Thermal and Electrical Properties of Irradiated Styrene Butadiene Rubber-Metal Composites

S.E. Gwaily, G.M.Nasr* and M.M. Badawy*

National Center for Radiation Research and Technology,
Nasr City, P.O.Box 29, Cairo, Egypt.
** Phys. Dept., Faculty of Science, Cairo University, Giza, Egypt.*

The effect of γ- radiation on both the electrical and thermal properties of styrene butadiene rubber (SBR) loaded with different concentration ratios of copper (Cu) and iron (Fe) fine powder has been studied. The d.c. electrical conductivity σ for all loaded SBR composites was highly affected by γ - radiation dose. The addition of different fillers do not contribute much to the thermal properties of these composites. The filler – filler inter-spacing distance was found to be highly affected by the γ- radiation dose, which in turn influences the electrical conductivity of these composites.

Introduction:

The majority of polymeric materials are electric insulators in nature[1]. However, they can be rendered conductive by different methods:

(a) Creation of conjugated double bonds in the backbone chain of polymers [2,3].

(b) Introduction of donor-acceptor complex in the polymer matrix [4], and

(c) Adding conductive fillers such as metallic powders and carbon black [5-8].

One of the goals of materials research is to create new materials with physical properties tailored to a particular application and to understand the mechanisms controlling these properties.

Irradiation of different types of rubber was early studied by Tarssova et al [9]. The effect of the polymer composition on radiation induced crosslinking was studied by many workers [10-12].

It is well known that electrical conduction in polymers can be considerably enhanced by irradiation [13]. The increase in conductivity of irradiated polymers may be attributed to the formation of conjugated structures [14]. Also, the irregularity in the polymer chain may give rise to a hopping mechanism that will enhance the conductivity [15].

The present investigation aims to clarify the effect of γ-radiation on both the electrical and thermal properties of styrene butadiene rubber (SBR) loaded with mixed concentration ratio of Cu and Fe metal fine powder. Moreover, the filler-filler interspacing distance is calculated empirically as a function of both γ- dose and filler content.

Experimental

2.1 Sample preparation

The styrene butadiene rubber (SBR) and the other conventional additives were mixed with different concentration ratios of Cu and Fe powders as shown in Table (1) on a roll mill, under typical industrial mixing conditions.

The investigated rubber specimens were shaped during the vulcanization process (under 78.4 MPa pressure at 160^{o}C for 60 min.) into the form of discs of radii 0.75 cm for the thermal and 0.5 cm for the electrical measurements and a common thickness of 0.2 cm.

Table (1): Composition of SBR composite samples with different concentration ratios of Cu / Fe fine powder.

Ingredients (phr)[a]	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**
SBR (1502)	100	100	100	100	100	100
Stearic acid	2	2	2	2	2	2
Processing oil	10	10	10	10	10	10
Fe	0	10	30	50	70	90
Cu	0	90	70	50	30	10
MBTS[b]	2	2	2	2	2	2
PBN[C]	1	1	1	1	1	1
ZnO	5	5	5	5	5	5
Sulpher	2	2	2	2	2	2

1) part per hundred parts of rubber by weight
2) dibenthiazy1 disulphide
3) pheny1 – β - naphthylamine

2.2 Thermal Measurements

The thermal properties (thermal diffusivity, a, specific heat capacity, C_p, and the thermal conductivity, λ) were measured using the modified flash method technique [16].

The samples were shaped into discs with diameter 1.5 cm and thickness of about 2 mm. The amplifier used was Yokogawa model 3031 and the y-t recorder was Linseis LY 14100-11.

2.3 Electrical and Irradiation Measurements

The ammeter-voltmeter method was used for measuring the d.c.electrical conductivity. The electrical conductivity σ was calculated by using the following equation:

The essential device in the circuit is a Keithley 485 autoranging picoammeter .The circuit was also interfaced with a computer in order to obtain the I-V characteristics for the samples under investigation. The a.c. conductivity and dielectric constant were obtained by using LCR bridge type Hioki 3531Z, Japan. All samples were thermally aged at 70 ^{o}C for 30 days before irradiation, to ensure their structure stability. A ^{60}Co gamma source model GB150 type B manufactured by the Atomic Energy Agency of Canada and located at the National Center for Radiation Research and Technology, A.E.A. was used for irradiating the samples at a dose rate of 9.23 kGy/h, and a constant temperature 30 ^{o}C.

Results and Discussions:

3.1 D.C. Conductivity

The electrical conductivity for these tested composites was observed to be in the insulating range (10^{-12} Ω^{-1} cm^{-1}) even on loading with filler. This may be due to either the elastomeric nature of SBR which causes segregation of the metal filler particles after molding [17], or the interfacial effects between metals and polymers. The temperature dependence of conductivity (log σ versus 1/T) for samples containing different metallic fillers ratios is shown in Fig. (1). The distinct feature which is evident from Fig. (1) is that, in general, the conductivity increases with increasing temperature, thus showing a positive coefficient of conductivity (PTCC) all over the investigated temperature range except for the S4 ,S5 and S6 samples with Cu /Fe ratios (50/50, 30/70 and 10/90). In these samples anomalous decrease of conductivity with increasing temperature (-ve TCC) takes place at different temperature ranges shifted to higher temperatures with increasing Fe content (330-363 K for S4, 340-374 K for S5 and 350-375 K for S6).

Two regions in the curves of Fig. (1) may be considered, region I (up to 345 K), and region II (T > 363 K).The activation energy (ΔU) for electrical conductivity has determined from this graph is seen to be in the range of 0.1 eV - 2.5 eV for I and 0.2 eV - 0.76eV for II. The value of (ΔU) in each of these regions depends on the filler concentration ratio.

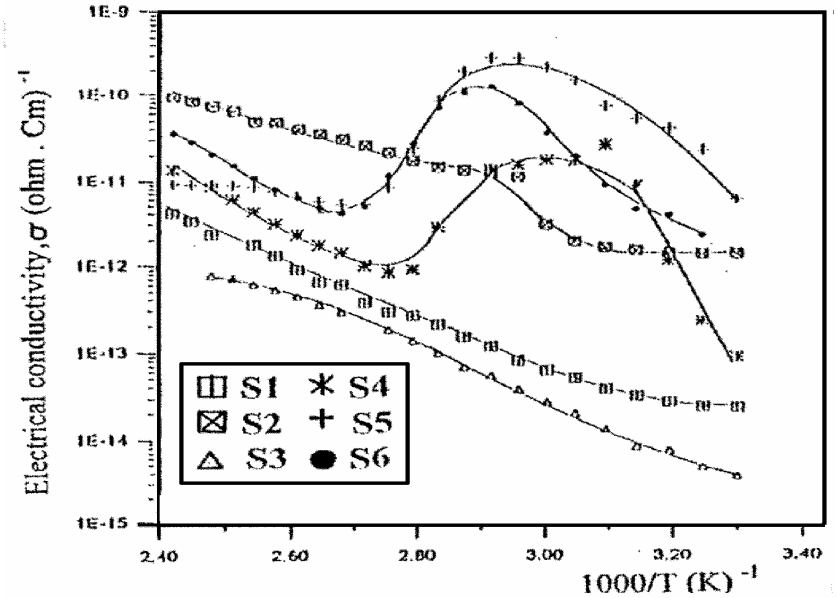

Fig. (1): The temperature dependence of the d.c. electrical conductivity for SBR samples loaded with different metallic filler (Fe/Cu) ratios.

The anomalous behaviour of conductivity detected as minima and maxima values ($\sigma_{min.}$ and $\sigma_{max.}$) in Fig.(1) might be due to the competition of two conduction mechanisms (the activated conduction mechanism and the hopping conduction one). The detected PTCC and NTCC for these composites consist with the suggestion that the interfacial phenomena control the temperature dependence of the conductivity behaviour of these composites[17].

3.2 Radiation Dose Dependence of the Electrical Properties

An appropriate method to detect different degrees of the filler dispersion in the rubber matrix is based on the measurements of the electrical conductivity of the rubber compound either with dc [18] or ac [19] mode. Figure (2 a-e) represent the dependence of the current density J as log J (Amp/m^2) versus the electric field E (Volt/m) at room temperature (30 ^oC) for all samples irradiated with different γ - doses. The dependence can readily be fitted to an empirical formula of the form [2]:

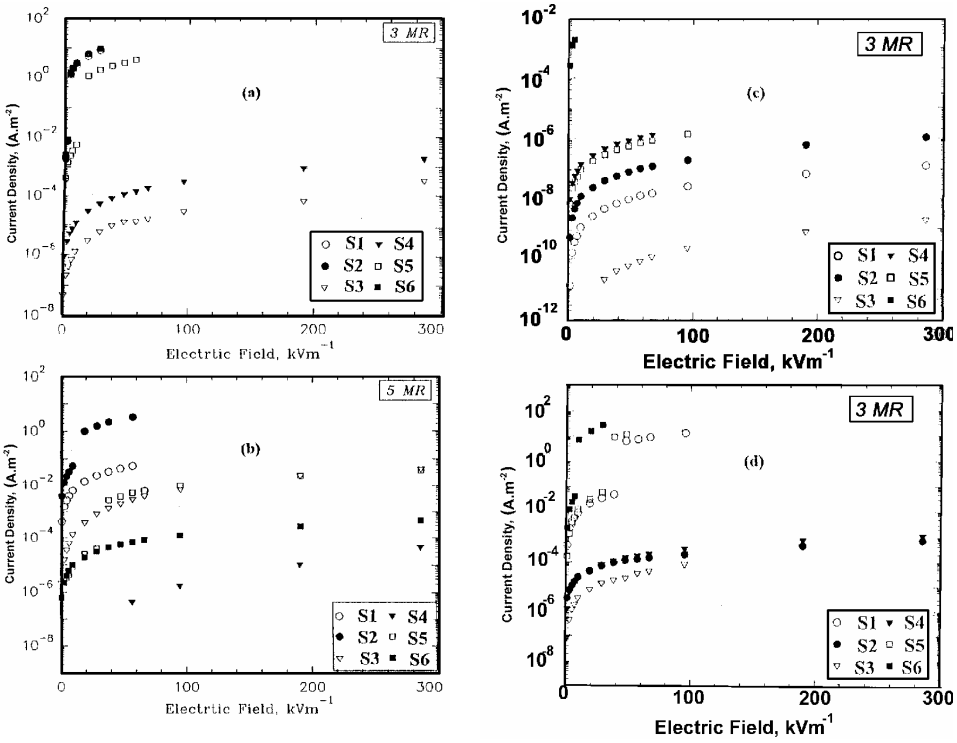

Fig. (2a-e): The current density-electric field characteristics for all samples irradiated with different γ-doses

$$J = J_o \sinh(\omega / 2kT)$$

where J_o is a fitting parameter that depends on both γ - dose and filler content in the SBR matrix , ω = deE, d , is the average separation distance between filler particles (Cu and/or Fe) , e is the electronic charge, k is the Boltzmann constant and T(K) is the ambient temperature. The estimated values of, d, could be obtained (by using the iterative method) from Fig. (2 a-e) and are tabulated in Table (2). The dependence of, d, on γ - dose is not quite the same for all samples , but an appreciable decrease in, d, was detected for most samples owing to the creation of free electrons by γ - dose in the filled SBR matrix.

Table (2): The interspacing distacne d between filler particles, and J_o for all samples irradiated with different γ- radiation doses.

Sample	γ-dose (M rad)	J_o (Amp.cm^{-2})	d(nm)
S1	3	8.5×10^{-3}	
	5	9.3×10^{-5}	
	10	2.5×10^{-6}	
S2	3	8.5×10^{-3}	1000
	5	2×15^{-3}	12
	10	2×10^{-6}	250
S3	3	5×10^{-6}	250
	5	10×10^{-6}	50
	10	2×10^{-8}	50
S4	3	8×10^{-8}	1450
	5	7×10^{-7}	1000
	10	5×10^{-6}	160
S5	3	8×10^{-1}	1760
	5	1×10^{-6}	500
	10	22×10^{-9}	60
S6	3	11×10^{-5}	800
	5	1×10^{-6}	8
	10	1.8×10^{-6}	16

In order to determine the charge transport mechanism, log J was re-plotted again versus the square root of the electric field $E^{1/2}$ as shown in Fig.(3).

This relation gave almost a linear behaviour at higher fields with an appreciable deviation from linearity at lower fields. This deviation. may be attributed to the accumulation of space charge at the electrodes [21].This linear variation between log J and $E^{1/2}$ suggests a conduction mechanism in which carriers can be released by thermal activation over a Coulombic potential

barrier that is decreased by the applied electric field [22]. The physical nature of such a potential barrier can be defined in terms of the slope value by one of two basic effects. It can be considered as a transition of electrons over the barrier between cathode and dielectric (Schottky effect). Alternatively, charge carriers can be released due to ionization of impurity centers in the dielectric (Poole- Frenkel effect). The conductivity σ is therefore given as;

$$\sigma = \sigma_o \quad \exp (\beta E^{1/2} / KT$$

where σ_o is the low field conductivity and β is a constant denoted as β_{RS} (for Schottkey effect) or β_{PF} (for Poole -Frenkle effect).

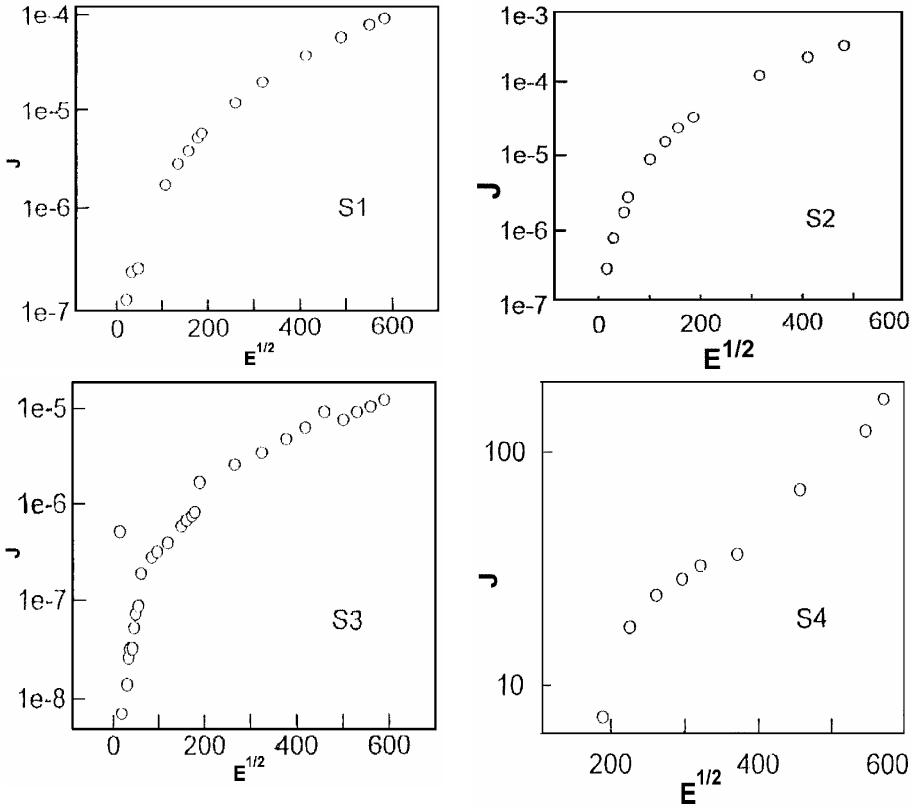

Fig. (3): Variation of log J with the square root of the electric field for all samples.

To determine the operating conduction mechanism, the values of β for samples with different γ - doses deduced from the slopes of the plots of log J against $E^{1/2}$ (Fig .4 for S4 as an example) are compared with the theoretical value the deduced from:

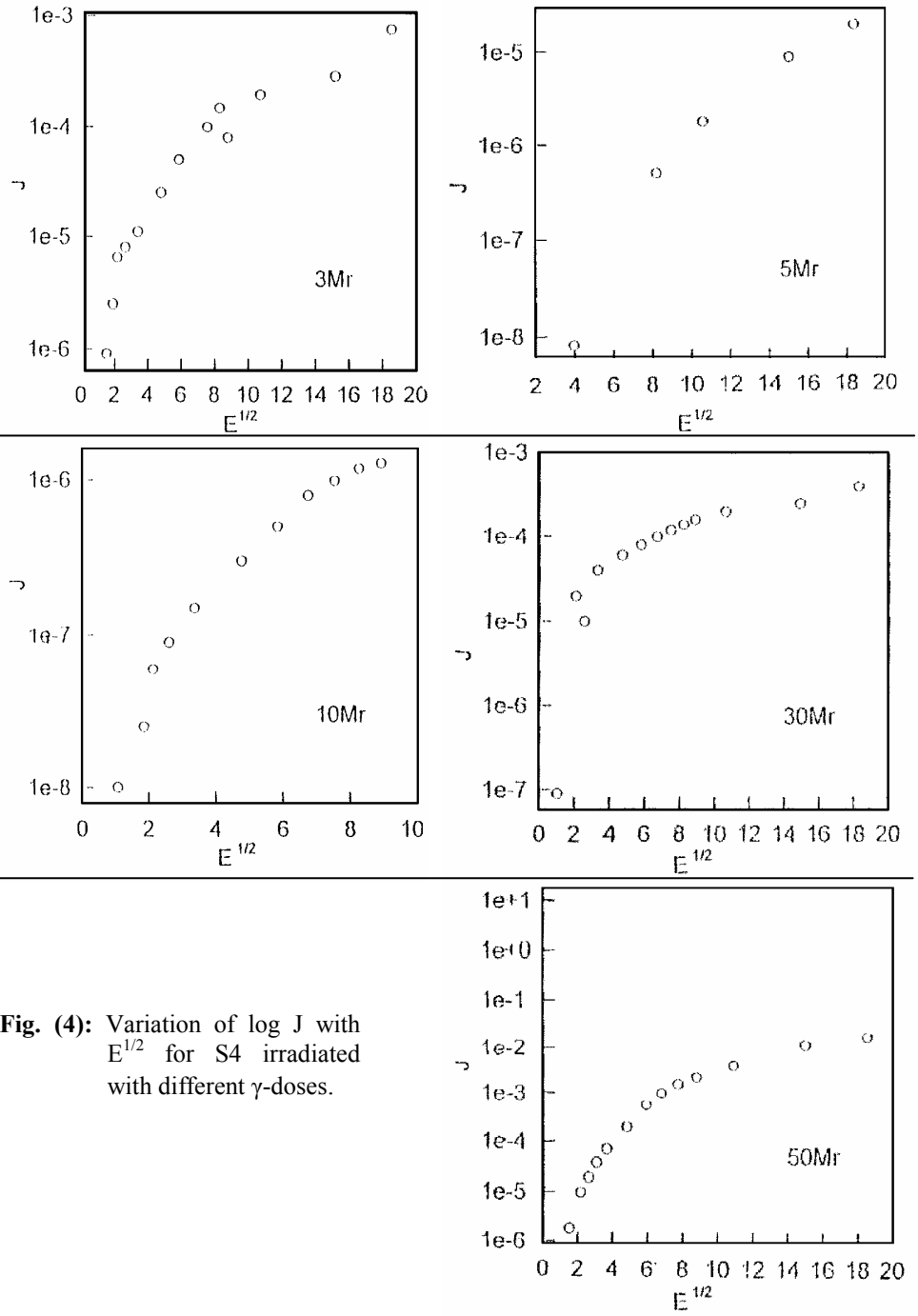

Fig. (4): Variation of log J with $E^{1/2}$ for S4 irradiated with different γ-doses.

$$\beta_{PF} = 2\ \beta_{RS} = 2\ (e / 4\pi\varepsilon\varepsilon_o)^{1/2} \quad (4)$$

where ε is the dielectric constant values of the samples that tabulated in Table (3) together with β values. The experimental value of β is in good agreement with β_{PF}. It may therefore be concluded that the Poole-Frenkel type of conduction mechanism is dominant in these samples even with γ - irradiation dose.

Table (3): The dielectric constant ε , and both the theortical and experimental β values for: (A) unirradiated samples .

Sample	ε measured	β_{PF} Theoretical $\times 10^{-5}$	β exp $\times 10^{-5}$
S1	14	2.03	2.0
S2	21	1.65	1.7
S3	13	2.1	2.2
S4	10.5	2.34	2.3
S5	20.0	1.69	1.6
S6	19.0	1.74	2.0

(B) For sample S4 at different γ- irradiation dose.

γ-dose Mrad	ε measured	β_{PF} Theoretical$\times 10^{-5}$	β exp $\times 10^{-5}$
3	10.5	2.34	2.3
5	14.7	2.0	1.98
10	7.7	2.75	2.73
30	24.9	1.52	1.3
50	25.0	1.5	1.16

The effect of gamma rays on the electrical conductivity of the investigated compounds is calculated with respect to six different doses 0, 30, 50, 100, 300 and 500 kGy at room temperature. From Fig. (5a,b), it is clear that at room temperature, the value of σ for unloaded SBR (S_1), initially, increased to approximately 10^{10} times its value upon irradiation by 30 kGy γ - dose and then decreased till < 100 kGy γ - dose. On the other hand,the values of σ for SBR loaded with mixed ratio of Cu and Fe fine powder showed an undulatory behavior with γ - dose. It may be presumed that the action of γ - rays on polymer, results in excitation of its molecules and creation of free electrons and ions [4]. Moreover, the filler particles were ionized by the action of gamma ray. These electrons and ions migrate through the polymer network till they are trapped leaving deficient regions. These induced electronic and ionic configurations cause the changes in the electrical properties of polymeric materials.

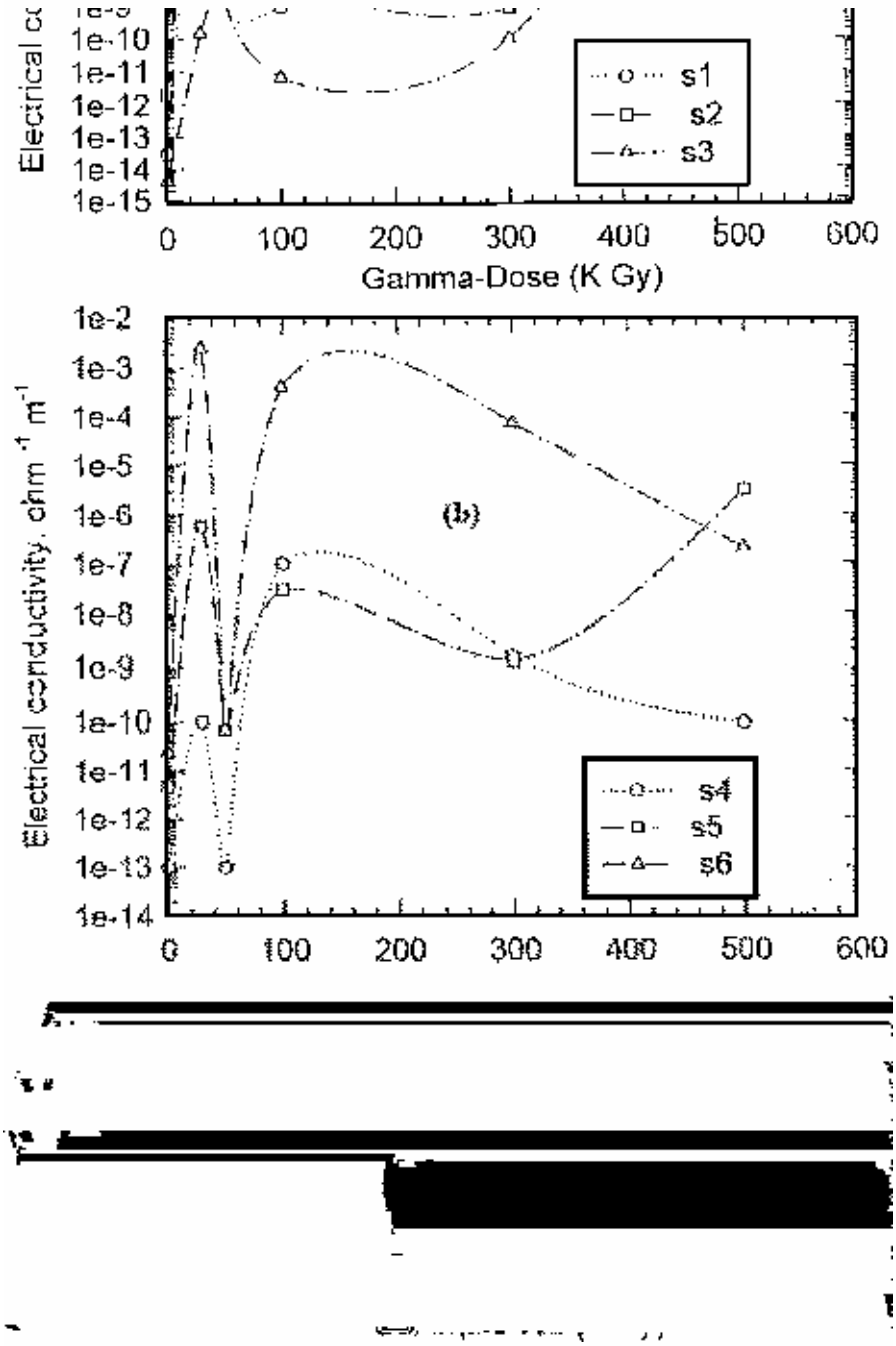

Fig. (5a,b): Variation of the d.c. electrical conductivity of SBR loaded with metallic filler ratios with γ-dose.

At a relatively high irradiation dose > 300 kGy there is an appreciable increase in σ (for S2 and S3) as a result of the increased crosslinking affected by the metal powder content. The two processes of degradation and crosslinking alternatively occur for the loaded SBR samples. The detected decreasing behaviour in σ_{dc} up to 100 kGy (S2 and S3) and up to 50 kGy (S4, S5 and S6) is mainly due to the dissociation of C-C and C-H bonds that leads to degradation process by which the separation between metal fine particles increases. For a dose greater than 300 kGy, the crosslinking process takes place leading to a close contact between metal fine powder which in turn causes an increase in σ_{dc} as it was detected for samples S_2, S_3 and S_5. Meanwhile, the de-agglomeration of Cu metal powder aggregation takes place at 100 kGy, for samples S_4 and S_6 which contain mixed ratio 50:50 and 10:90 of Cu:Fe metal powders, respectively.

3.1 Thermal properties of irradiated SBR loaded samples

As a rule, crosslinking and degradation occur simultaneously. However, the ratio of their rates depends on the chemical structure of the polymer, its physical state and the irradiation conditions [23].

Figure (6a-c) represent the dependence of the thermal properties (thermal diffusivity, a, specific heat C_p and thermal conductivity λ) on the filler content (Cu and Fe) at different γ - dose. The addition of filler powder (Fe and/or Cu) at different gamma doses (10-300 kGy), decreases both λ and C as shown in Fig. (6 b, c) owing to the increasing of phonon scattering. This effect could be due to both the liberation of scattered electrons from the metal atoms and/or the increased crosslinking density upon irradiation. This in turn decreases the transmittance of the thermal vibrations owing to the initially decreased distance between macromolecular lattice. Fig. (6a) represents the filler dependence of the thermal diffusivity of SBR composites at different γ - doses. The general features of these trends could be summarized as follows:

- Thermal diffusivity, a, decreases with increasing γ - dose (in the dose range 0 – 300 kGy) for sample loaded with Fe ≥ 30 phr.
- Thermal diffusivity, a, has a descending behavior with the filler ratio in the SBR composites at (30 -70) kGy γ - dose.

It might be concluded that the addition of Fe and /or Cu metal powders do not contribute well to the thermal diffusivity values and in addition, it lowered both λ and C_p for these SBR composites in the cocentration range (0-50 phr).

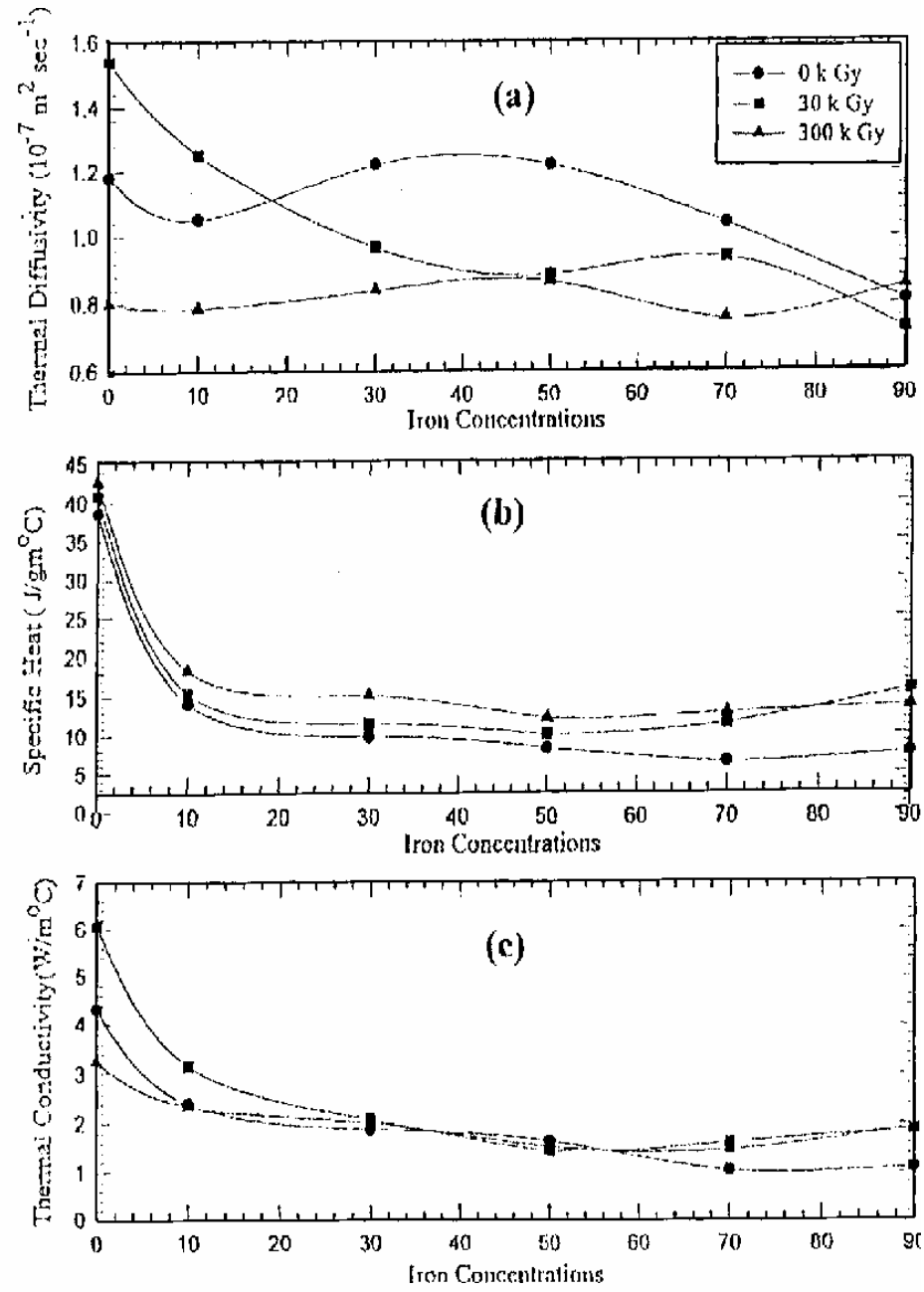

Fig.(6a,b,c): The dependence of (a) thermal diffusivity a,
(b) specific heat Cp and (c) thermal conductivity λ on the metallic filler ratios in samples irradiated with different γ-doses

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