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Property Enhancement of SiR-EPDM Blend Using Electron Beam Irradiation

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Abstract – Polymers are the most commonly used di-electrics because of their reliability, availability, ease of fabrication and cost. The commercial and industrial demand for advanced polymeric materials which are capable of being used in harsh environment is need of the hour. The study of the effect of electron beam irradiation on polymeric materials is an area of rapidly increasing interest. This paper discusses the resultant beneficial effects of electron beam irradiation on the SiR-EPDM blend having 50:50 composition. The changes in mechanical and electrical properties of SiR-EPDM blend which are exposed to three different doses of electron beam radiation namely 5 Mrad, 15 Mrad and 25 Mrad are presented. The irradiated blends are analyzed for their electro-mechanical and physico chemical properties. The electrical changes induced by irradiation are investigated by arc resistance, surface resistivity and volume resistivity measurements as per ASTM standards. The mechanical changes are observed by the measurement of tensile strength and elongation at break. Physico chemical investigation has been done using the FTIR, in order to investigate the irradiation induced chemical changes.

Keywords: Silicone Rubber (SiR), Ethylene Propylene Diene Monomer (EPDM), Fourier Transform Infrared Spectroscopy (FTIR), E-beam irradiation, Cross-linking, Chain scission

1. Introduction

The polymeric insulating materials play a key role in the performance and reliability of most of the electrical systems. The survival of an electrical system is mostly governed by the endurance limit of the di-electric material employed within such systems. The fundamental parameters of these di-electrics such as electrical, mechanical, thermal, chemical and environmental factors play a vital role in deciding the application. Now a days, the polymeric insulating materials are increasingly being used in nuclear reactors, radiation facilities etc., necessitating the development of novel polymeric insulating materials capable of handling such harsh environmental stresses such as radiation. Also, the restricted properties and limited use of homo-polymers has given rise to the exploration of composites, co-polymers and blends etc.

Mixing of the widely used polymeric material gives a new composite material having good flexibility and high resistance to environmental stresses. Blending of polymers is an attractive way of producing a new material as it does not involve cost and technical un-certainties as that of synthesizing a new one. Amidst polymers, EPDM and SiR are the commonly used elastomer materials in harsh environments. Many researchers have investigated the performance of these commonly used polymers [1, 2] and also their blends [3-7]. However the property modification by E-beam irradiation on these blends has never been reported. Low energy electron beam irradiation of polymers has been used in variety of fields. This process has been effectively utilized in power cable industry and has been identified as one of the most advanced industrial process.

The polymeric materials are sensitive to varying degrees of low energy radiation. For example, they may experience different alterations in their structure, such as simultaneous scission and cross linking, upon exposure to irradiation. As a result, changes in their physical and / or chemical properties occur that could prematurely terminate the useful life of the dielectric before electrical failure. The type and the degree of damage experienced by a material due to radiation depend greatly on several factors, such as radiation type, dose and dose rate, presence of oxygen and high temperatures, etc. Radiation may tend to induce changes in some materials while others may not be affected. In addition, some of these changes are transitory, while others may be permanent. The temporary changes occur primarily due to the production of gas pockets and the generation of local ionized particles, which may disappear or become trapped some time after the irradiation has ended. Permanent changes, on the other hand, result from structural damages to the material such as surface oxidation, cracks and chemical decomposition byproducts. The effects of E-beam irradiation on the electrical, mechanical, physico-chemical properties of SiR-EPDM blend are reported in this paper. These effects are

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categorized according to property classification. A correlation often exists between electrical, mechanical, and chemical properties. For instance, changes in electrical properties are usually associated with chemical reactions or mechanical degradation. These, in turn, are intimately connected with the physical state of the material which is governed by its chemical structure. Thus the properties that are important for a material in a harsh environment will depend in particular on the type of application and how the material is being used [7].

Some researchers have reported the treatment of polymer blends by E-beam irradiation [8-10]. For example, EVA-LDPE blend properties could be enhanced by the irradiating the rubber prior to melt blending [11]. E-beam irradiation has been used to improve the di-electric properties of Poly Ether Ether Ketone(PEEK) [12, 13]. The compatibility modification of PET/PP/PE/EVA blend by e-beam was reported [12].

The samples of SiR-EPDM blend are irradiated up to 5, 15 and 25 Mrad doses using an electron source of 1.5 MeV rating. The objective of the present work is to investigate the mechanical and electrical properties of SiR-EPDM blend of 50:50 composition at various doses of electron beam irradiation. The effect of the E-beam irradiation induced reactions such as cross-linking and chain scission on the electro-mechanical properties of the SiR-EPDM blend are interpreted through the FTIR.

2. Materials and Methods

2.1 Materials

The raw materials used are Silicone Rubber (SiR) and Ethylene Propylene Diene Monomer (EPDM) without any filler and additives). They are supplied by M/S Joy Rubbers, India.

2.2 Blend preparation

For the present investigations the blend ratio of 50:50 is selected [4, 5]. The Silicone rubber and EPDM with blend ratio of 50:50 were mixed in two roll mixing mill (Shoail make). The mixing was done for 30 minutes as per rubber manufacturing standards. The various additives like C, ZnO_2, MBT, TMTD, Stearic acid were added during the blending process. The vulcanization was carried out in a electrically heated press (RNKM make) for 3 minutes at a optimum temperature of 90º C, and then they were post cured as per standard.

2.3 Electron beam accelerator

The electron beam irradiation was carried out in air using an electron accelerator with a beam energy of 1.5 MeV(M/S Siechem Industries). The blends were exposed to three different doses (5 Mrad, 15 Mrad and 25 Mrad) of electron beam radiation. Three samples were exposed to the same dose of E-beam irradiation and investigations were carried out. All the results presented here are the average of the three investigations made at the same test conditions.

3. Characterization of SiR-EPDM Blend

The samples of SiR-EPDM have been characterized by their electrical and mechanical properties, as per IEC and ASTM standards, before and after electron beam irradiation.

3.1 Physico-chemical characterization

Fourier Transform Infrared Spectroscopy - FTIR is used for detecting functional groups and for characterizing the materials. It generates an infrared (IR) spectra of samples that absorb IR light. It provides information about the chemical bonding or molecular structure of materials. The FTIR technique enables the measurement of the changes in the nature and amount of different chemical groups by measuring the changes in the absorbance of wavelengths of IR light which are specific to those functional groups. The changes due to irradiation can be quantified in comparison to virgin. FTIR spectra of all the E-beam irradiated samples and virgin samples were taken using Perkin Elmer spectrophotometer, in the wave number ranging from 500 cm^{-1} to 4000 cm^{-1}.

3.2 Electro-Mechanical characterization

3.2.1 Mechanical characterization

The influence of E-beam radiation on the mechanical properties of a particular blend depends largely on the chemical transformations that take place within it during E-beam exposure. The applied load and the elongation of the dumb-bell shaped specimen are measured as per ASTM D 412 using a universal testing machine (Make - Hounsfield) at room temperature. Hardness is measured using Shore A Duo. The sample dimensions is 5x5x0.3 cm square shaped specimen.

3.2.2 Electrical characterization

The virgin and E-beam irradiated blends samples are tested for the electrical parameters like volume resistivity, surface resistivity and arc resistance. The electrical properties are dependent on the chemical composition of the di-electric, they usually suffer degradation after mechanical deterioration has taken place. The volume and surface resistivities were measured using a test cell along with mega ohm meter (Prestige Electronics) with a sample size of $10 \times 10 \times 0.3$cm (square shaped specimen) as per ASTM D257. A constant voltage of 500V DC is applied between main and guard electrode. The arc resistance was measured as per ASTM D495 (SEV Electricals). The sample of size $5 \times 5 \times 0.3$cm square shaped specimen was used for this measurement. 12.5 kV AC was applied to the sample.

4. Results and Discussion

4.1 Fourier transform infrared spectroscopy-FTIR

The performance of insulation systems may be affected by the various chemical reactions which has been occurred during the blending process / E-beam irradiation. The analysis of these chemical reactions in insulation material is necessary in material designs. Hence FTIR analysis has been done on E-beam irradiated samples and the spectra of the virgin SiR-EPDM sample was taken as reference. The FTIR spectra of virgin sample and E-beam irradiated samples of SiR-EPDM blend are given in Figs. 1(a), (b), (c) and (d).

The formation of various new functional groups during blending and E-beam irradiation is depicted in Figs. 2(a) and (b) respectively.

Tables 1(a) and (b) show the band numbers and the wave numbers for various functional groups of virgin sample and E-beam irradiated samples along with their absorbance values.

The investigations on the IR spectra of the virgin blend revealed the following facts. The formation of new functional groups such as Si-H, Si-CH_3-CH_2,=C-H(alkene, bending, strong), C=C (alkene, asymmetric stretch, strong) and C-H (alkane, bending, variable) have been noticed in addition to the various functional groups of component polymers in virgin sample. This indicates that the self cross linking has occurred between SiR and EPDM during blending itself due to the additives. The formation of new functional groups may be due to the cleavage of C-C, C-H bonds in EPDM and Si-CH_3, Si-O bonds in SiR, which will happen in the order of their bond energies. In EPDM, the cleavage of C-C bond will happen first followed by C-H bond cleavage, as their bonding energies are 348 (KJ/mol) and 413 (KJ/mol) respectively. Similarly in SiR, the cleavage of Si-CH_3 which occurs first is followed by the cleavage of Si-C bond as their bonding energies are 360 (KJ/mol) and 452 (KJ/mol) respectively.

The FTIR investigations on E-beam irradiated samples revealed that the irradiation has induced the chemical and morphological changes. The molecular changes occurring in polymers as a result of E-beam irradiation-induced chemical reactions may be classified as (i) chain cross-linking and (ii) chain scission. The cross-linking results in an increase in molecular weight and formation of macroscopic network. The chain scission results in decrease in molecular weight.

From the FTIR spectra of E-beam irradiated samples, the following points are observed. The hydrophilic (O-H) group content is found to increase initially with increase in dose compared to virgin. This ensures that the chain scission reaction has resulted in formation of more number of methyl groups as well as free hydrogen atoms. The mechanical and electrical parameters are subjected to a major change due to chain scission. At 15Mrad and 25

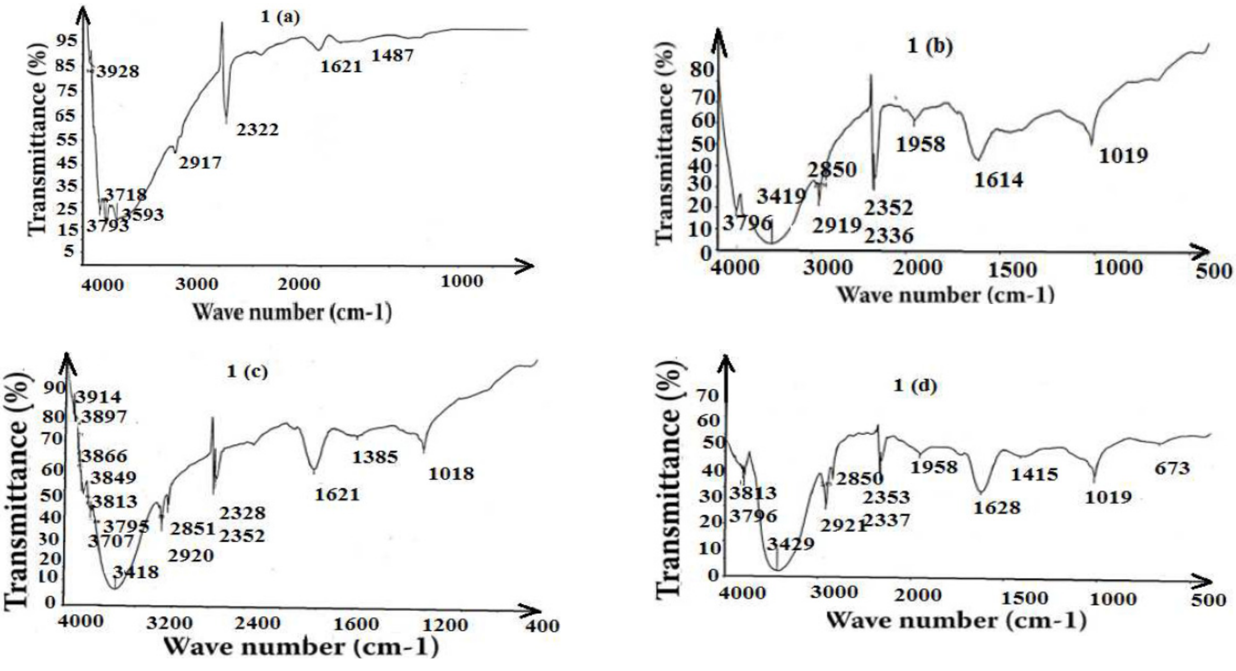

Fig. 1. FTIR Spectra SiR-EPDM Blend irradiated by various doses of E-beam: (a) 0 Mrad (virgin sample); (b) 5 Mrad; (c) 15 Mrad and (d) 25 Mrad

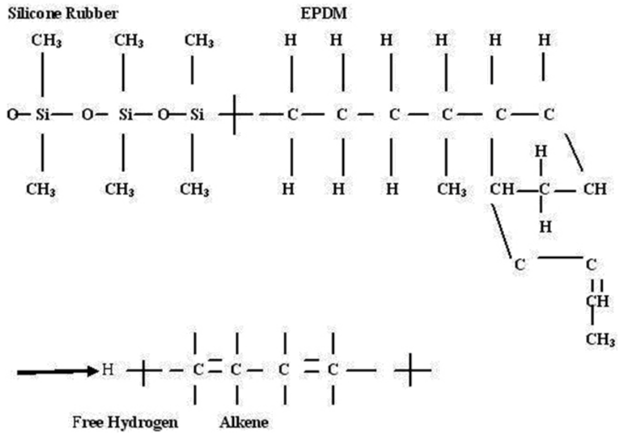

Fig. 2(a). Formation of various functional groups during the blending process

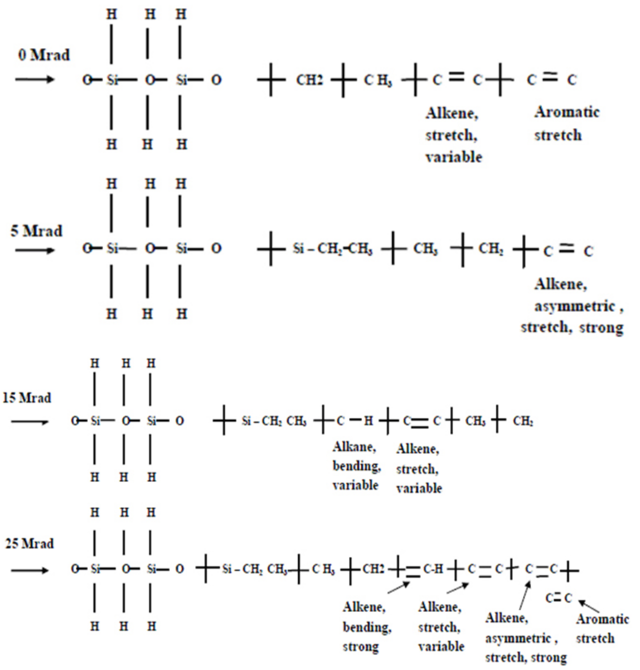

Fig. 2(b). Formation of various functional groups during the E-beam exposure [0 Mrad, 5 Mrad15 Mrad and 25 Mrad]

Table 1(a). FTIR Investigations of Virgin sample and E-beam irradiated samples (5 Mrad)

Functional groups	Absorption band	15 Marad		25 Marad	
		WN (cm^{-1})	Absorption %	WN (cm^{-1})	Absorption %
Hydrophilic (OH)	3200-3600	3418	119	3429	148
Hydrophobic CH_3-CH_2	2850-3000	2920 2851	49 40	2921 2850	39 26
Si-H	2100-2360	2353 2328	33 27	2353 2337	20 18
C=C, alkene, stretch, variable	1620-1640	1018	20	1628	31
Si-CH_3-CH_2	1000-1200	-	-	1019	16
C=C, alkene, asymmetric, variable	1900-2000	1385	16	-	-
C-H, alkene, bending, variable	1350-1480	-	-	1416	16
C=C aromatic stretch	1400-1600	-	-	673	11
=C-H alkene, bending, strong	675-1000	-	-		

Table 1(b). FTIR Investigations of Electron beam irradiated samples (15 Mrad and 25 Mrad)

Functional groups	Absorption band	15 Marad		25 Marad	
		WN (cm^{-1})	Absorption %	WN (cm^{-1})	Absorption %
Hydrophilic (OH)	3200-3600	3593	75	3419	149
Hydrophobic CH_3-CH_2	2850-3000	2917	35	2919 2851	62 46
Si-H	2100-2360	2322	22	2353 2336	50 46
C=C, alkene, stretch, variable	1620-1640	1621	6	-	-
Si-CH_3-CH_2	1000-1200	-		1019	29
C=C, alkene, asymmetric, variable	1900-2000	-		1958	21
C-H, alkene, bending, variable	1350-1480	-	-	-	-
C=C aromatic stretch	1400-1600	1488	4		-
=C-H alkene, bending, strong	675-1000	-	-		-

Mrad dosages, the hydrophilic OH group is found to decrease at wave numbers 3418 cm^{-1} and 3429 cm^{-1}. This may be attributed to the immobile nature of the segments of the macromolecules caused by radiation induced cross-linking.

At 5Mrad dose, because of chain scission reaction, the CH_3-CH_2 (hydrophobic) group has been found to have a higher absorbance values (of 77% and 31% with respect to the virgin sample) at 2919 cm^{-1} and 2851 cm^{-1}. Also the Si-H group content has been found to increase (to the values of 127% and 109% respectively with respect to the virgin sample) at wave numbers 2353 cm^{-1}, 2336 cm^{-1}. The formation of new groups such as alkene (C=C asymmetric, stretch, strong) and Si- CH_2-CH_3 have been noticed at 1958 cm^{-1} and 1019 cm^{-1} respectively with the absorbance values of 21% and 29%. This is due to chain scission taking place in SiR and EPDM side chains at 5 Mrad.

But at still higher dose of 15Mrad, due to the cross-linking, a significant reduction of the CH_3-CH_2 group have been noticed at 2920 cm^{-1} and 2851 cm^{-1} with the absorbance values of 40% and 14% (with respect to virgin). Also the reduction of Si-H group content is observed at 2353 cm^{-1} and 2328 cm^{-1} with the absorbance values of 50% and 23% (with respect to virgin). A significant increase (77% with respect to the virgin sample) in C=C alkene, stretch, variable has been noticed at 1621 cm^{-1}.

Also a 31% drop of $Si\text{-}CH_2\text{-}CH_3$ group is observed at 1018 cm^{-1}. A new C-H(alkane, bending variable) group have been noticed at 1385 cm^{-1} with the absorbance of 16%. This may be due to the increased availability of H atoms which are released from the EPDM during cross-linking.

At 25 Mrad, due to the continued cross-linking, a significant reduction of the $CH_3\text{-}CH_2$ group have been noticed at 2921 cm^{-1} and 2850 cm^{-1} with the absorbance values of 11% and 25% (with respect to the virgin). Also the reduction of Si-H group content is observed at 2353 cm^{-1} and 2337 cm^{-1} with the absorbance values of 9% and 18% respectively. A significant increase of 81% (with respect to the virgin sample) in C=C alkene, stretch, variable group has been noticed at 1621 cm^{-1}. Also a 21% drop of $Si\text{-}CH_2\text{-}CH_3$ group is observed at 1019 cm^{-1}. A new C-H(alkane, bending variable) group have been noticed at 1416 cm^{-1} with the absorbance of 16%. Also a new group =C-H (alkene),bending, strong has been noticed at wave number 673 cm^{-1}. This may be due to the increased availability of H atoms which are released from the EPDM during cross-linking.

4.2 Interpretation of mechanical parameters using FTIR

In particular, cross-linking and chain scission are believed to play an influential role on the rate of deterioration of SiR-EPDM blend. The tensile strength is mostly governed by the overall tendency of the material to cross-link or to undergo chain scission upon exposure to radiation. As mentioned before, the cross-linking effect is characterized by an increase in tensile strength and a decrease in the elongation at break point. In polymers where cross-linking predominates, the tensile strength often increases to a maximum. The elongation at break and tensile strength of the virgin sample and E-beam irradiated samples are plotted against the various doses of E-beam as shown in Figs. 3 and 4.

All the values indicated are the mean of 3 tests conducted. A slight decrease in elongation at break have been noticed (7.5% compared to virgin) at 5and 15 Mrad. This is due to the formation of double bonds which are initiated by chain scission mechanism of E-beam

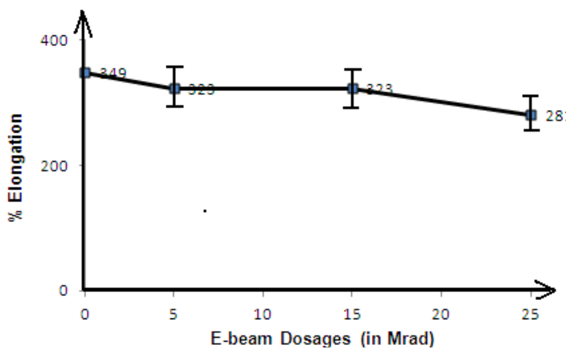

Fig. 3. Percentage Elongation of SiR-EPDM Blend

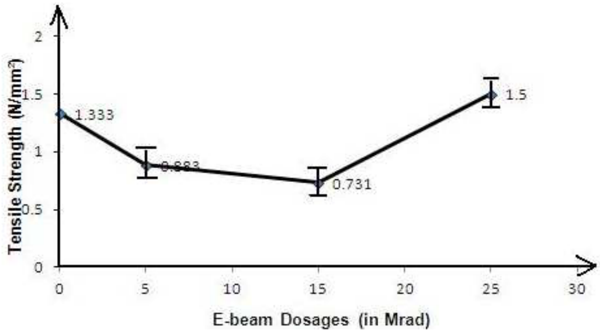

Fig. 4. Tensile strength of SiR-EPDM Blend

irradiation. It is also evident from FTIR that the formation of C=C (alkene, asymmetric, stretch, strong) bonds at 1958 cm^{-1} with 21% absorbance value has been noticed at 5 Mrad. At 15 Mrad, the existence of C=C (alkene, stretch, variable) group has been noticed at 1621 cm^{-1} with 26% absorbance. At higher dose of 25Mrad, a large decrease in elongation at break (19.5%) has been observed. This may be attributed to the reduced segmental mobility of polymer chains on account of cross-link formation in the amorphous region. The appearance of new group =C-H (alkene), bending, strong noticed at wave number 673 cm^{-1} with 11 % absorbance is responsible for the drop in elongation. The reduction of 34% and 45% tensile strength values have been noticed at 5 and 15 Mrad respectively. This is due to the increase in Si-H content at 2353 cm^{-1} with absorbance values of 127% and 50% respectively (with respect to the virgin). At 25 Mrad, the tensile strength of the blend is increased to 12.5%. It is validated by the corresponding decrease of 9% in Si-H group at 2353 cm^{-1}. This is due to the predominating effect of the cross-linking reaction which is initiated by the E-beam irradiation. Also 81% increase in C=C (alkene, stretch, variable) group at 1621 cm^{-1} (when compared to virgin) has been noticed from FTIR spectra.

4.3 Interpretation of electrical parameters using FTIR

The surface resistivity, volume resistivity and arc resistances of the virgin sample and E-beam irradiated samples are plotted against various doses of E-beam and are shown in Figs. 5, 6 and 7.

It is observed that both the volume and surface resistivity of the E-beam irradiated samples are found to drop till 15 Mrad dose. This may be due to the chain scission reaction, which has occurred at low dose level. It is validated by the absence of =C-H (alkene), bending, strong group. But a 73% increase in volume resistivity and lower deterioration in elongation has been noticed at 25 Mrad. This is proved by the appearance of new =C-H (alkene, strong) group at 673 cm^{-1} with 11% absorbance in FTIR spectra.

The arc withstanding time is found to increase with

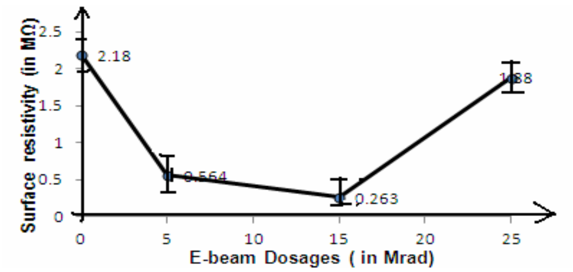

Fig. 5. Surface Resistivity of SiR-EPDM Blend

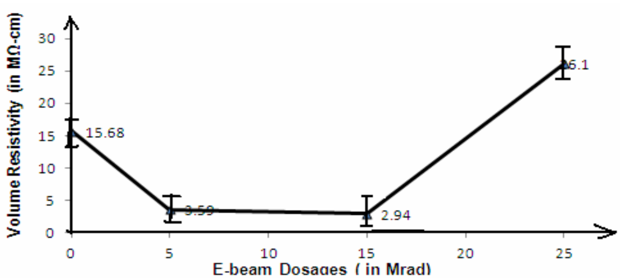

Fig. 6. Volume Resistivity of SiR-EPDM Blend

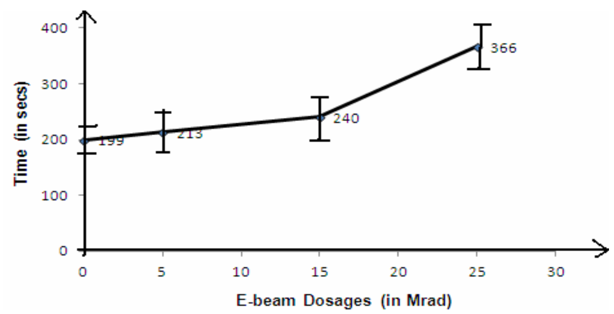

Fig. 7. Arc resistance of SiR-EPDM Blend

increase in E- beam dose. At 5 and 15 Mrad, the blend has withstood only 10 mA current. But at 25 Mrad dose, the current withstanding capability of the blend is found to be 40 mA for a duration of 366 seconds. The factor behind this effect is the E-beam induced cross-linking.The increase in the molecular weight leads to an increase in charging ability of polymer blend. Also from FTIR, the presence of more number of double bonds have been noticed at 1628 cm^{-1}, 1915 cm^{-1} 1416 cm^{-1} and 673 cm^{-1} for a 25 Mrad exposure.

5. Conclusion

The property (electrical/mechanical) modification of the SiR-EPDM blend at various doses of E-beam irradiation has been analyzed. The action of E-beam radiation on polymeric materials promotes mainly the two processes (a) cross-linking - formation of chemical links between adjacent molecular chains. (b) Scission of polymer chains, which destroys its molecular structure. These chemical transformations result in changes in the physical, mechanical and electrical properties of polymers. Although these effects occur simultaneously, one plays a dominating role depending on the chemical structure of the polymer and radiation dose. Cross-linking improves electrical properties (volume resistivity, surface resistivity, arc resistance) and one of the mechanical properties (tensile strength). E-beam exposure improves most of the parameters, and the cross-linking phenomenon is the key factor.

Based on the investigations, both the electrical and mechanical properties of the blend are found to be better than of the virgin sample, when treated between the doses of 15-25 Mrad. This study also proves that the SiR-EPDM polymer blend posses the superior characteristics of the SiR (electrical properties) and EPDM (mechanical properties). A radiation dose of 15-25 Mrad is found to be optimum for achieving the best balance in properties of SiR-EPDM blend. The changes in electro- mechanical properties of the SiR-EPDM blend before and after the E-beam exposure has been supported by FTIR investigations also. Hence it is concluded that with the optimal E-beam dose of 15-25 Mrad, the properties of the di-electrics can be enhanced. In this research, parameters like surface resistivity, volume resistivity and arc resistance alone are considered. The other important electrical parameters like dielectric strength and dielectric constant may be included for the future investigations.

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