

Styrene–Butadiene Rubber/Lead Oxide Composites as Gamma Radiation Shields

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SYNOPSIS

Composites of styrene–butadiene rubber were prepared with three different types of lead oxide, namely, monolead oxide (PbO), lead dioxide (PbO₂), and red lead oxide (Pb₃O₄). Concentrations of Pb₃O₄ ranging between 17 and 88 wt % were utilized, whereas 87 wt % was used for PbO and PbO₂. The prepared composites were investigated for their gamma radiation shielding properties. Moreover, physical and mechanical properties, and electrical conductivity were measured for both the unirradiated and irradiated composites. The highest value obtained for the linear absorption coefficient was 0.424 cm⁻¹ for 88% Pb₃O₄.

INTRODUCTION

Lead is the most common shielding material used to protect against γ - and X-rays. However, the presence of a rapidly changing magnetic field, which induces eddy current in a conductor, makes the use of ordinary metallic lead unacceptable.¹ Therefore, it is sometimes desirable that the shielding material should be an electric nonconductor. This requirement may be satisfied by using various combinations of metal powders in a polymer matrix.²

Polymeric composites containing various amounts of inorganic additives were previously prepared by other investigators^{3–9} for the purpose of studying their shielding properties toward γ -radiation. The additives may be any of the appropriate high-electron density materials such as lead oxides, lead silicate, lead sulfide, etc., dispersed in a plastic matrix¹⁰ or materials containing lead acrylate.¹¹ In addition, molten sulfur was used to form shielding materials when loaded with iron oxide and lead oxide.¹² An effective filler must have high shielding effectiveness against gamma rays and yet will not conduct electric current so that it may be used close to the target zone of an electron accelerator.

The purpose of the present work is to prepare

various styrene-butadiene rubber/lead oxides composites as gamma radiation shielding materials and to study the effect of these oxides on the chemical, physical, electrical and mechanical properties of the produced composites as well as their capabilities as shielding materials.

EXPERIMENTAL

Materials and Chemicals

Styrene–butadiene rubber (SBR-1502, from Good-year Tire and Rubber Company) was investigated. Monolead oxide (PbO), lead–dioxide (PbO₂), and red lead oxide (Pb₃O₄) were used as filler. Part of these oxides were surface modified and mixed at various concentrations with the following recipe:

SBR-1502	100 parts
HAF-carbon black	20 parts
Zinc oxide	5 parts
Stearic acid	1 part
PBN (antioxidant)	1 part
Sulphur	2.5 parts
MBT (accelerator)	2 parts

Except for specific samples of lead oxide, all chemicals in this recipe were of commercial grade and used without modification or further treatment.

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TECHNIQUES

Surface Modification of Filler

The surface modification of the lead oxides was carried out by the adsorption of different concentrations of stearic acid in benzene. The adsorbed amounts increased with equilibrium concentration to saturation. This point represent the formation of a monolayer on the surface. The time necessary to attain complete adsorption was about 48 h.¹³

Mixing

All rubber mixes were prepared on a two roll mill 170 mm diameter, with a working distance of 300 mm and RPM ratio of 1 : 1.4. The time of mastication was controlled by measuring the intrinsic viscosity of the raw rubber. The average time was 5 min.¹⁴ The ingredients were then added in the following sequence: fillers, lubricant, antioxidant, sulfur, and finally the accelerator.

Sample Preparation

The masticated sheets were cut into slabs and then compression molded at 141°C and 6 MPa for about 20 min.¹⁵ The thickness of the sheet was 2 mm.

Irradiation Procedure

A cobalt-60 source (Gammacell-40GS 6500), manufactured by the Atomic Energy of Canada, was used for irradiation. The dose rate used was about 25 kGy/h. The specimens were irradiated to a dose of about 30 kGy under atmospheric conditions and inside a special container. A rectangular lead box with dimensions of 120 × 120 × 160 mm was used as a sample container. The container was bored at the center of the upper face as a cylinder (35 mm diameter and 120 mm depth) in which the sample was put and subjected to the gamma radiation.

Radiation Dose Measurement

The gamma ray attenuation coefficients were determined by using red perspex dosimeter type 4034 L. The samples were cut with dimensions equal to those of the red perspex dosimeter (10 × 30 mm) and a thickness of 4 mm. Two film dosimeters were fixed in front and behind each sample and then surrounded with a metallic lead disk holder (with an outer diameter of 35 mm and 10 mm height) before insertion in the lead container for irradiation. The

opening of the cell container was placed facing the plaque source of the irradiator. The samples were placed at a distance of 100 cm from the ⁶⁰Co source. These conditions as well as the system geometry were proposed to avoid scattered radiation reaching the detectors.

Optical density measurements of unirradiated and irradiated dosimeter films were carried out by using a Pye Unicam model SP 200 UV-VIS, spectrophotometer, at 640 cm⁻¹.

Mechanical Properties

Mechanical properties of the specimen were tested by using an Instron tensile machine model 1195 and according to the standard test method.¹⁶

Swelling Number (SN) Determination

SN determination was carried out volumetrically by using a Swallowmeter and dried benzene containing phenyl-β-naphthylamine at 25°C. The measurements were carried out after 24 h.¹⁵

Electrical Properties

The electrical conductivity was measured indirectly by using the method described by Own¹⁷ which is based on the measurement of the resistivity. The relatively high resistance of the composite samples was measured by using a Multi Mega Ohm meter type MOM11 and a measuring cell ODW2 (WTW Co., W. Germany).

We have taken the different kinds of oxides to find out whether the nature of the oxides has any effect on its shielding properties.

RESULTS AND DISCUSSION

Attenuation Coefficients of Gamma Rays in Different Materials

The attenuation resulting from the interactions of γ-photons with matter is expressed quantitatively in terms of a linear attenuation coefficient μ (cm⁻¹), which is a measure of the probability of an interaction per unit distance through the matter and is given by the relationship¹⁸

$$D_i = D_0 e^{-\mu x}$$

where D_0 represents the dose of incident radiation on the absorbing material, and D_i represents the dose of radiation passing through a thickness x (cm). Other calculated properties describing radiation attenuation are: μ/ρ (cm^2/g) is the mass attenuation coefficient, and is usually independent of the density (ρ) and the physical state of the absorbing material and the half value layer (HVL) defined as $(\ln 2)/\mu$.

The values of μ , μ/ρ , and the half value layer HVL for ^{60}Co gamma radiation in the rubber composites are given in Table I as well as Figures 1 and 2. The results show that the value of μ of the rubber composites increased and their HVL decreased as the volume concentration of the lead oxide in the composites increased.

Figure 1 shows that, initially, the values of μ increased sharply with lead oxide up to a saturation volume of 5.6 vol % oxide. When the filler content exceeded 6 vol %, the rate of increase in μ diminished by almost a factor of 18. From this figure we see two distinct regions, a filler-diluted region and a filler-concentrated region. A concentration of 5.6 vol % oxide is found to be a critical volume, where photon attenuation parameters change from a matrix-predominant to a filler-predominant values, and this is because of the sensitivity of μ to the lead content in the samples. This becomes clear if we consider the variation of μ with the volume fraction of metallic lead content, in samples containing different lead

oxides in the same rubber recipes, as shown in the figure. These μ values extrapolate linearly down to the matrix value in the first region. Similarly, in the high filler concentration region, the μ values represent an oxide diluted by a rubber matrix and, therefore, extrapolate to the lead value at 100 vol % Pb.

We note from Table I that the values of μ of the matrix (SBR) as well as the filled composites are superior to the values of concrete and water^{19,20} for the same ^{60}Co energy. This relatively high resistance to radiation is believed to be partially due to the presence of the benzene rings in the styrene segments of the rubber molecule which dissipates much of the energy received.²¹

Figure 2, shows the mass attenuation coefficient as a function of oxide and of Pb content in the composites. It appears to be generally independent of the filler content. A variation occurs at low vol % oxide where the mass attenuation coefficient was found to increase sharply with the Pb_3O_4 content producing a peak at 6 vol % filler. It is interesting to note that μ/ρ values plotted as a function of vol % Pb extrapolate linearly to the value for pure lead.

Physicomechanical Properties

The type and the concentration of the lead oxides used in these experiments are given in Table I. Some

Table I The Types and the Concentrations of the Lead Oxides Used and the Values of Attenuation Coefficients and Half Value Layer (HVL) for Co60 Gamma Rays in the Rubber Composites

Sample No.	Density d (g/cm^3)	Types of Filler	Filler Concn (wt %)	Metal Content (wt %) ^a	Filler Concn (vol %)	Metal Content (vol %)	μ (cm^{-1})	μ/d (cm^2/g)	HVL (cm)
1	1.063	None	0	0	0	0	0.143	0.134	4.86
2	1.265	Pb_3O_4	17	15.4	2.4	1.7	0.238	0.188	2.91
4	1.335	Pb_3O_4	38.1	34.5	5.6	4.9	0.346	0.259	2
4 ^b	1.335	Pb_3O_4	38.1	34.5	5.6	4.9	0.37	0.277	1.87
8	3.59	Pb_3O_4	77.4	70.1	30.5	20.9	0.393	0.109	1.76
9 ^b	4.73	Pb_3O_4	87.7	79.5	45.6	33.2	0.424	0.09	1.63
10 ^b	5.14	PbO	87.4	80.7	47.2	34.1	0.401	0.078	1.73
11 ^b	4.33	PbO_2	87.5	75.8	40.4	31.6	0.409	0.094	1.69
Lead ^c	11.34						0.674	0.059	1.03
Water ^c	1						0.064	0.058	5.13
Concrete ^c	2.34						0.135	0.058	5.13
Air ^c	0.00129						0.000074	0.058	9370
	at NTP								

^a Metal content in the composite (wt %).

^b Surface modified.

^c Sources: Refs. 19 and 20.

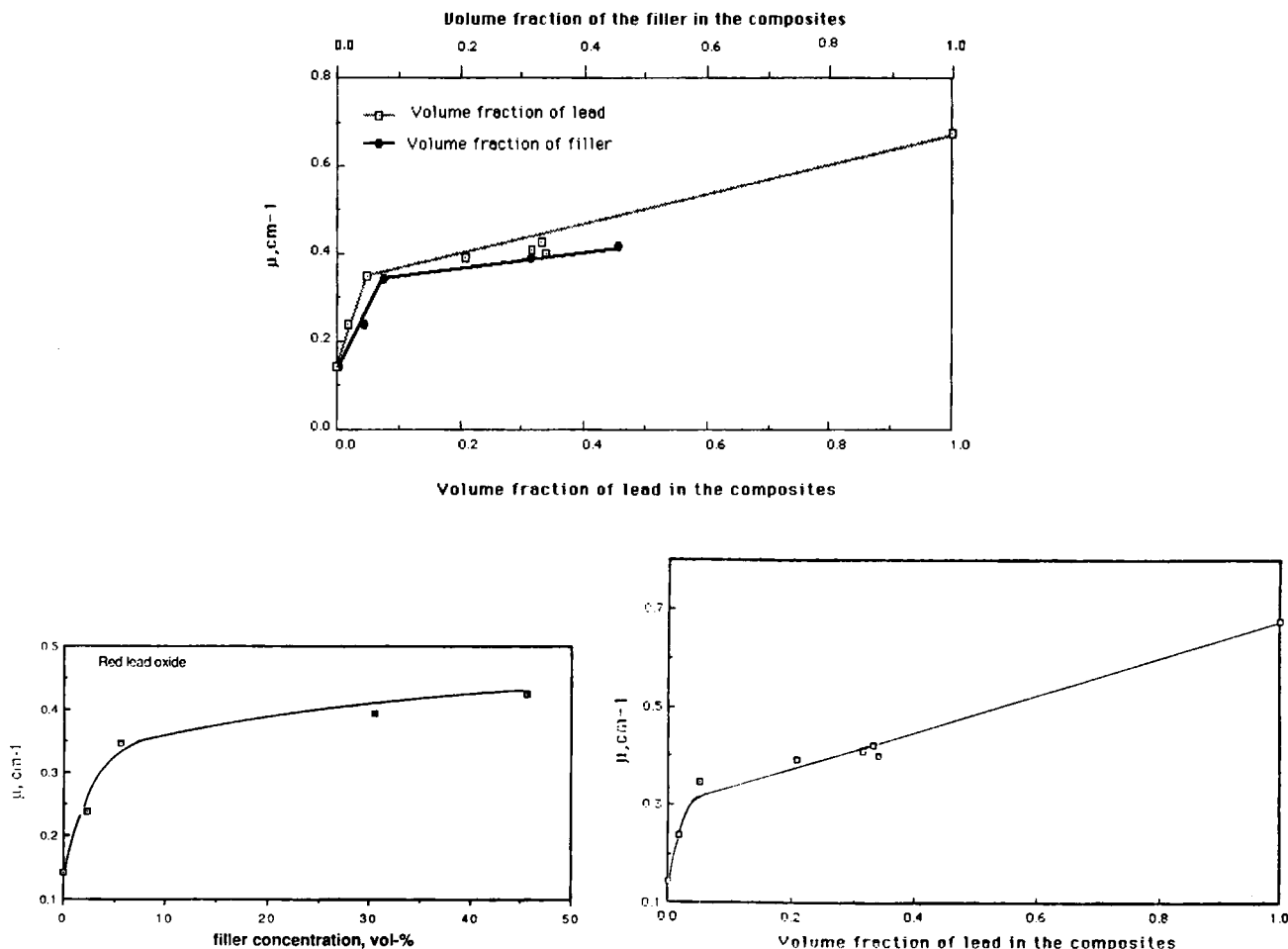


Figure 1 The linear absorption coefficient of the composites as a function of the lead oxide as well as the lead contents.

of each oxide sample was surface modified prior to their incorporation into the rubber matrix without changing the matrix recipe. In this modification, the surface of the oxide was coated with stearic acid to increase the compatibility between the inorganic oxide and the organic rubber. This modification is expected to enhance the physico-mechanical properties of the rubber composites. Figures 3–5 show the tensile strength (TS), the elongation at break (E) and the swelling number (SN) as a function of the filler loading in the rubber before and after irradiation. All these properties show the same trend. They decrease as the vol % of the filler increases with a faster drop in these properties below 6 vol % filler. It should be noted that the upper experimental loading level was 46 vol % (88 wt %) filler which could not be exceeded because of problems with dispersibility, processability of the rubber/filler mix-

tures, and serious loss of the rubbery characteristic of the composites. At this maximum loading, the filled rubber still retained 200–300% elongation, but its strength was reduced to half the unfilled value. It is expected that the incorporation of a particulate filler will result in the noted reduction in strength and elongation. Particulate fillers do not carry mechanical load and create defects within the matrix which result in stress concentration and molecular separation at the filler matrix interface. This molecular separation may also reduce the effectiveness of crosslinking in the interfacial region. When these samples were exposed to γ -radiation (a dose of 30 kGy), an increase of about 7% in strength and a reduction of about 20% in elongation were observed. This effect is due in part to an increase in the crosslink density with dose. It is interesting to note that the reduction in strength at low volume fraction of

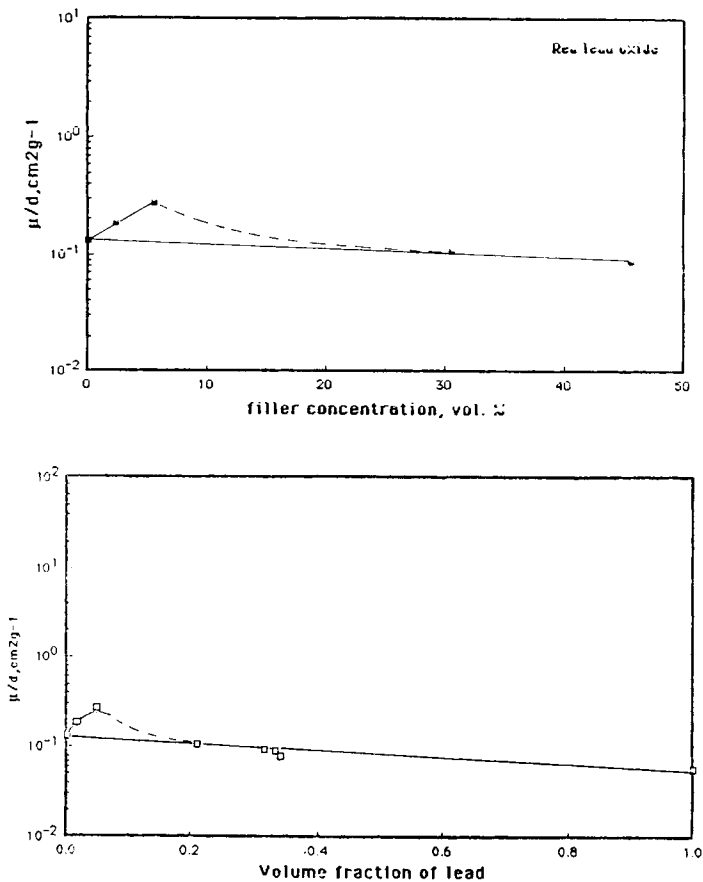


Figure 2 The mass attenuation coefficient as a function of filler content and the lead metal content in the composites.

filler ($V_f < 0.1$) is below the calculated values using the composite law of mixtures when the load is carried solely by the matrix: $(TS)_{\text{composite}} = (TS)_m V_m$, where V_m is the volume fraction of the matrix. This

may be explained by variations in the distribution of the filler within the viscous matrix which is more pronounced at the lower concentrations. At higher loading, more mixing is used to insure sample ho-

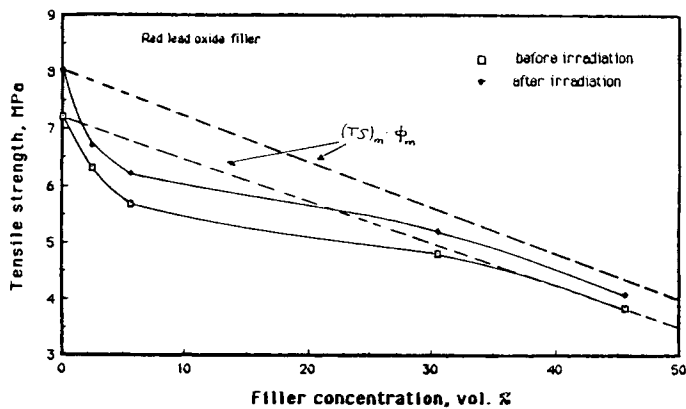


Figure 3 Tensile strength as a function of filler content in the composites.

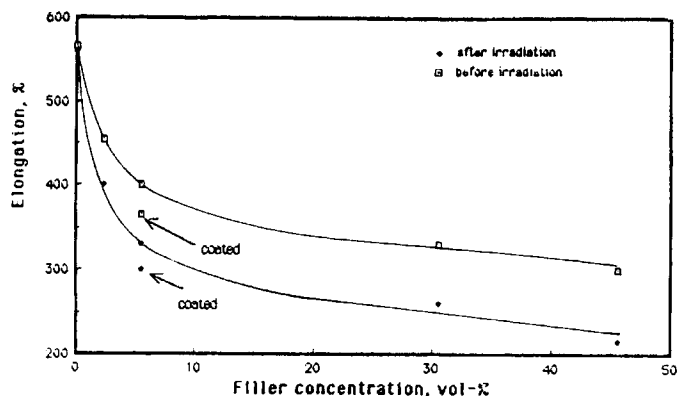


Figure 4 The elongation at break of the composites as a function of filler content.

mogeneity and, therefore, the TS was proportional to the calculated matrix contribution.

Figure 5 shows the change in swelling number (SN) with filler content. From the reduction in tensile strength with filler, it is expected that the SN will be increased. This, however, was not the case. The SN decreased sharply with vol % filler up to about 5 vol % and then continued to decrease with filler at a lower rate. Incorporation of filler particles resulted in a dramatic increase in the stiffness of the matrix. This stiffness increased the resistance of the matrix to deformation and hence reduced the SN. The results in Figure 6 also show that the effect of radiation crosslinking on the SN was not significant compared to the influence of the filler. An indication of sample stiffness may also be predicted from the values of the modulus as a function of filler content. Figure 6 shows the modulus, measured as the tensile strength at 300% elongation, versus the

filler content. It is apparent that a pronounced increase occurred initially up to a filler concentration of 6 vol %. This increase is in agreement with the previous results showing a sharp reduction in SN in the same range of filler concentration. This definition of modulus, however, is not a true measure of stiffness, (e.g., samples with 30 or 45 vol % filler were much stiffer and very difficult to mix compared to 5.6 vol % loading). This increase in stiffness is not shown in the almost constant values of the modulus between 6 and 45 vol % filler range and this may be attributed to the filler-rubber interaction rather than to rubber crosslinking.

The dependence of DC conductivity on filler concentration is illustrated in Figure 7. We note from this figure that the incorporation of oxide caused a slight increase in the conductivity of the stock material. We should, however, note that the incorporation of carbon black in the rubber stock caused

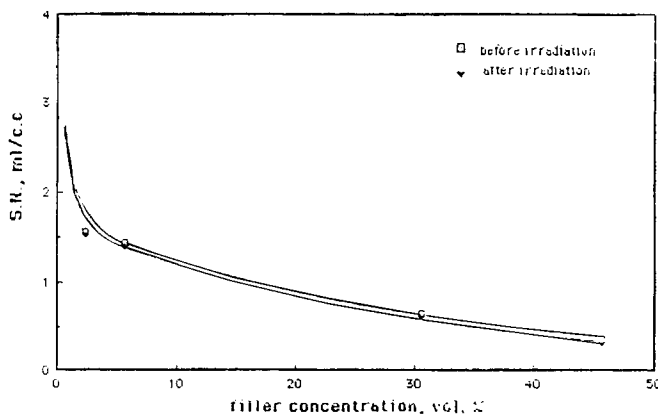


Figure 5 The swelling number of the composites (in benzene) as a function of filler content.

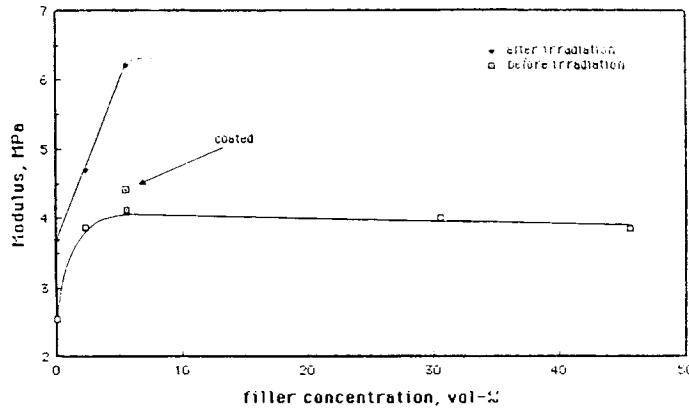


Figure 6 The modulus (at 300% elongation) as a function of filler content in the composites.

also an increase in conductivity which depends on the level of carbon black. When the oxide is added to that recipe, an initial decrease is noted due to the separation of the carbon black network. These changes, however, are not very significant since all the results are in the insulation range 10^{-14} – $10^{-15} (\Omega \text{ cm})^{-1}$. A correlation of conductivity with filler can be estimated as:

$$\sigma_{\text{composite}} = (0.01 + 0.045V_f + 2.34V_f^2 + 2.15V_f^3) 10^{-1} + 2.34V_f^2 + 2.15V_f^3) 10^{-1}$$

which is represented by the solid line in Figure 7. From these results a value of $\sigma_{\text{oxide}} = 4.5 \times 10^{-13} (\Omega \text{ cm})^{-1}$ can be predicted. We should note that a filler volume concentration of 6% gave a minimum conductivity which is a desirable property for the use of these composites in radiation shielding.

CONCLUSION

The SBR loaded with lead oxide powder can attain up to about 63% of the shielding capacity of pure lead. The nature of the oxide has no great significance on the shielding character of the composites. The advantages of the rubber filled system are the low density, the ease of fabrication into many products and shapes including personnel garments for use during radiotherapy and other isotope handling services. Another major advantage of these composites is the lack of radiation induced conductivity which is very desirable in shielding materials. The elasticity of the rubber composites at low filler loadings makes them readily conform to the shielded surface. The major feature of this work is the change in dependence of the absorption coefficient on the lead oxide concentration at about 6 vol %. At this volume of filler we can attain the maximum benefits

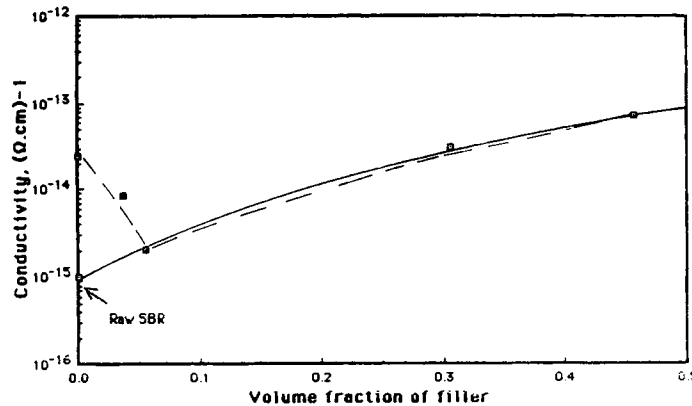


Figure 7 The electric conductivity of the composites as a function of the filler content.

from the incorporation with lead oxide without sacrificing the elasticity and strength of the material.

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