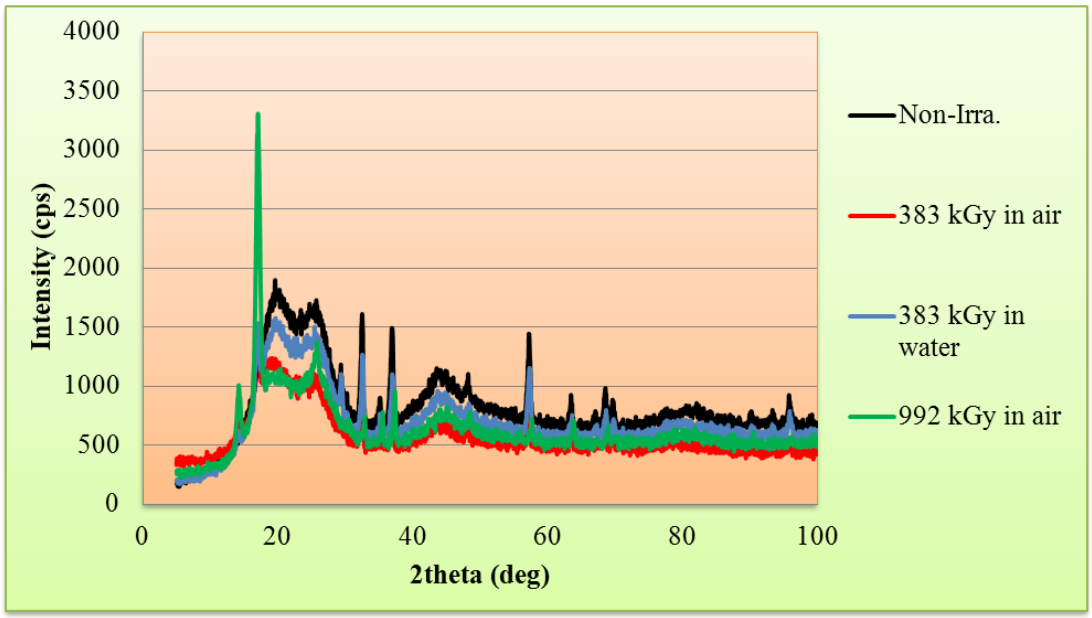

Fig. 3.22 Comparisons of XRD patterns of non-irradiated and irradiated EPDM-1 samples

* The first 2 notable reflections as shown in all XRD spectra came from the sticker which was used to hold the samples during XRD analysis. The XRD spectrum for the sticker is shown in Appendix B.

3.3. SCANNING ELECTRON MICROSCOPY (SEM)

Four different dose (non-irradiated, 383 kGy, 383 kGy at water, 990 kGy) irradiated EPDM-1 samples were investigated in Scanning Electron Microscopy (SEM). There are eight images shown in Figure 3.23 and 3.24. Image '**a**' belongs to non-irradiated EPDM sample. As shown from image '**a**', the surface of EPDM is clear and there are no fractures. In image '**b**' belonging to 383 kGy irradiated EPDM sample there were fractures on the surface. It shows that radiation deformation started on the surface. Image '**c**' belongs to the EPDM sample, which was irradiated to 383 kGy in water. It is understood from image '**c**' that water probably shielded radiation and it partially inhibited deformation. Lastly, it is understood from image '**d**', the most decomposed EPDM sample via irradiation was found in 992 kGy irradiated EPDM sample. Decomposition is understood from the clearly visible fractures on the EPDM surface. Additionally, it shows that high dose radiation caused high deformation in the surface. Figures 3.23 and 3.24 show Scanning Electron Microscope (SEM) images of irradiated EPDM-1 samples which were monitored at 1.000 X and 10.000 X respectively.

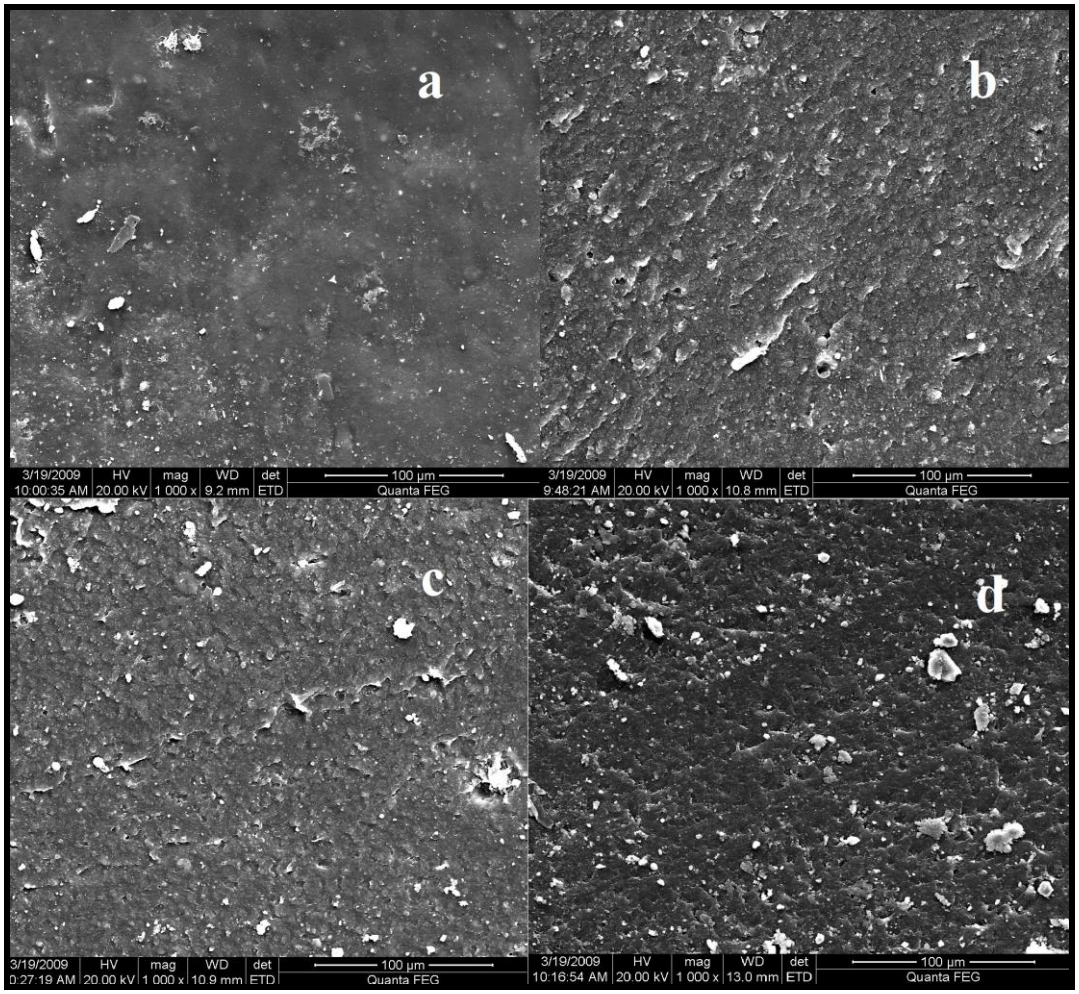

Fig. 3.23 SEM images of EPDM-1 samples monitored at magnitude 1.000 X

- **a.** Non-irradiated EPDM sample
- **b.** 383 kGy irradiated EPDM sample in atmosphere condition
- **c.** 383 kGy irradiated EPDM sample in water condition
- **d.** 992 kGy irradiated EPDM sample

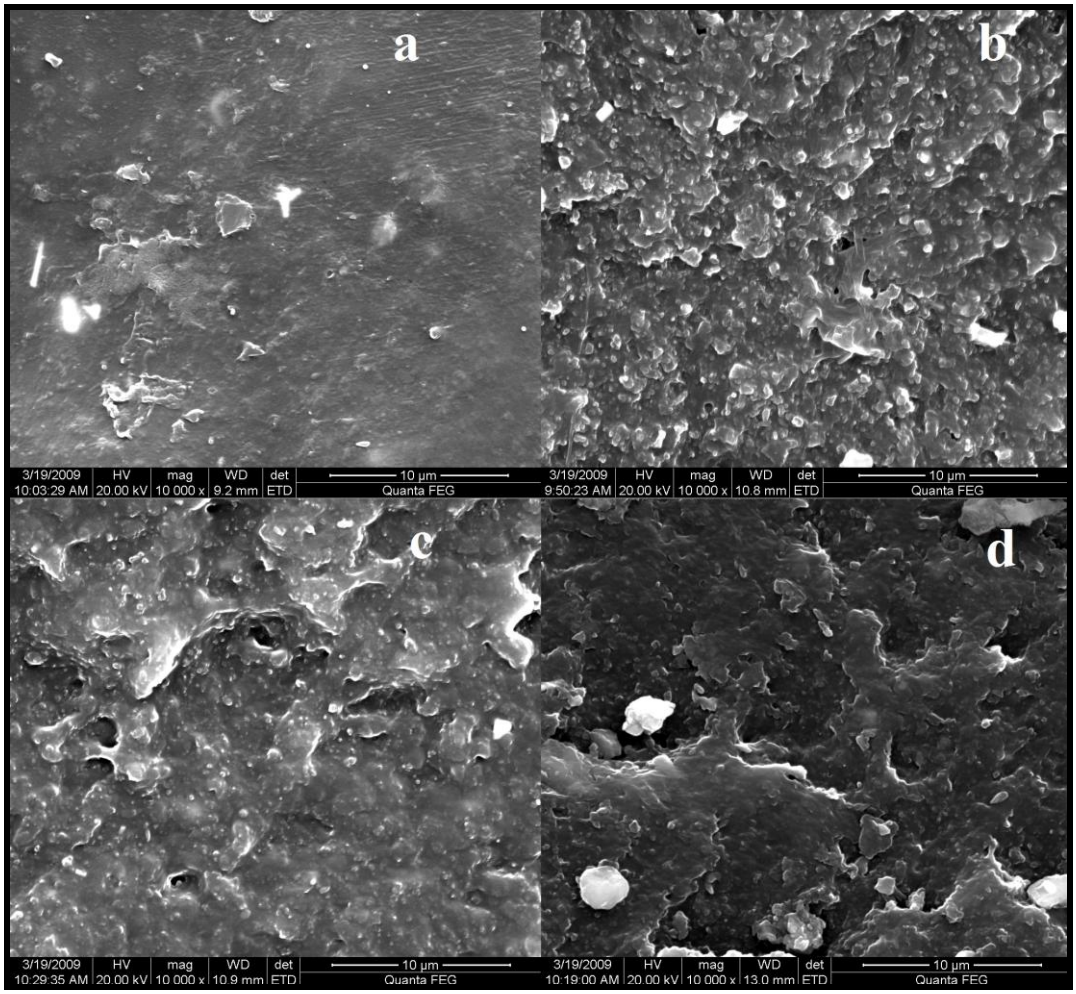

Fig. 3.24 SEM images of EPDM-1 samples monitored at magnitude 10.000 X

- **a.** Non-irradiated EPDM sample
- **b.** 383 kGy irradiated EPDM sample in atmosphere condition
- **c.** 383 kGy irradiated EPDM sample in water condition
- **d.** 992 kGy irradiated EPDM sample

3.4. THERMOGRAVIMETRIC ANALYSIS (TGA-FTIR)

According to TGA results, all EPDM-1 samples were stable up to 300 ^{o}C, at which no significant weight loss was observed. Between 300 ^{o}C and 400 ^{o}C, thermal decomposition slightly increased. After 400 ^{o}C to 500 ^{o}C, significant thermal decomposition was observed in all EPDM-1 samples. Between 500 ^{o}C and 800 ^{o}C, all EPDM-1 samples were not significantly decomposed. According to thermogravimetric curves, remaining weights of all irradiated EPDM samples (except 1178 kGy irradiated sample) at 300 ^{o}C, 350 ^{o}C, 400 ^{o}C, 500 ^{o}C and 600 ^{o}C were higher than the remaining weights of the non-irradiated sample. In addition, the temperatures at which maximum weight loss and 50 % decomposition is observed, can be taken as a reference point for thermal stability. Maximum weight loss was calculated from differential thermogravimetric (DTG) curves. In all irradiated EPDM-1 samples, 50 % decomposition and maximum weight loss occured at higher temperatures with respect to non-irradiated samples. The EPDM-1 sample which was irradiated to 383 kGy in water condition showed higher thermal stability than all other samples. The thermal stability of sample, which was irradiated in air to 160 kGy, was more stable than the sample that was irradiated to equal doses in water. It can be understood from the mechanical and the thermogravimetric analysis that the initial stage of irradiation caused crosslinking reaction as dominant mechanism. Moreover, it can be concluded that water shielded the radiation, therefore it reduced radiation effects on EPDM. Up to 178 kGy, real absorbed doses of the EPDM sample in water was probably less than the absorbed doses of EPDM in air. Moreover, according to thermogravimetric curves shown in Figure 3.25, the thermal stability of the 160 kGy irradiated (in air) sample was higher than the thermal stability of the 383 kGy irradiated (in air) sample. This was probably due to an increase in chain scission. Between 383 kGy and 992 kGy, increase in thermal stability was detected. Increase in thermal stability was a result of the increase in the crosslinking reactions and the formation of carbonyl groups which have higher dissociation energy than CH, CH_2 and CH_3 groups present in the main chain of EPDM. Moreover, after 992 kGy, a reduction in thermal stability was observed. The reason behind this might be

due to the occurrence of more chain scission and oxidative reactions (occurrence of hydroxyl and hydroperoxide group) which were observed in ATR spectra.

Tables 3.14 and 3.15 show decomposition temperatures and remaining weights of the EPDM-1 samples at various weight loses and at different temperatures respectively. Figure 3.25 displays TGA thermograms of irradiated EPDM-1 samples.

Table 3.14 Decomposition temperatures of EPDM-1 samples

EPDM-1 Samples	**Decomposition temperatures (^{o}C) at various weights loses**				
	10%	**20%**	**40%**	**50%**	**T max(^{o}C)**
Non-irra	360.67	442.51	468.21	477.06	468.70
160 kGy	368.15	462.77	488.32	498.43	486.82
160 kGy in water	360.75	459.13	484.25	494.26	482.57
383 kGy	373.51	460.73	487.25	497.37	484.71
383 kGy in water	386.16	467.55	492.89	503.51	490.55
727 kGy	360.60	461.95	488.43	498.80	486.59
992 kGy	375.91	461.64	488.38	498.82	489.22
1178 kGy	354.65	452.63	480.00	490.53	479.77

Table 3.15 Remained weight (%) of EPDM-1 samples at different temperatures

EPDM Samples	Remained weight (%) at different temperatures				
	300 °C	350 °C	400 °C	500 °C	600 °C
Non-irra	96.47	91.13	86.41	44.43	43.28
160 kGy	96.94	92.03	87.23	48.90	43.51
160 kGy in water	96.57	91.22	86.76	46.17	43.38
383kGy	97.04	92.61	87.50	48.06	43.23
383 kGy in water	97.65	93.60	88.82	52.88	43.59
727 kGy	96.32	91.20	86.87	49.12	43.42
992 kGy	96.75	92.59	87.94	49.18	43.28
1178 kGy	95.58	90.45	86.62	44.78	43.24

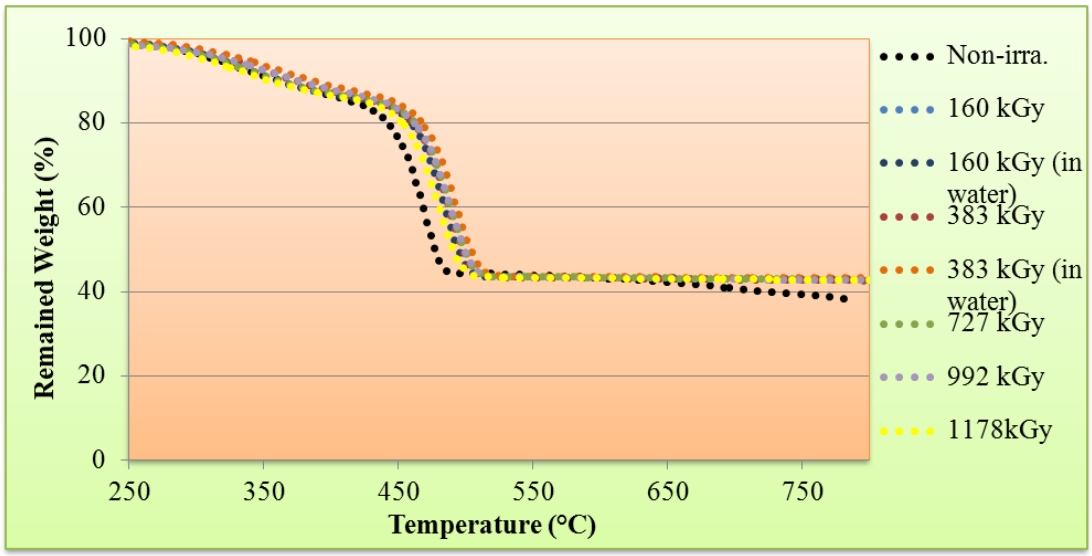

Fig. 3.25 Thermogravimetric (TG) curves of EPDM-1 samples

Figure 3.26 shows differential thermogravimetric (DTG) curves of EPDM-1 samples.

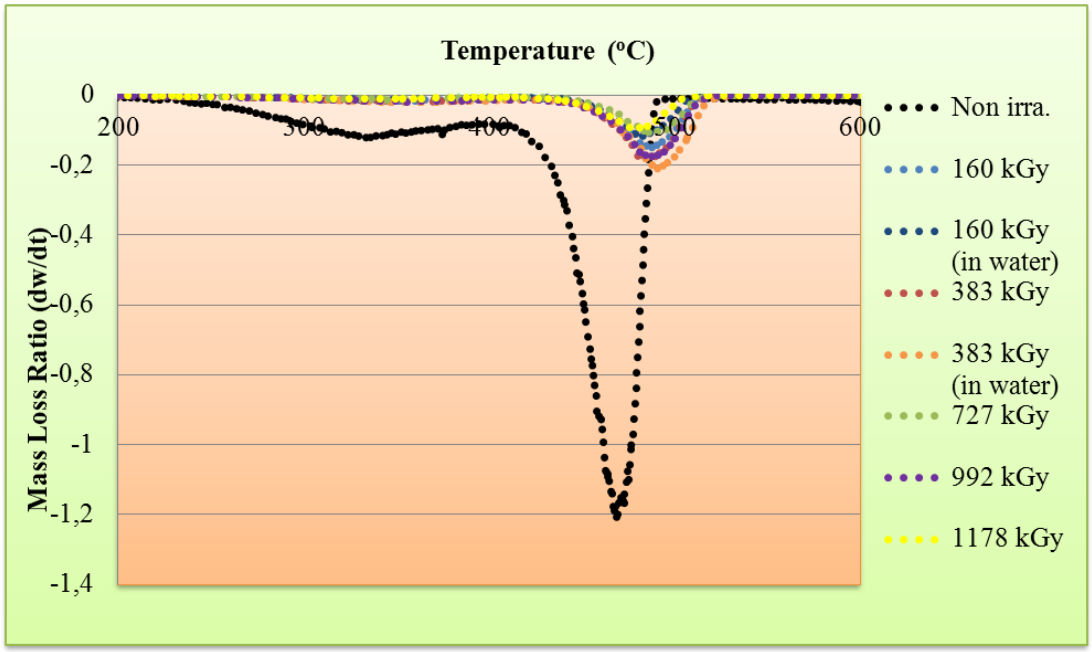

Fig. 3.26 Differential thermogravimetric (DTG) curves of EPDM-1 samples

According to the FTIR spectra of pyrolysis products emitted from TGA at 350 ^{o}C and 495 ^{o}C, intensities of FTIR peaks at 350 ^{o}C were higher than intensities at 495 ^{o}C. At 350 ^{o}C and 495 ^{o}C specific C-H stretching vibrations were observed around 2992 cm^{-1} with high intensities [45]. Peaks around 2350 cm^{-1} and between 3750-3550 cm^{-1}, indicating the presence of carbon dioxide were results of combustion [34]. Around 3400 cm^{-1}, the presence of hydroxyl and hydroperoxide, peaks disappeared at 495 ^{o}C [45]. Additionally, around 1700 and 1200 cm^{-1}, the presence of carbonyl and ether groups respectively, a significant decrease in the peak intensities is detected [45]. In other words at 495 ^{o}C, the FTIR spectrum of the volatile product closely resembled the FTIR spectra of the raw EPDM. At higher temperatures to 495 ^{o}C, additives used in compounding of EPDM were almost decomposed.

FTIR spectra of the pyrolysis samples (727 kGy irradiated) emitted from TGA were given in Figure 3.27, 3.28.

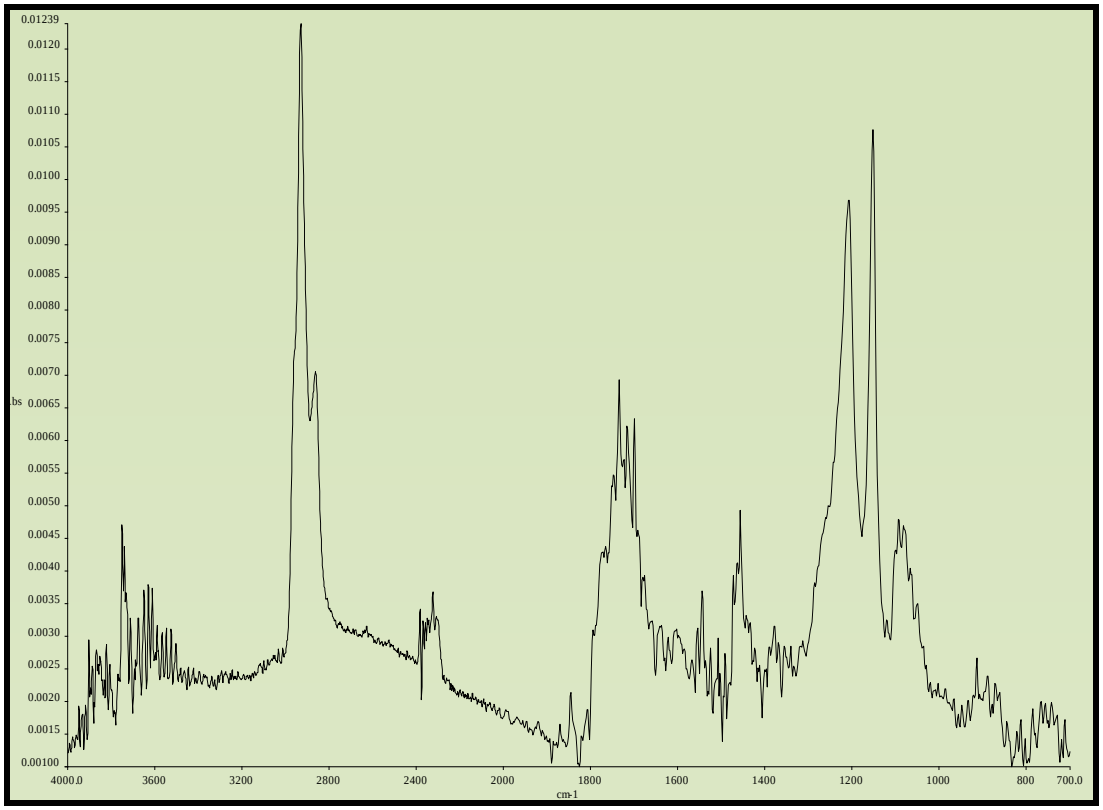

Fig. 3.27 FTIR spectrum of 727 kGy irradiated EPDM-1 sample's pyrolysis product emitted from TGA at 350 ^{o}C

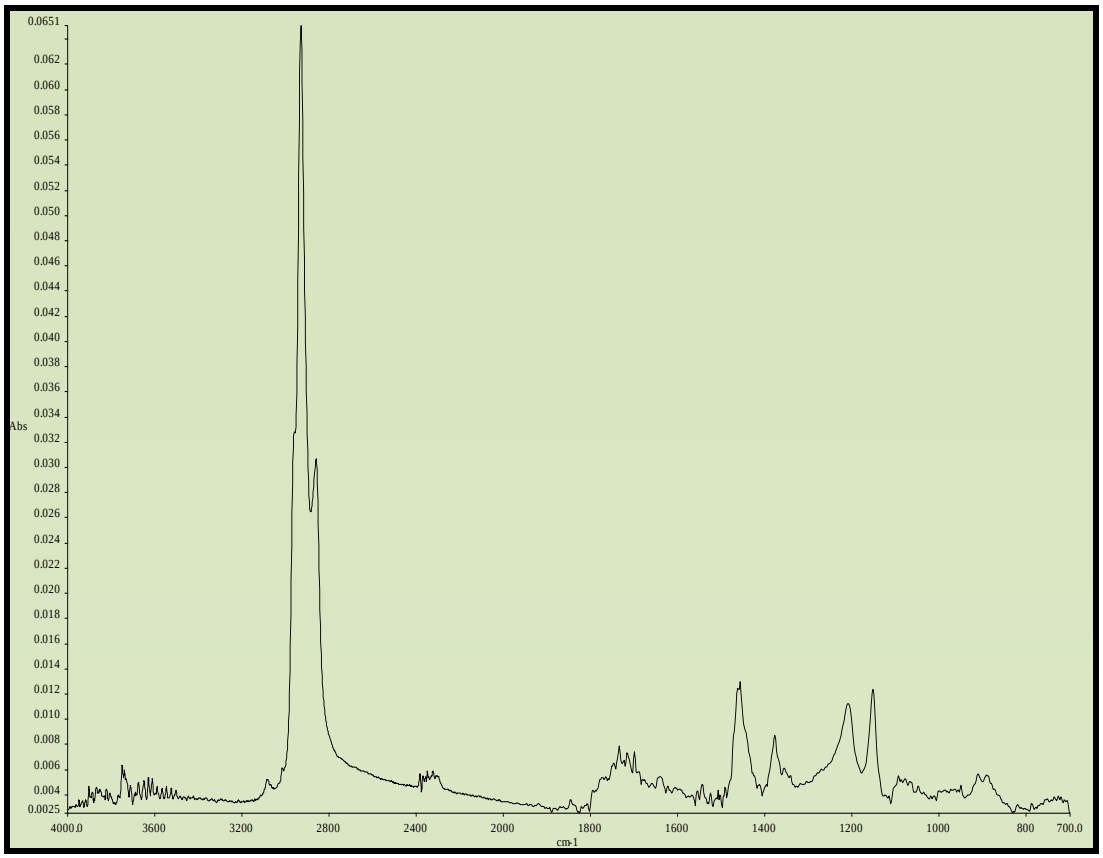

Fig. 3.28 FTIR spectrum of 727 kGy irradiated EPDM-1 sample's pyrolysis products emitted from TGA at 495 ^{o}C

3.5. DYNAMIC MECHANICAL ANALYSIS (DMA)

Change in the dynamic mechanical properties of the EPDM-1 samples via radiation was studied. Samples were irradiated to 3 different doses in water and in air conditions. According to storage modulus results; via radiation, storage modulus increased in all irradiated samples. Storage modulus is related to stiffness, therefore increase in stiffness can be explained by the fact that relative degree of crosslinking increased via radiation up to 426 kGy. According to Figure 3.29, the sample irradiated to 383 kGy in water showed the highest storage modulus values. This means that greatest increase in the relative degree of crosslinking with irradiation was occurred in the 383 kGy irradiated (in water) EPDM sample. The reason behind the higher relative degree of crosslinking in water via irradiation can be explained by the fact that water generates highly reactive radicals like $OH^{\bullet}$ and these reactive radicals are capable of hydrogen abstraction from EPDM structure, and this hydrogen abstraction increases yield of crosslinking [49].

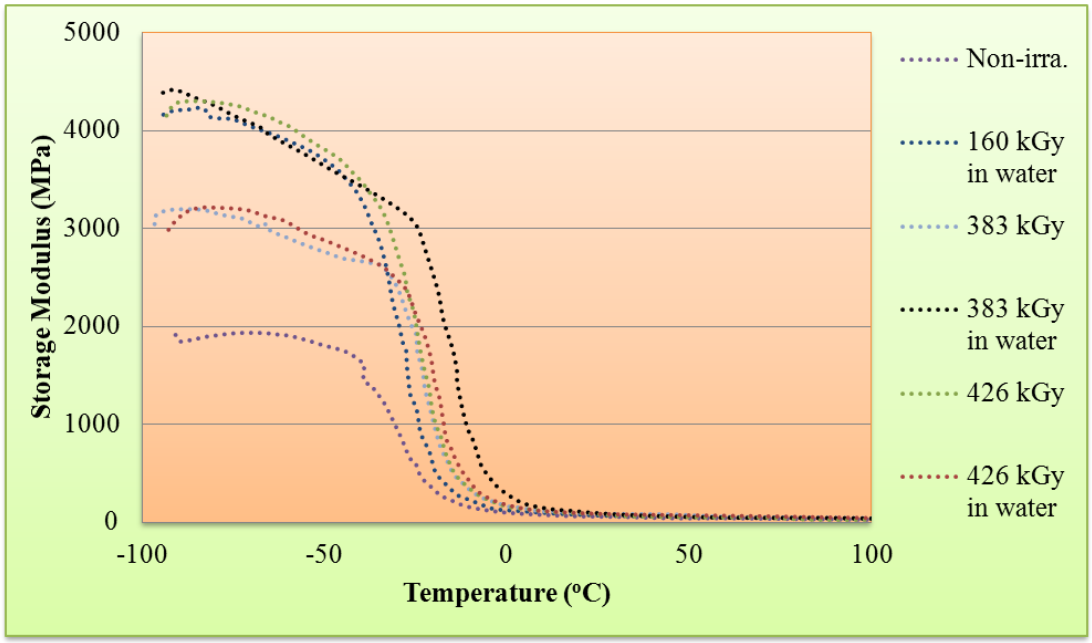

Fig. 3.29 Comparison of storage modulus values of irradiated EPDM-1 samples

In addition to storage modulus, change in the damping factor peak temperature was analyzed by using tan delta (δ) vs temperature (^{o}C) graph. According to Figure 3.30 and Table 3.16, damping peak temperature increased with irradiation. Damping peak temperatures (referring to Tg) of irradiated in water samples were higher than the peak temperatures of samples irradiated in air. The reason behind the increase in Tg values was due to the increase in crosslinking in the structure via irradiation to 426 kGy. Moreover, in water conditions, water prevented the destructive effects of radiation to 426 kGy and increases the yield of constructive reactions in the structure dominantly, therefore the Tg values of irradiated (in water) samples were higher compared with the samples irradiated in air.

Table 3.16 Glass transition temperatures (Tg) of irradiated EPDM-1 samples

Samples	Glass Transition Tempreatures (^{o}C)
Non-Irradiated	- 25.04
160 kGy irradiated in water	- 21.41
383 kGy irradiated	- 17.85
383 kGy irradiated in water	- 7.09
426 kGy irradiated	- 15.20
426 kGy irradiated in water	- 11.70

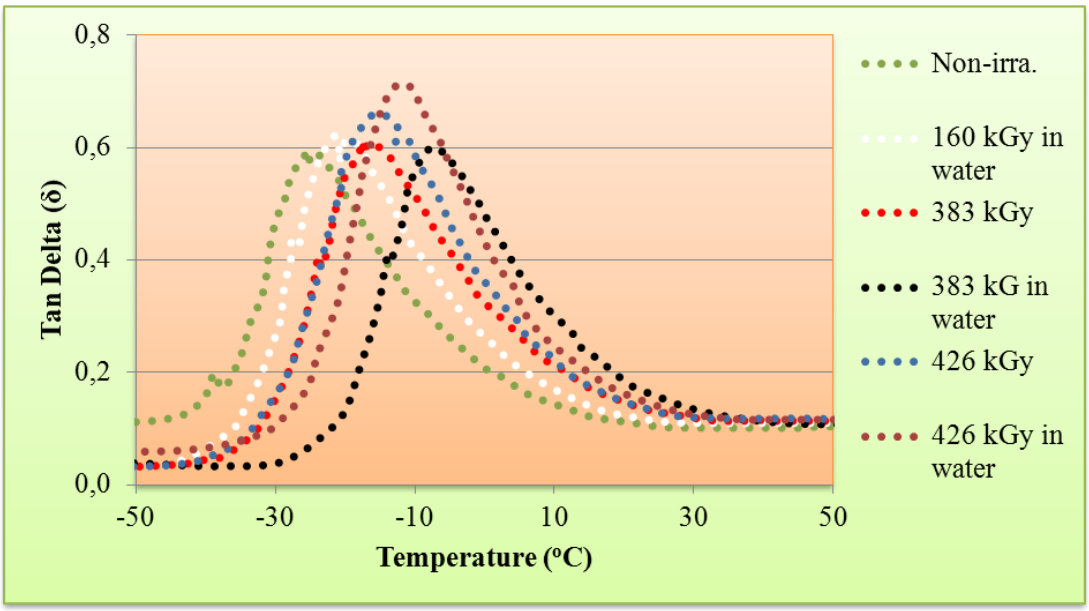

Figure 3.30 DMA spectra of irradiated EPDM-1 samples

3.10. ATTENUATED TOTAL REFLECTION FOURIER TRANSFORM INFRARED SPECTROSCOPY (ATR-FTIR)

ATR-FTIR results of the non-irradiated and the irradiated EPDM-1 samples aid in estimating the possible reactions which occurred in EPDM's structure via radiation. According to FTIR spectra shown in Figure 3.31, which belong to the non-irradiated, 992 kGy and 1178 kGy irradiated EPDM-1's; intensity changes in bands were observed via radiation. First of all, a significant rise in intensities at peaks approximately 3200 and 3300 cm^{-1} were observed in the irradiated samples. Peaks at approximately 3200-3500 cm^{-1}, reveal the presence of hydroxyl and hyrdroperoxide groups [34]. Intensity increases at 3278 cm^{-1} in 992 kGy and 1178 kGy irradiated samples which indicated the formation of the O-H groups by oxidative reactions. When comparing spectra of the 992 and the 1178 kGy irradiated samples, peak intensities at approximately 3270 cm^{-1} were higher in the 1178 kGy irradiated sample. Moreover, in 1178 kGy irradiated samples' spectrum, there were additional peaks at approximately 3600 and 3700 cm^{-1}. Therefore, it can be concluded that increment in the total dose resulted in higher oxidative reactions. Secondly, in 992 kGy irradiated sample's spectrum, there was a peak at 950 cm^{-1} which implies the presence of –CH=CH- [45]. On the other hand, the peak at 950 cm^{-1} was not observed in the non-irradiated and 1178 kGy irradiated samples' spectrum. It can be inferred that the double bonds formation occured in EPDM via ionizing radiation to 992 kGy. Further irradiation after 992 kGy consumed newly occurred double bonds. In addition, a new peak around 1320 cm^{-1} [34,45,47], which infers the presence of quaternary carbon, was detected in the 992 kGy irradiated sample. It may be concluded that radiation abstracted the hydrogen atom from the ethylene and the propylene unit to form radicals and this radical formation led to crosslinking between radicalic propylene units. After crosslinking, a quaternary carbon was produced. Quaternary carbon was the least radiation sensitive unit and existence of quaternary carbon led to chain scission reactions. Further irradiation broke the C-C bonds of quaternary carbon in the propylene unit. Therefore, the peak at 1320 cm^{-1} was not observed in 1178 kGy irradiated sample's spectrum due to chain scission [34]. Apart from the results discussed above, peak intensity at 1415 and 1360 cm^{-1} were highest

in the 1178 kGy irradiated samples' spectrum. Peak intensity at 1415 cm^{-1}, corresponding to the C-H asymmetric stretching of methyl ketone, indicated the presence of oxidation [34,45]. Intensity increase around 1360 cm^{-1} indicated the rise in the methyl composition of EPDM. High intensity peaks which were observed at 1731 $cm^{-1,}$ 1646 cm^{-1} and 1030 cm^{-1} in the irradiated samples' spectra showed carbonyl, carbon-carbon double bond and ether formation in the structure respectively [45]. Carbonyl and ether formations were a characteristic result of ionizing radiation in presence of oxygen. Additionaly, peak intensity at 870 cm^{-1} was observed in 1178 kGy irradiated samples'spectrum and this peak corresponds to the epoxide (cyclic ether) formation [47]. The cyclic ether formation was probably owing to the double bond consumption by further irradiation. Figure 3.31 shows ATR-FTIR spectra of non-irradiated and irradiated EPDM-1 samples.

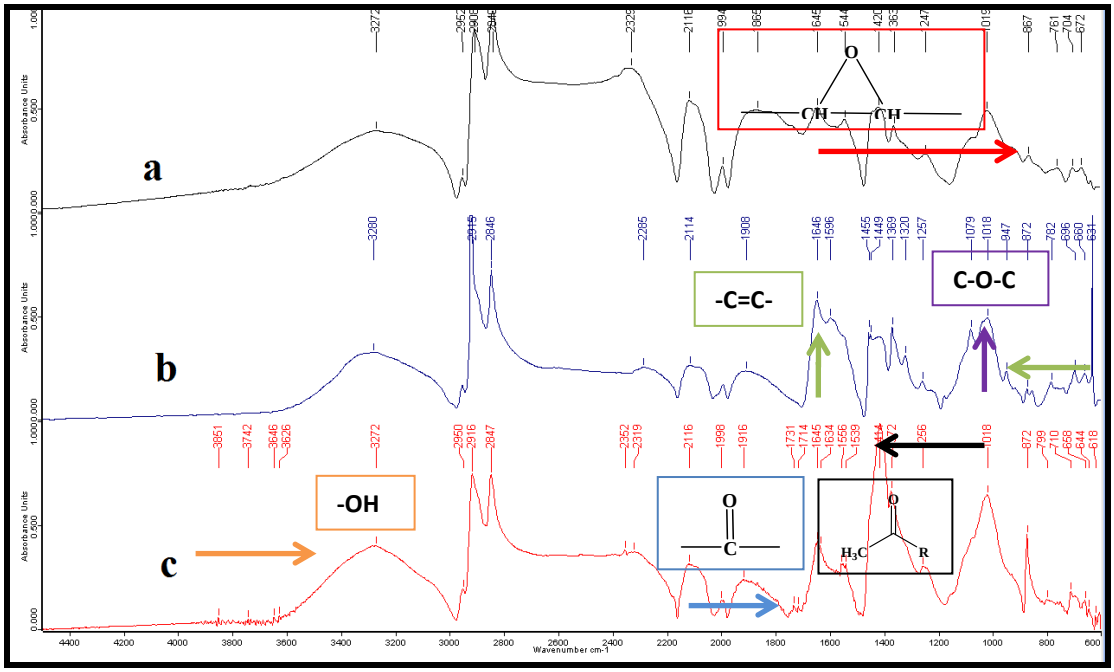

Fig. 3.31 Comparison of ATR-FTIR spectra of EPDM-1 samples

a. Non-irradiated EPDM sample

b. 992 kGy irradiated EPDM sample

c. 1178 kGy irradiated EPDM sample

According to ATR-FTIR analysis, possible reaction types on EPDM structure via irradiation are shown in Figures 3.32, 3.33, 3.34, 3.35, 3.36 and 3.37 [50-52].

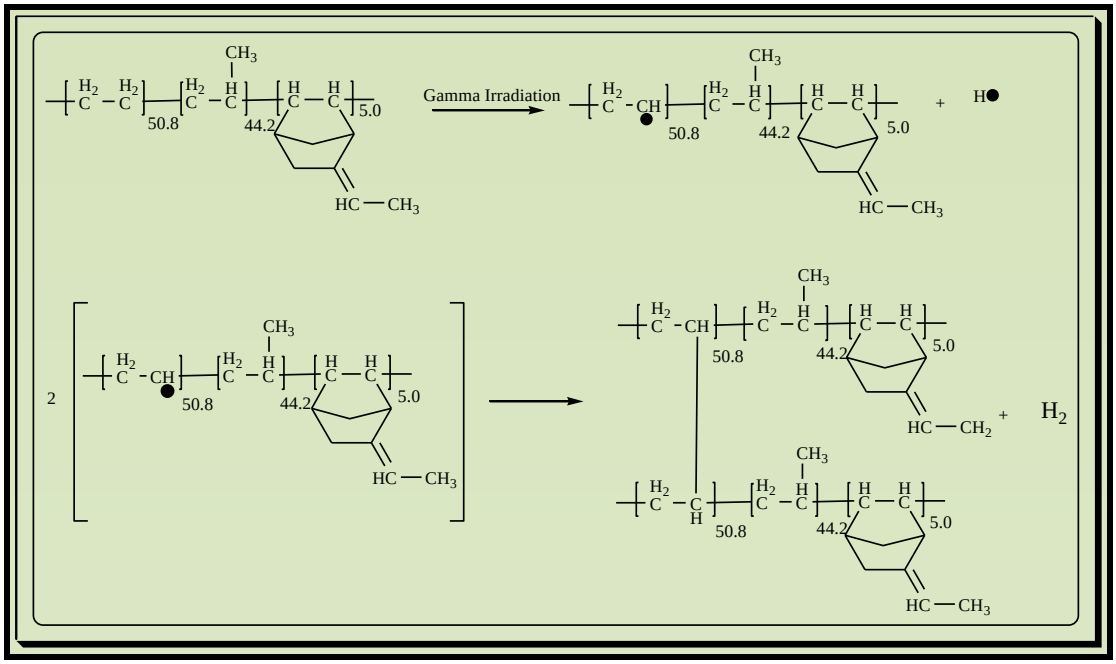

Fig. 3.32 Crosslinking reactions of EPDM (from ethylene parts) via irradiation

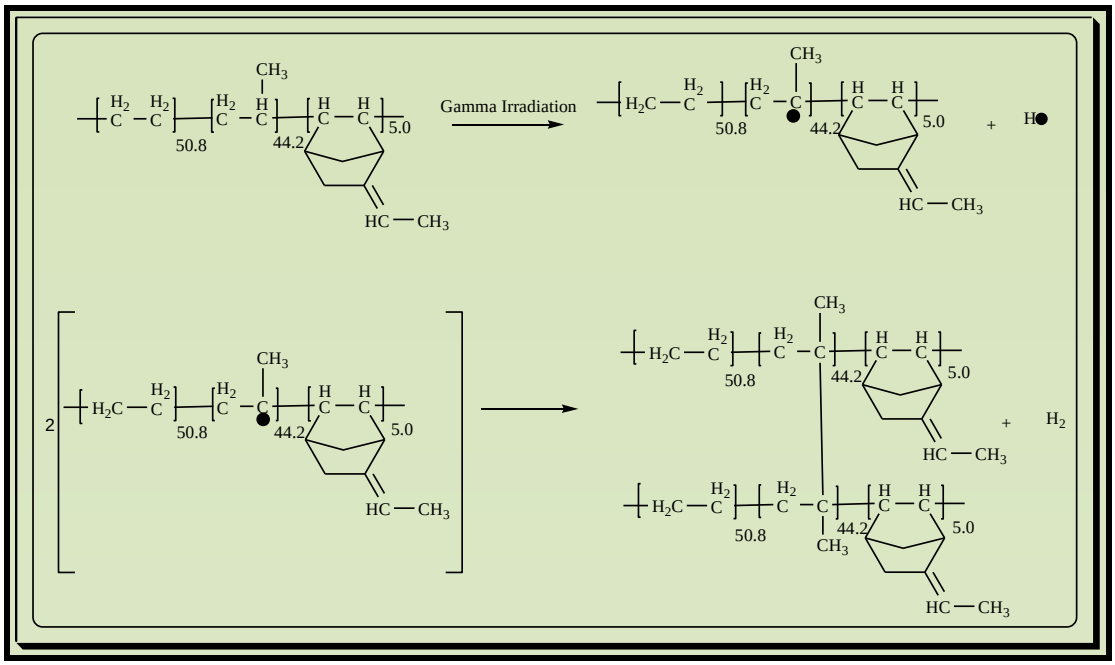

Fig. 3.33 Crosslinking reactions of EPDM (from propylene parts) via irradiation

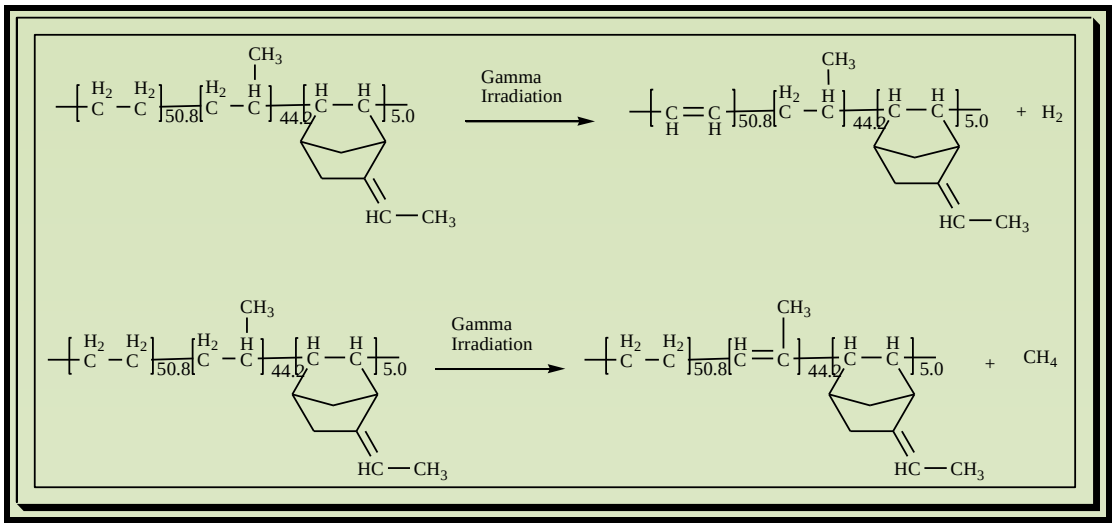

Fig. 3.34 Double bond formation of EPDM via irradiation

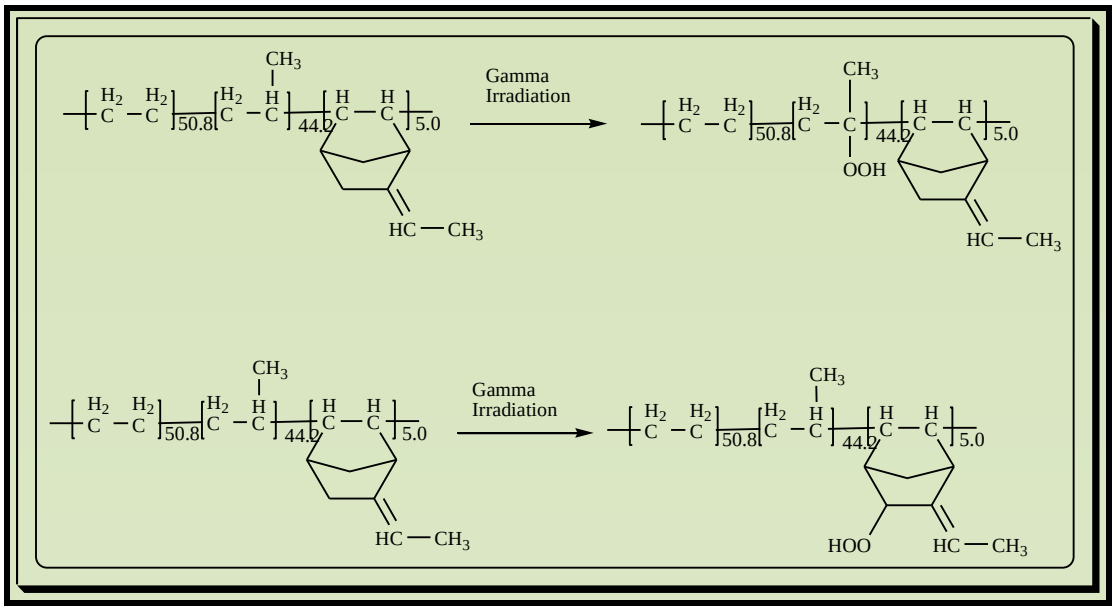

Fig. 3.35 Oxidation of EPDM via irradiation

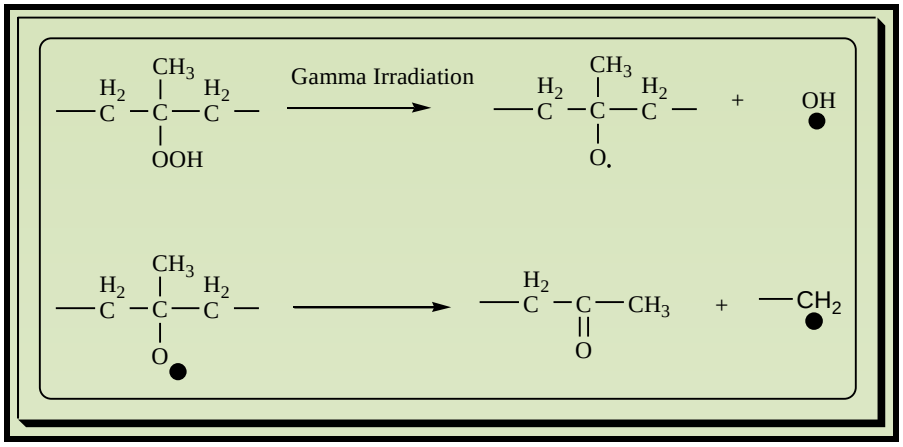

Fig. 3.36 Carbonyl formation of EPDM (from propylene unit) via irradiation

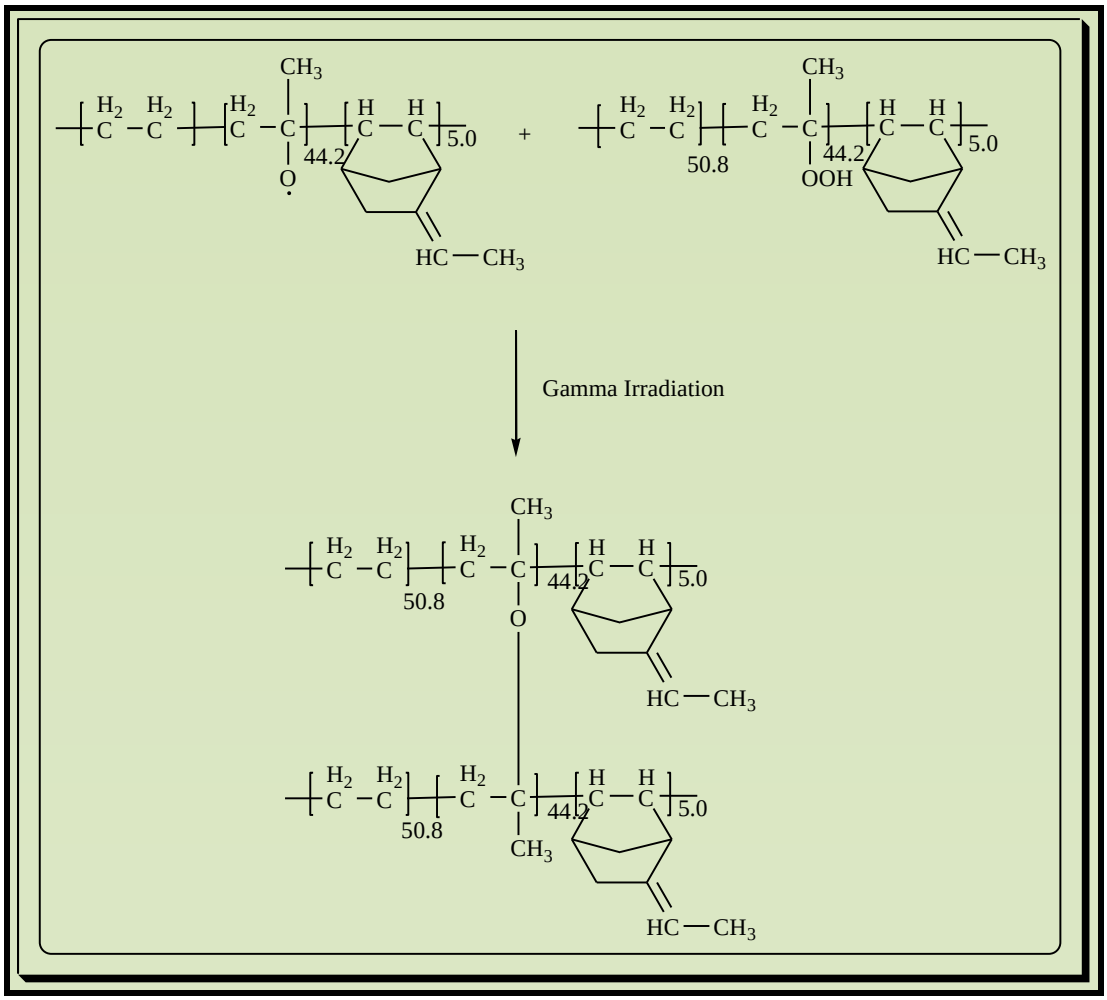

Fig. 3.37 Ether formation of EPDM (from propylene unit) via irradiation

CHAPTER 4

CONCLUSIONS

According to results of experimental investigation of this study, following conclusions can be revealed:

- According to mechanical results, elastomeric properties of EPDM ter-polymers diminished via irradiation. Stiffness, hardness and brittleness increased via irradiation. Experimentally, the highest total dose that EPDM resisted was 2157 kGy which was carried out in high dose rate. Theoretically, EPDM can resist to radiation to approximately 4000 kGy which was calculated from the extrapolation of elongation at break data. According to the IAEA [48], half life of low and medium level radioactive waste is generally 30 years. Considering 300 years storage of wastes theoretically, radioactive wastes having maximum initial dose rate of 10.56 Gy/h can be immobilized in to EPDM rubbers.

- Compression set results showed that initial stage of irradiation causes crosslinking reactions as dominant mechanism; further irradiation makes chain scission reactions dominant in the structure.

- Increase in compression set, hardness, elastic modulus and decrease in elongation at break, maximum stress at break values at higher doses could be also explained by additive effects. Plasticizers were probably destroyed via irradiation. Moreover, content of carbon black were as high as content of EPDM. This means that at higher doses due to chain scission, length of chains decreased so that carbon blacks made EPDM harder. In other words, via irradiation EPDM petrified because of high content of carbon black and destruction of plasticizer.

- Peroxide type used in vulcanization of EPDM was not so important regarding radiation stability. Both aliphatic and aromatic types of peroxides have similar effects on EPDM via irradiation. In addition, aromatic type of peroxide and allylic type of coagents included EPDM samples were slightly more resistant to radiation than aliphatic type peroxide and acrylic type of coagent included EPDM.

- Mechanical tests showed that dose rate was important parameter in determining radiation stability. The degradation of samples in low dose radiation was more significant than the degradation of samples in high dose radiation. HVD (elongation) values, which were calculated from extrapolation of the mechanical results, were higher in high dose rate irradiated samples. The reason behind more significant degradation in low dose rate was due to oxygen effect that diffused more deeply to the structure and caused oxidation which was destructive. It can be suggested that in estimating initial dose rates of radioactive wastes that is predicted to be immobilized in to polymer, irradiations in low dose rate give probably better results.

- According to SEM and XRD investigations, morphology of polymer decomposed via irradiation. There were fracture formations observed in SEM images with irradiation. Intensity decreases in XRD patterns were observed. This decrease clearly explained the destruction of additives like peroxides and plasticizers which gave crystallinity to EPDM.

- ATR-FTIR analysis showed that at high doses increase in oxidation were observed. Hydroxyl, carbonyl, ether, epoxide and double bond formation were recorded. In addition, after observing double bond formation in 992 kGy irradiated EPDM sample, double bond consumption were recorded via further irradiation to 1178 kGy.

- Thermal investigations revealed that irradiation improved thermal properties up to 992 kGy. After 992 kGy decrease in thermal stability were recorded.

- Dynamic Mechanical Analysis (DMA) shows that in water conditions, storage modulus and glass transition (Tg) values of irradiated samples were higher

with respect to in air conditions. It can be concluded that irradiations in water increased the relative crosslinking yield of EPDM samples via abstracting H atoms by highly reactive water radicals.

- Results of EPDM samples irradiated in water had better and more suitable than results of irradiated samples in air condition. The reason behind this is self shielding and scavenger property of water that reduces radiation destructive effects.

- The 383 kGy irradiated (in water) EPDM sample was found the most resistant sample to radiation in all irradiated EPDM samples.

- As a result of whole experimental investigation, EPDM ter-polymer used in this study can be possibly be used in the radioactive waste management.

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APPENDIX A

DOSE RATES OF LOW DOSE RATE AND HIGH DOSE RATE IRRADIATION SOURCES

Changes in the dose rates of low dose rate and high dose rate irradiation sources are given in Table A.1 and Table A.2 respectively.

Table A.1 Dose rates of low dose rate irradiation source

Period	Dose Rate (Gy/h)
January 2008	54.77
February 2008	54.17
March 2008	53.58
April 2008	53.00
May 2008	52.42
June 2008	51.85
July 2008	51.28
August 2008	50.73
September 2008	50.17
October 2008	49.63
November 2008	49.09
December 2008	48.55
January 2009	48.02
February 2009	47.50
March 2009	46.98
April 2009	46.47
May 2009	45.96
June 2009	45.46
July 2009	44.96
August 2009	44.47
September 2009	43.99

Table A.1 continue…	
Period	**Dose Rate (Gy/h)**
October 2009	43.51
November 2009	43.04
December 2009	42.57
January 2010	42.10
February 2010	41.64
March 2010	41.19
April 2010	40.74
May 2010	40.30
June 2010	39.86
July 2010	39.42
August 2010	38.99

Table A.2 Dose rates of high dose rate irradiation source

Period	Dose Rate (Gy/h)
January 2008	1096
February 2008	1084
March 2008	1072
April 2008	1060
May 2008	1049
June 2008	1037
July 2008	1026
August 2008	1015
September 2008	1004
October 2008	993
November 2008	982
December 2008	971
January 2009	961
February 2009	950
March 2009	940
April 2009	930
May 2009	920
June 2009	910
July 2009	900
August 2009	890
September 2009	880
October 2009	870
November 2009	861
December 2009	852
January 2010	842
February 2010	833
March 2010	824
April 2010	815
May 2010	806
June 2010	797
July 2010	789
August 2010	780

APPENDIX B

XRD PEAK SEARCHS OF EPDM-1 SAMPLES

XRD peak search of sticker and EPDM-1 samples which were irradiated in low dose rate are shown in Tables B.1, B.2, B.3, B.4 and B.5.

Table B.1 XRD peak search of sticker

Peak No.	2theta	FWHM	d-value	Intensity	I/I_0
1	9.45	0.176	9.3508	245	2
2	14.00	0.529	6.3203	2591	19
3	16.90	0.529	5.2417	14120	100
4	18.35	0.118	4.8307	166	2
5	25.50	0.529	3.4901	2014	15
6	27.95	0.118	3.1895	91	1
7	28.65	0.235	3.1131	478	4
8	31.45	0.235	2.8421	71	1

Table B.2 XRD peak search of non-irradiated EPDM-1 samples

Peak No.	2theta	FWHM	d-value	Intensity	I/I_0
1	10.15	-	8.7074	51	9
2	19.30	0.118	4.5950	97	16
3	19.60	0.176	4.5253	127	21
4	20.20	0.118	3.3923	76	13
5	20.45	0.118	4.3391	78	13
6	24.70	0.176	3.6013	74	12
7	29.20	0.118	3.0557	116	19
8	29.35	0.235	3.0404	162	27
9	30.20	0.118	2.9568	87	15
10	32.05	0.118	2.7902	106	18
11	32.30	0.118	2.7692	327	54
12	32.45	0.294	2.7567	615	100
13	32.80	0.118	2.7281	76	13
14	34.90	0.118	2.5686	112	19
15	35.15	0.118	2.5509	169	28
16	36.40	0.118	2.4661	108	18
17	36.60	0.118	2.4531	205	34
18	36.90	0.412	2.4338	520	85
19	41.50	0.118	2.1741	75	13
20	43.55	0.118	2.0764	89	15
21	44.10	0.118	2.0517	71	12
22	48.20	0.176	1.8864	126	21
23	44.10	0.118	1.8790	73	12
24	48.20	0.235	1.7493	83	21
25	48.40	0.176	1.6780	74	12
26	52.25	0.118	1.6639	85	14
27	54.65	0.118	1.6300	79	13
28	55.15	0.118	1.6117	357	14
29	56.40	0.176	1.6078	494	13
30	57.10	0.118	1.5417	74	59
31	63.10	0.176	1.4721	102	17
32	63.45	0.235	1.4648	205	34
33	66.75	0.176	1.4002	72	12
34	68.05	0.176	1.3766	74	13
35	68.50	0.294	1.3686	235	39
36	69.45	0.118	1.3522	122	20
37	69.70	0.176	1.3479	133	22
38	73.05	0.176	1.2942	81	14

Table B.2 continue...					
Peak No.	**2theta**	**FWHM**	**d-value**	**Intensity**	**I/I_0**
39	74.55	0.118	1.2718	75	13
40	89.95	0.235	1.0898	87	15
41	90.20	0.118	1.0874	74	12
42	93.35	0.176	1.0588	83	14
43	95.35	0.176	1.0402	80	14
44	95.75	0.235	1.0385	180	30

Table B.3 XRD peak search of 383 kGy irradiated (in air) EPDM-1 samples

Peak No.	2theta	FWHM	d-value	Intensity	I/I_0
1	13.95	0.118	6.3429	65	24
2	14.25	0.118	6.2100	59	22
3	16.95	0.353	5.2264	278	100
4	24.90	0.118	3.5728	54	20
5	25.80	0.118	3.4502	66	24
6	30.15	0.176	2.9616	67	25
7	32.15	0.118	2.7818	125	45
8	32.40	0.294	2.7609	179	65
9	35.05	0.118	2.5580	59	22
10	35.50	0.118	2.4596	76	28
11	36.80	0.176	2.4402	206	75
12	42.15	0.118	2.1420	60	22
13	45.75	0.118	1.9815	52	19
14	47.90	0.176	1.8975	53	20
15	48.15	0.118	1.8882	58	21
16	56.95	0.176	1.6156	160	58
17	57.25	0.176	1.6078	168	61
18	61.50	0.176	1.5065	52	19
19	61.85	0.235	1.4988	68	25
20	63.30	0.235	1.4679	100	37
21	63.65	0.118	1.4607	61	22
22	64.90	0.235	1.4355	54	20
23	65.25	0.176	1.4287	63	23
24	68.50	0.294	1.3686	94	34
25	69.55	0.118	1.3505	78	29
26	69.65	0.118	1.3488	56	21
27	74.10	0.118	1.2784	53	19
28	99.00	0.235	1.0130	66	24

Table B.4 XRD peak search of 383 kGy irradiated (in water) EPDM-1 samples

Peak No.	2theta	FWHM	d-value	Intensity	I/I_0
1	14.15	-	6.2537	68	16
2	16.50	0.176	5.3358	139	32
3	16.95	-	5.2264	324	74
4	17.25	0.118	5.1362	168	39
5	19.65	0.118	4.5139	88	21
6	25.40	0.118	3.5036	81	19
7	25.65	0.118	3.4700	90	21
8	26.50	0.176	3.3606	73	17
9	27.30	0.176	3.2639	72	17
10	29.35	0.176	3.0404	205	47
11	29.50	0.118	3.0253	158	36
12	32.20	0.118	2.7775	120	28
13	32.50	0.353	2.7526	440	100
14	35.15	0.118	2.5509	132	30
15	35.30	0.118	2.5404	113	26
16	36.60	0.118	2.4531	96	22
17	36.80	0.118	2.4402	218	50
18	37.00	0.176	2.4275	325	74
19	37.15	0.176	2.4180	245	56
20	41.45	0.118	2.1766	71	17
21	43.70	0.118	2.0696	92	21
22	48.25	0.176	1.8845	104	24
23	49.20	0.118	1.8503	75	18
24	56.75	0.118	1.6208	75	17
25	57.30	0.353	1.6065	373	85
26	63.40	0.176	1.4658	94	22
27	63.60	0.118	1.4617	110	26
28	68.40	0.118	1.3704	104	24
29	68.70	0.176	1.3651	143	33
30	69.70	0.118	1.3479	108	25
31	90.25	-	1.0869	79	18
32	93.25	0.118	1.0597	77	18
33	96.00	0.176	1.0365	89	21
34	98.95	0.176	1.0133	80	19

Table B.5 XRD peak search of 992 kGy irradiated EPDM-1 samples

Peak No	2theta	FWHM	d-value	Intensity	I/I_0
1	13.95	0.118	6.3429	137	12
2	14.15	0.176	6.2537	226	20
3	14.30	0.176	6.1884	215	19
4	17.00	0.294	5.2111	1168	100
5	24.00	0.118	3.7047	53	5
6	25.50	0.118	3.4901	101	9
7	25.75	0.118	3.4568	136	12
8	30.45	0.118	3.9331	57	5
9	30.55	0.118	2.9237	53	5
10	32.80	0.235	2.7281	112	10
11	32.95	0.353	2.7160	79	7
12	35.50	0.118	2.5266	160	14
13	37.35	0.235	2.4055	252	22
14	48.40	0.176	1.8790	78	7
15	48.55	0.118	1.8736	80	7
16	57.60	0.176	1.5989	113	10
17	63.80	0.118	1.4576	137	12
18	68.90	0.235	1.3616	88	8
19	70.10	0.176	1.3412	56	5
20	85.60	0.294	1.1337	58	5
21	90.40	0.118	1.0855	62	6
22	99.35	0.294	1.0103	73	7

Figure B.1 show XRD patterns of sticker which was used to hold the EPDM-1 samples during XRD analysis.

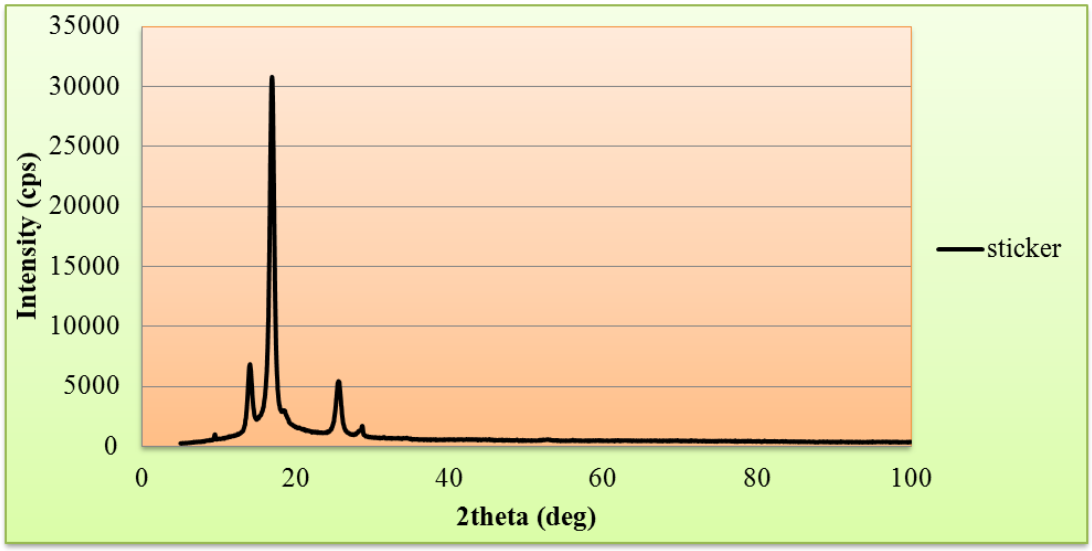

Fig. B.1 XRD patterns of sticker which was used to hold EPDM-1 samples during XRD analysis

APPENDIX C

FTIR SPECTRA OF PYROLYSIS EPDM-1 SAMPLES EMITTED FROM TGA AT 350 ^{O}C AND 495 ^{O}C

FTIR spectra of pyrolysis EPDM-1 samples (irradiated) which were emitted from TGA at 350 ^{o}C and 495 ^{o}C are shown in Figures C.1, C.2, C.3 and C.4.

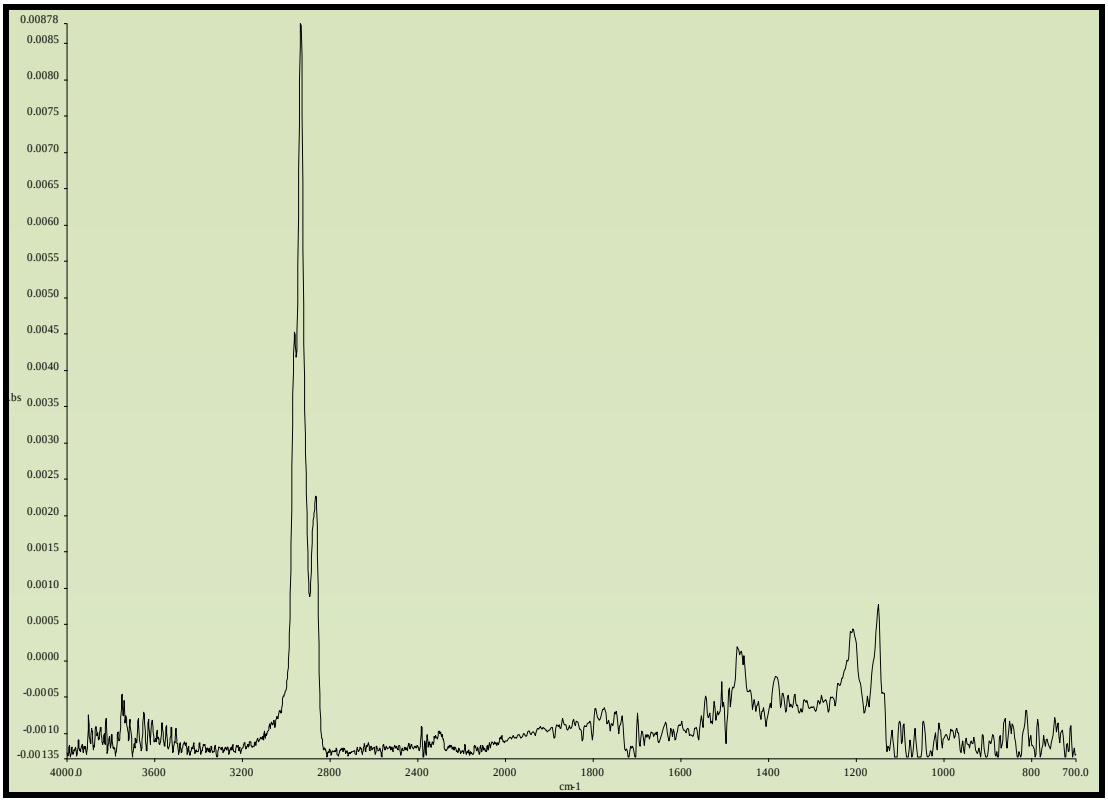

Fig. C.1 FTIR spectrum of pyrolysis EPDM-1 samples which were irradiated to 383 kGy in water, at 350 ^{o}C

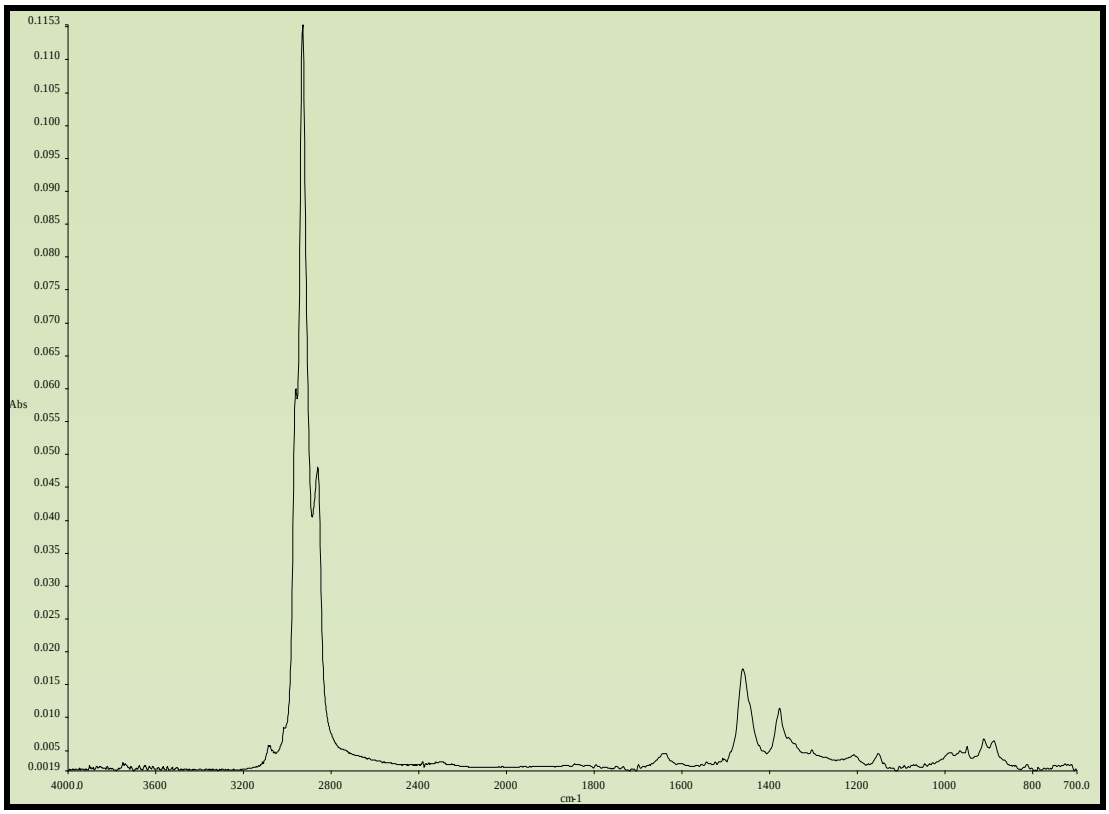

Fig. C.2 FTIR spectrum of pyrolysis EPDM-1 samples which were irradiated to 383 kGy in water, at 495 ^{o}C

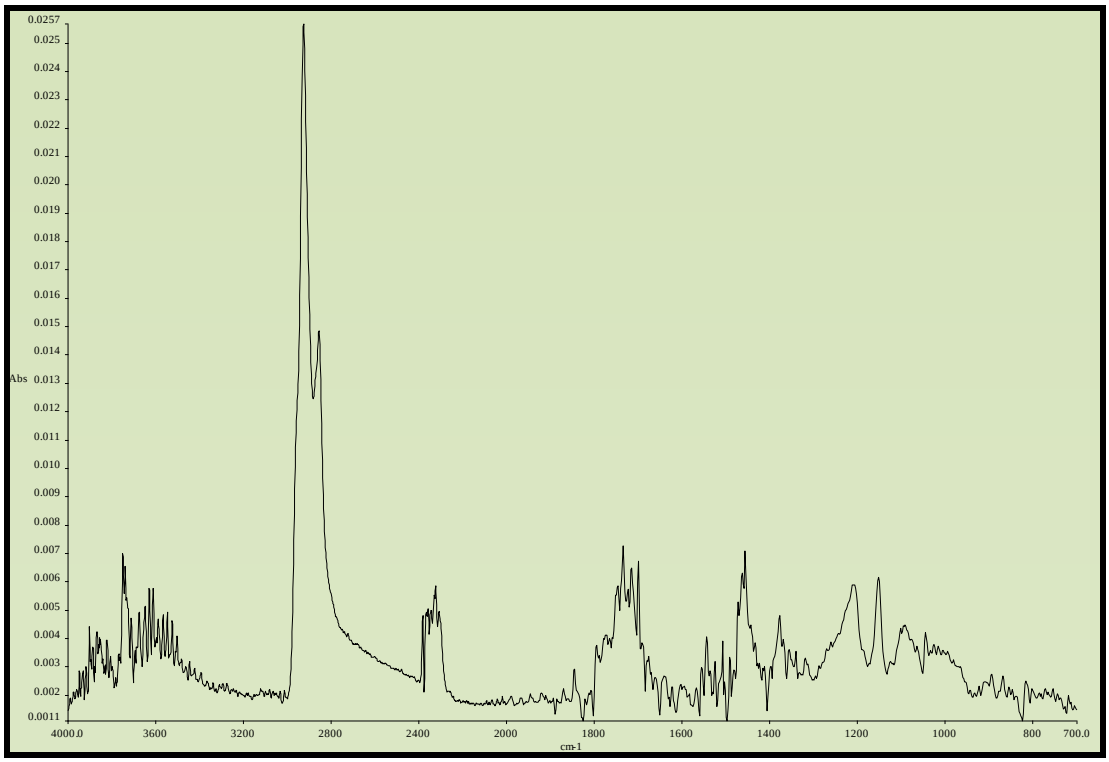

Fig. C.3 FTIR spectrum of pyrolysis EPDM-1 samples which were irradiated to 992 kGy, at 350 ^{o}C

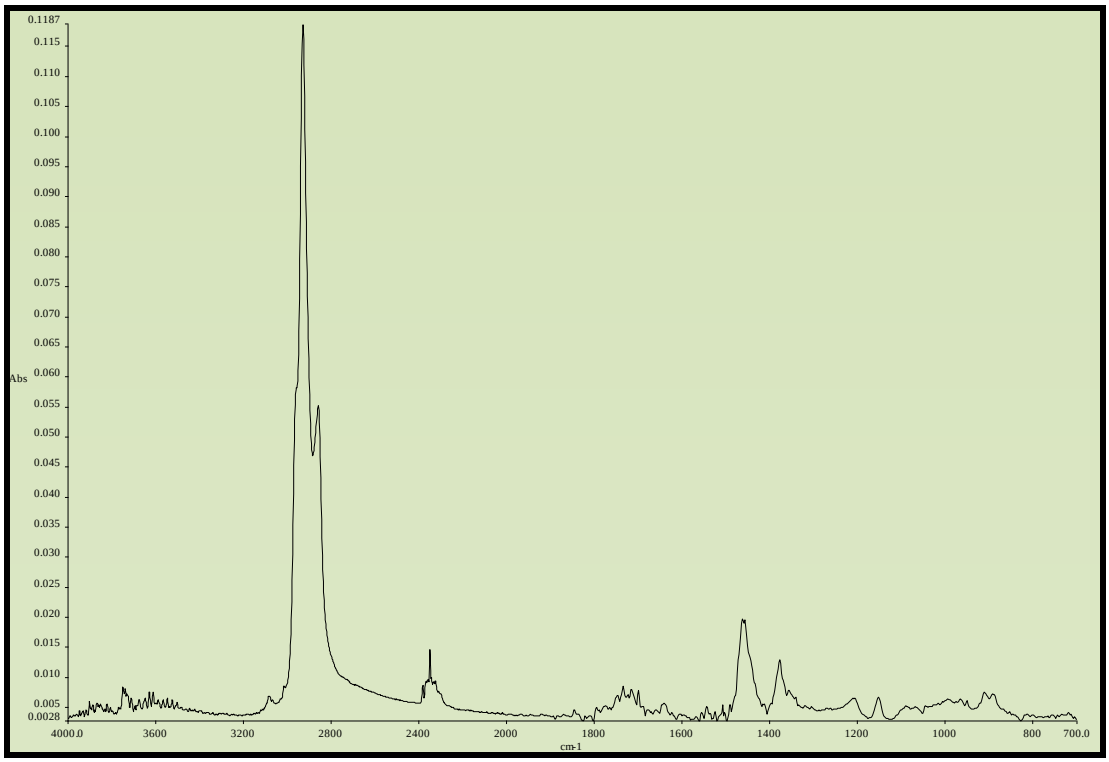

Fig. C.4 FTIR spectrum of pyrolysis EPDM-1 samples which were irradiated to 992 kGy, at 495 ^{o}C

APPENDIX D

SCANNING ELECTRON MICROSCOPE IMAGES OF IRRADIATED EPDM-1 SAMPLES

Scanning electron microscope images of irradiated EPDM-1 samples which were monitored at magnitude 5.000 X and 30.000 X are shown in Figures D.1 and D.2.

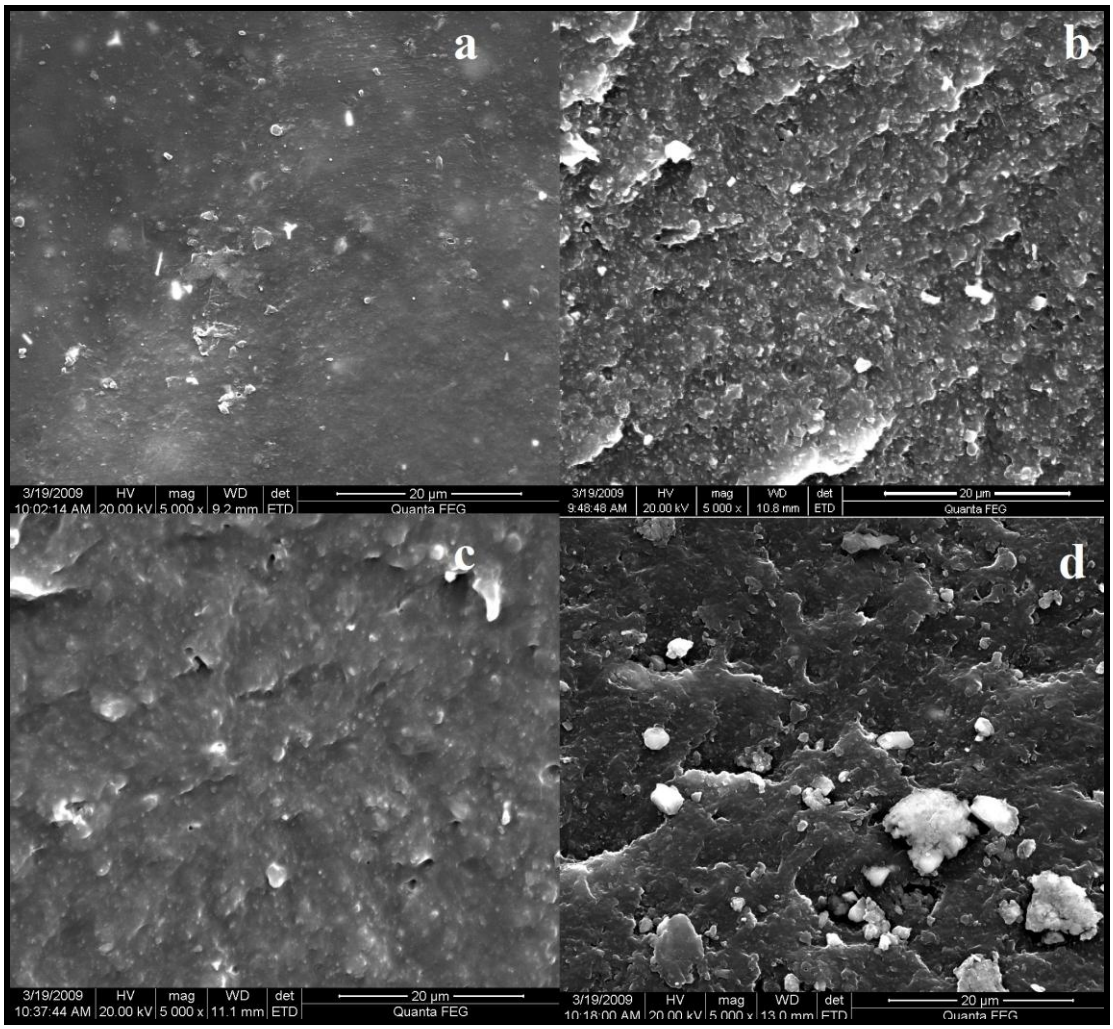

Fig. D.1 SEM images of EPDM-1 samples monitored at magnitude 5.000 X

- **a.** Non-irradiated EPDM sample
- **b.** 383 kGy irradiated EPDM sample in atmosphere condition
- **c.** 383 kGy irradiated EPDM sample in water condition
- **d.** 992 kGy irradiated EPDM sample

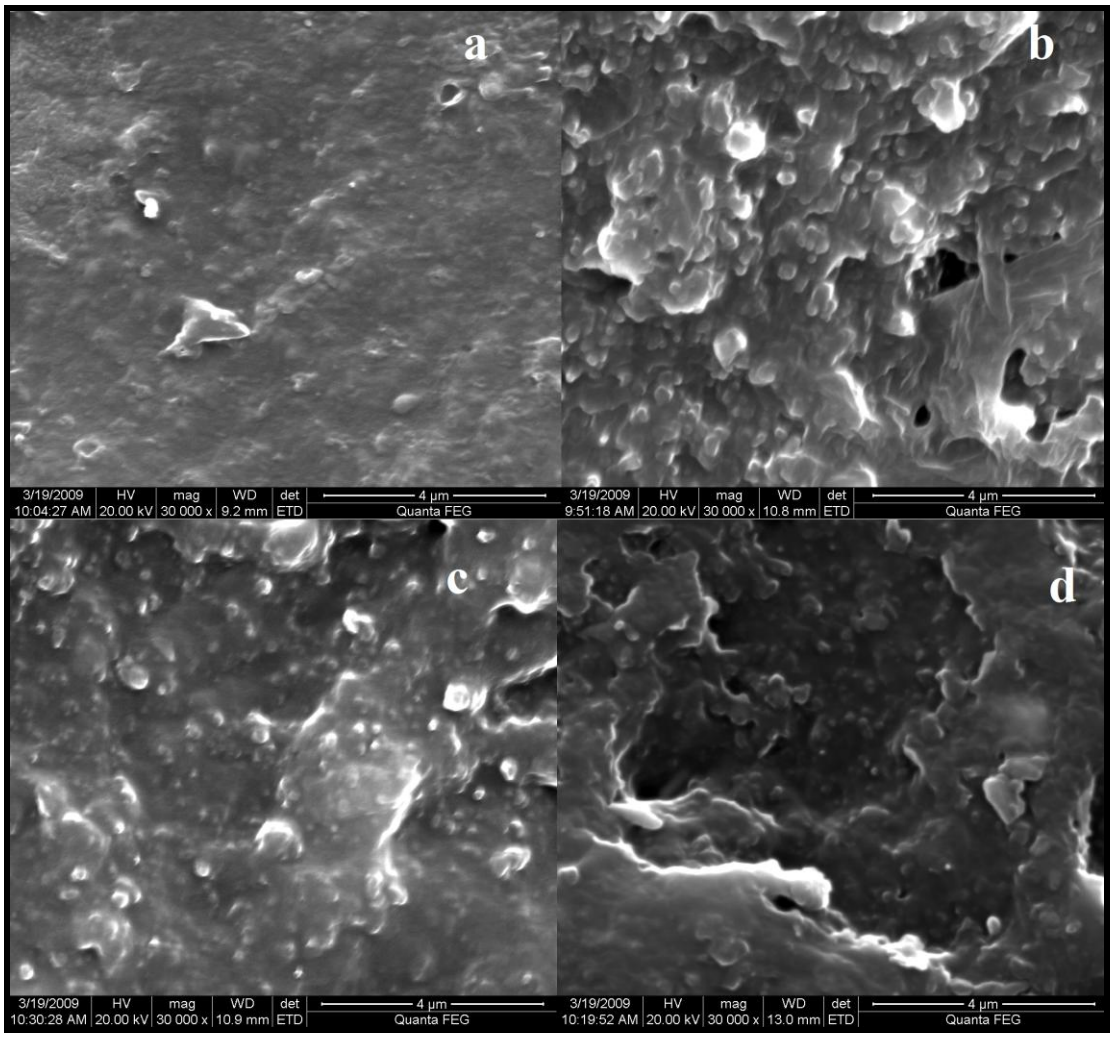

Fig. D.2 SEM images of EPDM-1 samples monitored at magnitude 30.000 X

- **a.** Non-irradiated EPDM sample
- **b.** 383 kGy irradiated EPDM sample in atmosphere condition
- **c.** 383 kGy irradiated EPDM sample in water condition
- **d.** 992 kGy irradiated EPDM sample

APPENDIX E

STRUCTURES OF PEROXIDES, COAGENTS AND ACTIVATORS USED IN EPDM FORMULATION

Structures of peroxides, coagents and activators used in EPDM-1, EPDM-2 and EPDM-3 formulation are shown in Figures E.1, E.2, E.3, E.4 and E.5.

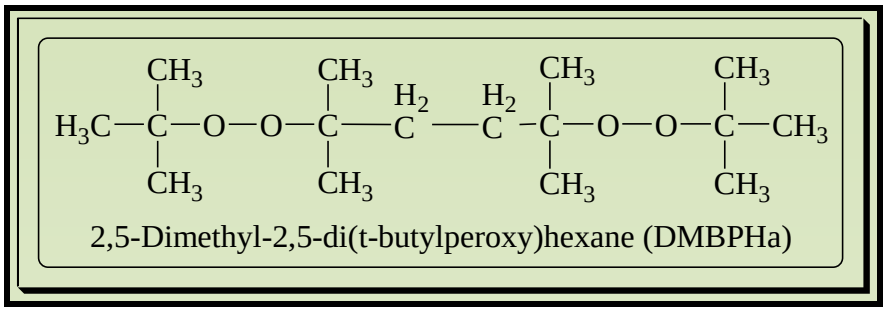

Fig. E.1 Structure of peroxide used in EPDM-1 and EPDM-2 formulation

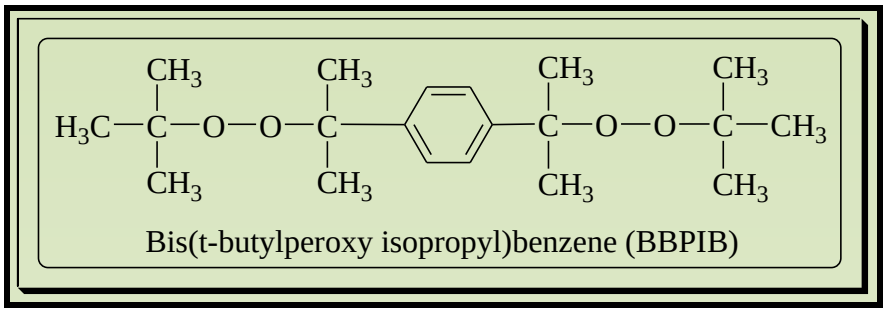

Fig. E.2 Structure of peroxide used in EPDM-3 formulation

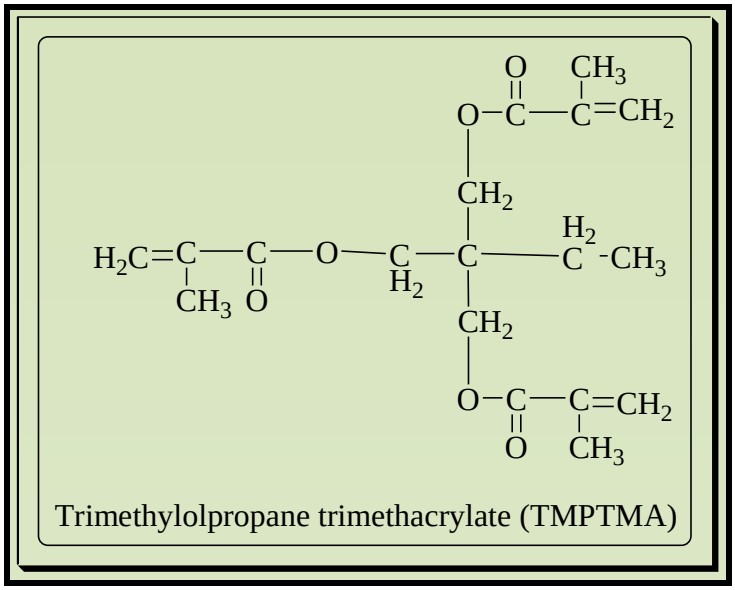

Fig. E.3 Structure of vulcanization coagent used in EPDM-1 and EPDM-2 formulation

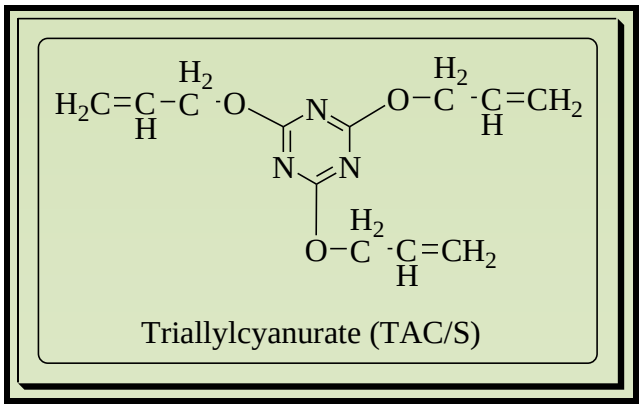

Fig. E.4 Structure of vulcanization coagent used in EPDM-3 formulation

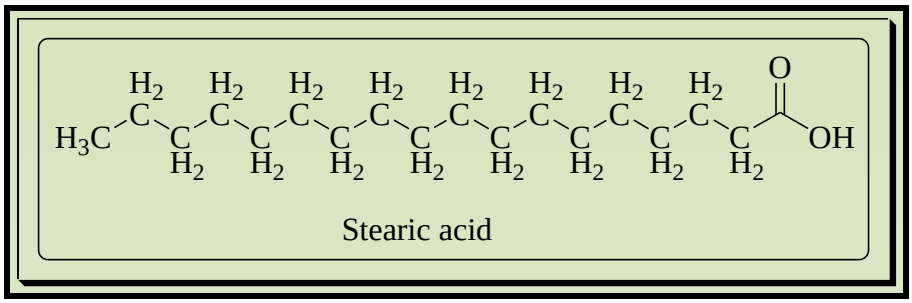

Fig. E.5 Structure of activator used in EPDM formulation