Application of radiation technology to rubber and tire industries

Kauçuk ve lastik sanayisinde radyasyon teknolojisi uygulamaları

Review Article

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ABSTRACT

Application of radiation technology to the rubber and tire industries is in progress and is being developed. In this review, recent studies on radiation processing in rubber and tire industries are reviewed. Both academic investigations and industrial applications in non-tire rubber goods, tire production and tire reinforcing materials are mentioned. Current trends, new challenges and opportunities of technologies and the tire reinforcing materials are also given.

Key Words
Radiation, radiation technology, rubber, tire.

ÖZET

Kauçuk ve araç lastiği sanayisinde radyasyon uygulamaları gelişerek devam etmektedir. Bu çalışmada, kauçuk ve lastik sanayisinde radyasyonla işleme çalışmalarındaki son gelişmeler gözden geçirilmiştir. Araç lastiği ve lastik eşya üretimi ile lastik takviye malzemeleri konularındaki akademik ve endüstriyel uygulamalar anlatılmıştır. Uygulamalardaki mevcut eğilimler, yeni fırsat ve zorluklara değinilerek tartışılmıştır.

Anahtar Kelimeler
Radyasyon, radyasyon teknolojisi, kauçuk, lastik.

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INTRODUCTION

Radiation is a powerful energy source for chemical processing applications in several industries. Nuclear radiation is ionizing; radiation-induced materials give positive ions, free electrons, free radicals, and excited molecules. A wide range of reactive species become available; they can be used as an origin for radiation-initiated reactions such as modification, cross linking, or degrading materials [1].

Radiation-initiated reactions can be categorically classified as two types: (1) cross linking and scission and (2) grafting and curing. Cross linking is intermolecular bond formation of polymer chains. The degree of cross linking is proportional to the radiation dose. Cross linking during irradiation does not require unsaturated or other more reactive groupings. The mechanism of cross linking generally varies with the polymers concerned. The universally hydrogen atom, followed by abstraction of a second hydrogen atom from a neighbouring chain to produce molecular hydrogen. Then two adjacent polymeric radicals combine to form a cross link. Scission is the opposite process of cross linking in which the rupturing of C—C bonds occurs. Cross linking increases the average molecular weight whereas the latter process reduces it. If the energy of the radiation is enough, chain breaking occurs through the cleavage of C—C bond [1]. The cross linking of elastomers during irradiation is most desirable reaction and can be enhanced by addition of small amount of molecules called as radiation cross link promoters or co-agents.

The final changes of polymer during irradiation are rather complex. There have been always competing reactions of cross linking and main chain scission simultaneously. The net effects of radiation depend on these competing reactions. Responses of different elastomers to the ionizing radiation are summarized in Table 1 [2].

The aim of radiation processing of polymers is to modify their physical and chemical properties by using ionizing radiation for improving their properties in order to add value. The industrial applications of radiation processing of polymer industry are an important part of the peaceful use of nuclear energy besides nuclear power generation.

Table 1. Classification of elastomers according to their response to ionizing radiation [2].

Polymers predominantly cross linking
Copolymer of styrene and butadiene (SBR)
Chlorinated polyethylene (CM)
Chlorosulfonated polyethylene (CSM)
Polybutadiene (BR or PB)
Natural rubber (NR)
Polychloroprene (CR)
Copolymer of acrylonitrile and butadiene (NBR)
Hydrogenated NBR (HNBR)
Ethylene-propylene rubber (EPM)
Ethylene-propylene-diene rubber (EPDM)
Polyurethanes (PUR)
Polydimethyl silicone (MQ)
Polydimethylphenylsylicone (PMQ)
Fluorocarbon elastomers, based on vinylidene fluoride (FKM)
Polymers predominantly degrading
Isobutylene-isoprene rubber or butyl rubber (IIR)
Chlorobutyl rubber (CIIR)
Bromobutyl rubber (BIIR)
Isobutylene rubber (IR)

There are two types of industrial sources of ionizing radiation: Gamma irradiators and electron beam (EB) accelerators. The γ-radiation has very high penetration and high dose rate when compared EB radiation.

There are lots of advantages of radiation technology. Some of these can be counted as no catalyst requirements for the reactions, no contamination due to the chemical initiator or modificators, sustainable reaction rates at lower temperatures and in any phase, etc. Radiation processing used to be applied lots of industrial areas such as biomedical, textile, electrical, membrane, cement, coating, rubber goods, tire and wheel, foam, footwear, printing rolls, aerospace and pharmaceutical industries [1]. In this review, it has been focused primarily on the radiation technology applications on rubber and tire technologies and the tire reinforcing materials.

Applications of Radiation Technology to the Rubber Industry

Polymers comprise the main fraction among the materials concerning radiation processing. Rubber and tire are also a big part of polymer industry [3]. In rubber and tire industries, radiation practices are focused on vulcanization (cross linking), pre-vulcanization, and devulcanization (for recycling rubber based wastes). Use of radiation in rubber industry provides some additional advantages. Radiation cross linking may be faster, less energy consuming and an environmentally-friendly alternative for traditional sulphur or peroxide curing systems. It is also possible to eliminate dispersion problems and high temperature defects in the products due to ambient processing conditions in radiation cross linking systems. These advantages become more significant for the rubbers which need longer vulcanization time such as ethylene propylene diene monomer rubber (EPDM) and butyl rubber (IIR).

Mohamad et al. studied vulcanization of natural rubber(NR)/styrene-butadiene rubber (SBR) based rubber compounds filled with different fillers with gamma irradiation (up to 250 kGy) [4]. The effects of irradiation dose and the fillers such as carbon black, silica, clay, and titanium dioxide were investigated in terms of vulcanizate properties. Silica and carbon black found to be efficient fillers in vulcanization by almost 150 kGy irradiation.

One of the successful industrial applications of radiation processing has been the pre-vulcanization of tires imparting shape stability prior to final vulcanization. It is important to keep the dimensional consistency of each component in due course of tire building and final vulcanization. The carcass, however, tends to deform and flow during assembly and to vulcanize due to an extensive transformation under high pressure, and results in the reduction thickness and uneven distribution of compounds in the tire. This phenomena is illustrated shematically in the Figure 1 [5].

NR based compounds for the carcass and halobutyl based compounds are generally used for radial tire production. The conventional tire technology overcomes this problem by using more thick and expensive compound layers. The

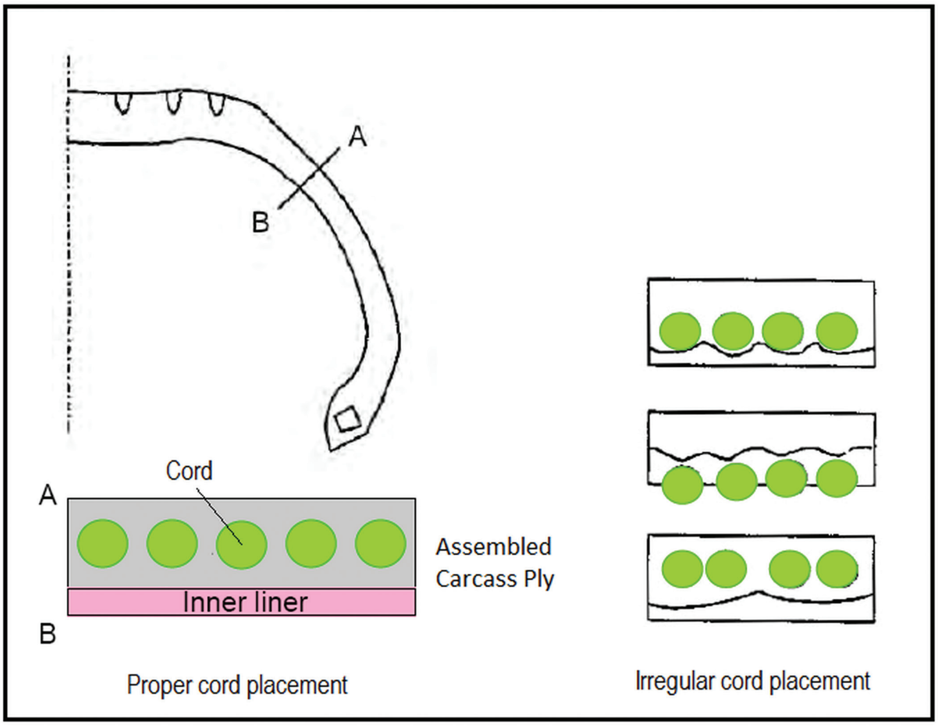

Figure 1. Cross section of a carcass ply [5,6].

results of pre-vulcanization are the improved green strength of the rubber compounds, especially of the inner liner and stabilization of carcass plies and higher quality tire with more uniform thickness and better balance [2,6]. Dose requirements for prevulcanization are in the range of 30–50 kGy [6,7]. EB irradiation in tire industry for pre-vulcanization is already being applied commercially worldwide, for example, major Japanese tire companies are using electron accelerators for the production of radial tires [6,8]. A low- to medium-energy (500–800 keV) electron accelerator is used in a radiation shielding cabinet for cross linking the carcass ply. The appropriate material handling system and transportation device for the carcass ply feeding and supporting facilities such as the suppliers of electricity, water and cooling air are required. Since the carcass ply is a composite material obtained by assembling of calendered cord fabric and innerliner compound at a calendering line, the electron accelerator parameters should be accurately set to control the degree of cross linking. The green strength of the carcass ply is enhanced because of cross linking of the compounds [6]. However, the cord is affected by radiation depending on type of cords used. Therefore, the influence of high energy irradiation on the reinforcing materials, i.e. on the textile cord needs to be investigated. Figure 2 shows shematic representation of irradiation [5].

One of the unique characteristics of high energy electrons is that a substantial portion of the curing process occurs in the body of the material, not on the surface. This may explain why tack is less affected than by other surface treatment methods [9].

Another EB radiation curing studies has been published by Chakraborty et al [10]. In that study, the effect of EB pretreatment on tire components has been investigated. Components of tire such as inner liner and tread were irradiated with optimum doses selected in line with the study conducted on the experimental and industrial compounds. These components were then used to build the green tire. Properties of compound and tire as a whole were checked and were reported.

It is known that EB radiation pretreatment of tire components improves the tack and green strength. Improvement in mechanical

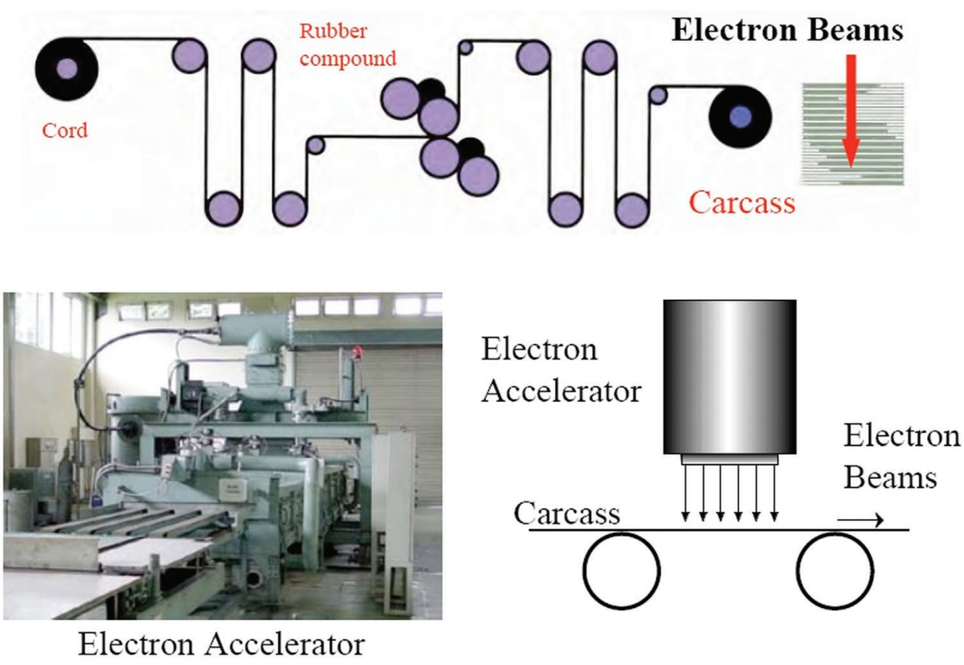

Figure 2. Irradiation of carcass ply with electron accelerator [5,6].

properties with a reduced cure time helps to produce premium quality tires in a less time. The productivity increased as that tire with 5 Mrad irradiated components was cured with 14% reduction in cure time [10]. But the properties of tire components were not deteriorated; moreover life of tire was extended. All these were attributed to the C-C cross links formed on radiation treatment. Moreover, finish and shape of the tires got better by using of irradiated components. The squeezing out of the innerliner through the carcass layers was almost nil for the irradiated inner liner on heat curing. This would make tire specialist enable to keep the exact gauge of the innerliner at the time of building the tire. Usually they used to keep thicker inner liner. This would facilitate material saving and cost reduction. Tire industries might look forward to pretreating tire components i.e., innerliner, tread, and plies, as the technique made it possible to produce superior quality tires, save material, and increase productivity.

In recent years, the production of rubber industry and the consumption of polymeric material increased tremendously in parallel to the rapid industrialization and civilization. Since the polymeric materials do not decompose easily, disposal of waste polymers is a major environmental problem both for the municipalities and the governments. Several global and national policies have been developed and proposed worldwide related to the disposal of solid wastes such as plastics and waste rubber tires. Since most of these wastes contain petroleum products, re-use and/or recycling of those wastes are very important to protect un-renewable natural resources. But unfortunately, used inner tires are also not directly re-usable, because of the three dimensional network structure of vulcanized rubber. Therefore, a devulcanization process or a suitable degradation process needs to be applied for regeneration or recovery of its materials.

Many academic and industrial attempts have been made for disposal of rubber products. The various reclaiming methods, including microwaving [11], milling [12] and ultrasonic devulcanization [13] have been studied. A comprehensive review on rubber recycling methods has been published [14]. For recycling of butyl rubbers, on the other hand, thermo-mechanical processes and irradiation methods have been reported [15, 16]. It is known that when devulcanized rubber is added to the virgin rubber compound, viscosity of the compound increases, scorch time decreases, and mechanical properties are deteriorated. Therefore, it has been reported that it could only be used as filler in virgin rubber compounds [17].

High energy irradiation offers unique solutions to the problem of recycling due to its ability to induce cross linking or scission of a wide range of material without introducing any chemical initiators and without dissolving the sample, thus, avoiding phase separation. This method can possess a significant economical and ecological advantage as compared to the conventional chemical, thermal and mechanical methods.

IIR (chemically a copolymer of isobutylene and isoprene) has very good properties including low gas permeability, good thermal and oxidative stability, and excellent moisture and chemical resistance. It has been used in a wide variety of tire and non-tire applications such as inner tubes, tire inner liners, and tire curing bladders due to its low unsaturation (generally less than 3%).

Unlike the majority of the elastomers with high levels of unsaturation, IIR exhibits significant degradation damage by ionizing radiation action. The molecular scission generates allyl radicals, which were detected with the ESR technique by Ranby and Rabek [18]. The main effect of high-energy photons, such as gamma rays, in organic polymers is generation of free radicals, accompanied by changes in electrical, optical and mechanical properties. As previously stated by Claugh [19], gamma rays induce a large destructive effect on IIR vulcanizates; this was particularly demonstrated by the sudden reduction of the relaxation effort. The IIR vulcanizates irradiation experiments were carried out by Drozdovskii and Mikhailova in their reclaim work [20]. Recycling of IIR from inner tubes using irradiation of cryogenically ground rubber crumbs is already being applied commercially in China. A pilot scale recycling plant is operating with a capacity of about 2000 tons per year [3].

It has been reported that gamma irradiated IIR removed from used sealing membrane can be reclaimed because of the radiation instability at low doses. The radiation processing of IIR in a dose range of 100-150 kGy brings about a medium plasticized material. With the addition of this regenerated elastomer into virgin rubber, a valuable material recovery and cost reduction can be obtained [21,22].

Şen et al investigated the effect of dose rate and irradiation atmosphere on the degradation of uncross linked, commercial IIR. They evaluated the effect of radiation-induced degradation on the molecular weight investigated by chromatographic and viscosimetric techniques [23]. Three commercial IIR samples were used in the experiments: Ex 165 (isoprene content: 0.8%) and Ex 268 (isoprene content: 1.7%) were obtained from Exxon company, and BK1685N (isoprene content: 1.7%) was obtained from the Nizhnekamsk company. IIR specimens of dimensions in 2 cm x 2 cm with 5 mm thicknesses were irradiated at ambient temperature in air and nitrogen purged and sealed glass ampoules in Gamma cell 220 type Canadian made γ-irradiator for low dose rate (0.18 kGy/h) irradiations and Isslodovately model Russian made γ-irradiator for high dose rate (3.0 kGy/h) irradiations.

In order to see the effect of irradiation dose rate and atmosphere on the degradation of rubber samples, the limiting viscosity numbers were determined. Figure 3 and 4 show the effect of atmosphere on the limiting viscosity number of IIR at low and high dose rate irradiations. Cross linking reactions occur in most elastomers when treated with ionizing radiation, but only a few rubber varieties such as IIR and whose structural units contain quaternary carbon atoms undergo appreciable degradation reactions [24].

As shown in the Figures, limiting viscosity values of rubber samples used in this study decrease signifiacantly up to 100 kGy irradiation dose but do not change appreciably beyond this dose value. Slightly higher values of degradation was observed for low dose rate irradiation in air than in nitrogen for a given absorbed dose value. This is presumably due to the longer contact of rubber with oxygen in air and resulting in higher chain scission reaction [25,26]. On the other hand, no significant dependence of limiting viscosity or average molecular weight on the irradiation atmosphere was observed for rubber samples following high dose rate irradiation, most probably due to shorter contact time of the rubber with oxygen as shown in Figure 3.

Viscosimetric and chromatographic studies show that, beside irradiation atmosphere, the irradiation dose rate is an important parameter for

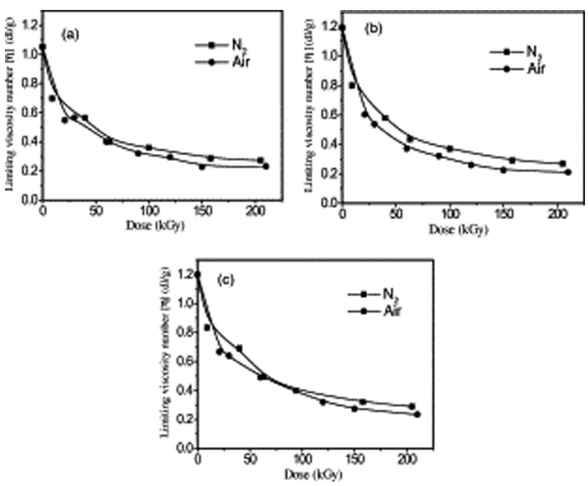

Figure 3. Variation of limiting viscosity numbers with irradiation dose, for low dose rate irradiation (0.18 kGy/h) in air and N_2; (a) Ex 165, (b) Ex 268, (c) BK1685N [23].

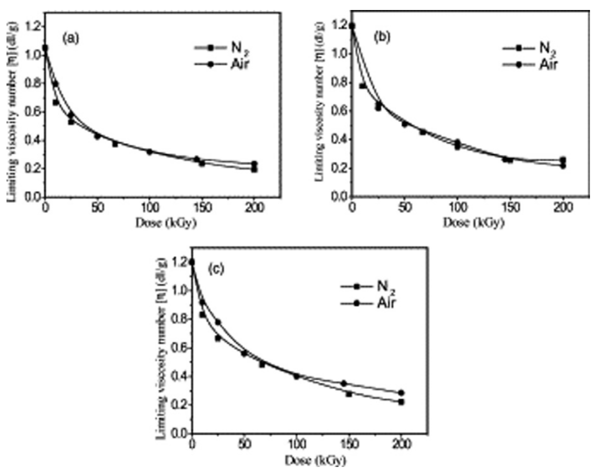

Figure 4. Variation of limiting viscosity numbers with irradiation for high dose rate irradiation (3.0 kGy/h)) in air and N_2; (a) Ex 165, (b) Ex 268, (c) BK1685N [23].

controlling at low dose rates. For doses exceeding 100 kGy, degradation of IIR becomes independent of atmosphere and dose rate, all rubber samples studied attain very similar average molecular weight and isoprene content at this dose value.

Karaağaç et al [27] studied recycling of gamma irradiated inner tubes in butyl based rubber compounds. Used inner tubes were irradiated with gamma irradiation in air at 100 and 120 kGy absorbed dose. The compatibility of irradiated inner tubes with virgin IIR was first checked. Similar experiments were also done by using the commercial butyl rubber crumbs devulcanized by conventional methods. The rheological and mechanical properties and carbon black dispersion degree for the both types of blends prepared by using inner tubes scraps and commercial butyl crumbs were measured and then were compared to the values of virgin IIR compound.

Used inner tubes were shredded and irradiated at ambient temperature in air with a Russian made Isslodovately model γ-irradiator at 3.0 kGy/h dose rate. The rubber compounds were prepared in an open two-roll mill. All of the recipes used in this study are shown in Table 2. In the table, C denotes the recipes prepared by recycling of the commercial IIR crumbs. I-100 and I-120 denote the recipes prepared by using gamma irradiated inner tubes at 100 and 120 kGy, respectively. The rheological and mechanical properties and carbon black dispersion degree for both types of compounds prepared by using inner tube scraps and commercial butyl crumbs were measured and then compared to the values of virgin IIR compound represented as "control compound".

The compatibility of gamma irradiated inner tubes up to 120 kGy absorbed dose with virgin IIR and with the commercially devulcanized IIR crumbs which is already being used in tire industry is practically almost the same level. Although mechanical properties are deteriorated when rubber crumb is added to the virgin compound, the decrease in the mechanical properties was much lower for the compounds prepared from the inner tube wastes irradiated at 120 kGy than the compounds prepared by using commercial butyl crumbs. This study emphasizes the effects of gamma irradiation on the recycling of used inner tubes. It has been concluded that gamma irradiated inner tubes are compatible with IIR and gamma irradiated used inner tubes can be recycled within IIR based compounds.

Scagliusi et al [28] have studied recently on the radiation-induced degradation of IIR vulcanized by three different cross linking systems. They prepared IIR based compounds and vulcanized

Table 2. The compound recipes used [27].

		C Recipes			I-100 Recipes			I-120 Recipes		
Compound (phr)	**Control**	**C-5**	**C-10**	**C-15**	**I-100-5**	**I-100-10**	**I-100-15**	**I-120-5**	**I-120-10**	**I-120-15**
Butyl BK 1675 N	100	95	90	85	95	90	85	95	90	85
Butyl reclaim (com.)		5	10	15						
Butyl irradiated					5	10	15	5	10	15
C/B N660	50	50	50	50	50	50	50	50	50	50
Paraffinic oil	20	20	20	20	20	20	20	20	20	20
TQM	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
6PPD	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Stearic acid	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Zinc oxide	3	3	3	3	3	3	3	3	3	3
Sulphur	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
MBT	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
TMTD	1	1	1	1	1	1	1	1	1	1

them by three different curing systems, such as the ones based on sulphur, sulphur donor and phenolic resin, to identify that which curing system was the most stable under irradiation. All vulcanizates were gamma irradiated with doses of 25, 50, 100, 150, and 200 kGy. Irradiated and non-irradiated samples were then characterized. It was observed that doses higher than 150 kGy practically destroy the assessed properties for all butyl compounds, irrespective of the vulcanization system used; however compounds cured with phenolic resin exhibited a decrease in properties proportional to the dose.

Hassan et al studied on the effects of γ-irradiation on some properties of reclaimed rubber powder (RRP) and nitrile/butadiene rubber (NBR) blends [29]. In that study, RRP was treated by the addition of glycidyl methacrylate (GMA) and the produced GMA-RRP was mixed with NBR in various compositions. The blends were irradiated with gamma radiation doses of 50–250 kGy. Results showed that the tensile strength, hardness and swelling resistance increased with increasing NBR content in the blends. It has been shown that the tensile strength increased with increasing dose. Similarly, hardness values, which were reported for the same composition, apparently increased with dose within the range of 50–250 kGy.

Smith et al have recently published an interesting paper on the radiochemical ageing of IIR for space applications [30]. They studied the effect of gamma irradiation in inert atmosphere at 25 °C and 70 °C on carbon black filled IIR. The properties have been investigated by SEM, ^{13}C NMR, swelling measurements and mechanical tests. Unlike previous in the literature, an increase in tensile strength of the material was observed during ageing. This increase was explained as due to a modification of the rubber network structure. Correlations between mechanical properties and cross link density were also presented. They concluded that the chain cross linking process predominates over the chain scission reactions at 25°C, whereas the two phenomena are in competition at the aging temperature of 70°C, at high irradiation doses.

Applications of Radiation Technology to the Non-tire Rubber Industry

There are many industrial application of radiation technology also on non-tire rubber goods. Various automobile components such as gaskets and seals are made of elastomers. Main elastomers used for non-tire rubber goods are ethylene propylene-diene monomer rubber (EPDM), ethylene propylene rubber (EPM), acrylonitrile–butadiene rubber (NBR), hydrogenated acrylonitrile butadiene rubber (HNBR), chloroprene rubber (CR), styrene butadiene rubber (SBR), polyacrylate rubber (ACM), silicone rubber (SR), and fluoroelastomer (FKM). These synthetic rubbers are generally cross linked by conventional peroxide based methods. Radiation cross linking is an option to apply in thin articles and high purity O-rings. In India, radiation cross linked SR gaskets in high temperature applications [5].

Mizote et al studied on the surface modification of vulcanized rubber by radiation grafting [31,32]. They performed graft polymerization of 2-hydroxyethylmethacrylate (HEMA), and hydrophobic monomer, 3-(methacryloyloxy) propyltris(trimethylsiloxy)silane (MPTS) by simultaneous irradiation of EB onto the vulcanized NR and investigated the characteristics of graft polymerization, the contact angle of water on the modified surface, and friction behavior at the semi-dry state. After graft polymerization of HEMA and MPTS, the composition of the modified surface could be determined by IR measurements. The contact angle of the trunk rubber, 92.6° was modified from 73.4° to 108.1°. This result suggests that the friction at the moment of semi-dry can be controlled by providing the hydrophobic properties with graft polymerization.

They also evaluated the HEMA-grafted NR by surface hardness, dry friction, wiping performance, and wear duration on the view point of the practical usage for car wiper [32]. When the composition ratio of HEMA to NR near the surface layer of the HEMA-grafted rubber was higher than 0.7; the coefficient of dry friction was lower than that of commercially available chlorinated rubber. Additionally, the wiping performance was more than 95%. These results indicate that the graft polymerization of HEMA on rubber surface provides sufficient characteristics as the wiper rubber and is promising surface treatment for the novel wiper rubber which can achieve both the reduction of dry friction and the holding of high wiping performance. The wear resistance of HEMA-grafted rubber was eight times higher than chlorinated rubber. This high performance of wear resistance gives the life of two years in the practical use as wiper rubber. It was concluded that the HEMA-grafted rubber is promising material for wiper rubber instead of the currently used chlorinated rubber.

EPDM is commonly used for rubber goods production for automobiles and household applications. Stelescu et al [33] studied the concentration effect of trimethylolpropane-trimethacrylate coagent, on the mechanical properties of filled and unfilled EPDM rubber vulcanized by EB. Mechanical properties of EB irradiated samples were compared with the dibenzoyl peroxide cured samples. Dependence of mechanical properties on irradiation dose was determined from a dose range of 0 kGy to 200 kGy. Dibenzoyl peroxide vulcanization at 160°C was carried out on the EPDM samples as well. The results showed that the optimum values of physicomechanical rubber parameters present a strong dependence on TMPT concentration and irradiation dose. It was concluded that EB curing of EPDM with an irradiation dose of 50 kGy is a quite efficient way to reach high cross linking densities.

Application of Radiation Technology to the Tire Reinforcing Materials

Tire is a composite material consists of reinforcing materials and rubber compounds. The reinforcing materials used in tires are mainly textile cords, steel cords, and steel bead wire [34]. The textile tire cord can be produced with different type of materials such as Nylon 6 (Ny 6), Nylon 66 (Ny 66), Poly (ethylene teraphthalate) (PET), Rayon (Ry) and Aramid (Ar). PET and Nylon tire cords are widely used reinforcing materials for automobile industry. Ar cords are used only high perfomance tires. The advantages of PET tire cord are high strength, good durability, high modulus, and lower creep. Polyester has good dimensional stability while having low adhesion and low fatigue resistance. On the other hand, Ny 66 is superior to most tire reinforcing materials. Ny 66 tire cord has higher strength, better adhesion and fatigue resistance but poor dimensional stability. Recently, tire cord producers have developed and produced new generation hybride reinforcing materials having either higher performance than the conventional cords or lower cost with similar performance with PET/Ny 66 or Ar/PET [35,36]. In line with rapidly changing in the tire technology, the investigation of the influence of high energy irradiation on the reinforcing materials had been investigated by Professor Olgun Guven and his co-workers [37,38].

Advantages of the use of irradiation in tire industry, such as improving of tire uniformity, and the possibility of saving materials and energy have long been acknowledged [6]. However, as it is known from the literature, there have been a few studies on the effects of high energy irradiation on the textile tire cord materials. Harmon [39] investigated the effect of different levels of gamma irradiation on some of the physical properties a group of textile cords. These textile cords were Dacron (DuPont polyester fiber), Nylon, cotton, Orlon (DuPont acrylic fiber), Fiberglass, Celanese 36 and Rayon. In that study, flex fatigue, creep rate, melt points, stress, strain and shrinkage were studied. He found that, shrinkage values of Nylon cords were improved and the creep values were reduced. While the tensile strength of the Dacron decreased 40%, the other cords lost 90% of the original tensile strength. In generally, the effect of gamma irradiation on the physical properties was to worsen of the cords evaluated. Aytaç et al [37] studied the effect of gamma irradiation on the properties of high tenacity Ny 66 and PET tire cords. They irradiated the untreated tire cords with different twist levels in air and measured the mechanical and thermal properties with absorbed dose. They found that the mechanical properties were deteriorated with the increasing radiation dose for Ny 66 cords, while it was almost unchanged for polyester cords (Figure 5). Hot shrinkage values for the Nylon cords were improved, i.e. were decreased. They observed a slight decrease in the hot shrinkage values of irradiated polyester cords. They found that the effect of irradiation on both the Ny 66 and polyester cords was not depending on the twist level of the cords. It was concluded that polyester cord has higher radiation resistance than Ny 66 cord.

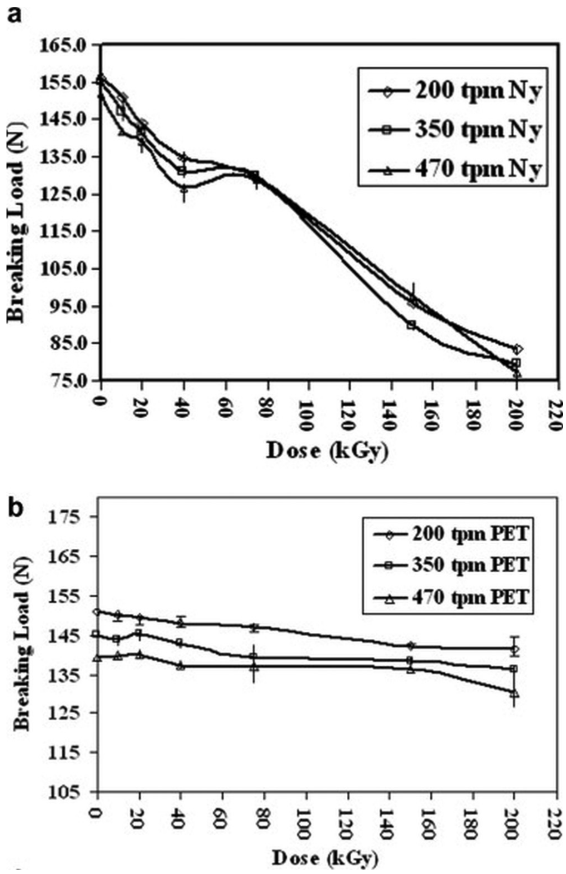

Figure 5. Tensile strength-dose curves with different twist levels (a) GreigeNy6.6 (b) Greige PET tire cords [37].

Aytaç et al [38] also investigated that the effects of gamma and EB irradiation on mechanical and structural properties of Nylon 66, Nylon 6 and PET fabrics used in tires. In that study, the untreated (greige) cords, treated cords, and calendered fabrics were irradiated at different doses. They found that the effects of high energy irradiation on greige and treated cords, and calendered fabrics were similar. Also they observed that no protective effect of compound coating used in calendering process to against radiation-induced oxidative degradation although calendering compounds had been some antidegredants. Besides, the deterioration effect of gamma irradiation on mechanical properties was much higher than that of EB irradiation for all sample types. This is a well known fact due to dose rate difference between gamma rays and EB. They concluded that PET calendered fabric had higher resistance to ionizing radiation and Nylon calendered fabrics were more sensitive even at low doses. The effect of irradiation strongly depends on the chemical structure of these polymers. It is well known that PET shows good resistance to radiation due to the presence of the aromatic rings on the main chain [40]. Limiting viscosity numbers were also determined to see the effects of gamma and EB irradiations on the structural properties of fabric materials in that study. They observed that limiting viscosity numbers of Nylon cords decreased up to 75 kGy, whereas remained almost unchanged for PET cords. The decrease in limiting viscosity number of Nylon cords was attributed to the radiation-induced oxidative degradation of the main chain which caused deterioration in the mechanical properties of the Nylon cords. Therefore, they concluded that the effects of high energy irradiation on tire cords had to be taken into consideration during tire design that is reinforced with particularly Nylon fabrics if high energy radiation is to be applied. PET/Ny 66 and Ar/Ny 66 hybrid cords should also be evaluated if EB irradiation will be used for pre-vulcanization.

Pramanik et al studied on the modification of Ny 66 by EB irradiation for the improvement of the properties [41]. Ny 66 was irradiated under the optimized dose rate of EB in the presence of suitable cross linkers. It has been observed that water absorption of Ny 66 was decreased substantially on irradiation and thermal stability was improved with increasing dose of irradiation. It was also showed that crystalline percent of polymer decreased leading to more amorphous character. Triallyl isocyanurate (TAIC) was found to be the best cross linker.

Future Prospects

The radiation technologies using gamma sources and electron accelerators for material processing are well-established processes. The number of industrial electron beam accelerators (EBA) is being increased every day all over the world.

According to IAEA reports, apart from the other applications, cross linking of selected thermoplastics for enhancing their performance and radiation vulcanization of elastomers and automobile tires are of great importance. The use of thermoplastics and/or rubber-thermoplastic components in automotive industry (OEM) is also increasing. Radiation cross linking is an option for the enhancement of compatibility of the blends.

It is well known that radiation cross linked engineering plastics offer OEM and end users in many branches of industry, have much more technical and economical advantages in comparison with high performance plastics. Although the cost of the radiation treatment depends on many factors; the cost of unit enhancement of performance will probably decrease when the radiation treatment is used at mass production process. Because radiation processing is a single, environmentally friendly, and efficient operation; it utilizes lower cost tooling, reduced cure times and needs low energy.

Carbon nanotubes are being widely used in rubber composites, recently. Different types of functionalized nanofillers are also becoming attractive. A radiation based process is recommended as alternative to functionalize some of nanofillers. Desired functional groups are provided from polymers and/or from monomers.

The surface modification of vulcanized rubber goods by radiation grafting is another interesting and novel technique. Graft polymerization is capable of providing the desired functions such as hydrophilicity, good mechanical properties, and core/shell morphology of composite in rubber. The studies on graft polymerization of polyfunctional monomers onto the vulcanized rubber will lead the improvement of the mechanical and surface characteristics of technical rubber goods used in OEM.

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