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Influence of Hydrostatic Pressure on the Electrical Conductivity of 100 phr* FEF Black-Loaded SBR with Different Concentration of Sulphur

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ABSTRACT

The effect of hydrostatic pressure on the electrical properties of conductive styrene butadiene rubber loaded with different concentrations of sulphur was elucidated. The separation distance between carbon black aggregates (calculated using an empirical formula) was found to be highly affected by hydrostatic pressure. Meanwhile, the conductivity of such composites was found to rise with pre-compression owing to both the change in contact resistance between adjacent carbon black aggregates in the rubber, softening and molecular orientation.

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* phr: part per hundred parts by weight of rubber

INTRODUCTION

Rubber is very poor conductor of electricity and any conductivity it does possess is due to additives, such as carbon black. The correlation between the degree of dispersion and electrical conductivity is very high, so, it is considered one of the current methods to determine the degree of dispersion of filler within the rubber compound.

One of the best methods of determining the degree of dispersion of a filler (blacks and others) within a rubber compound is the measurement of its electrical conductivity under different conditions. The hydrostatic pressure is known to have a profound influence on the development of structure and properties of polymers. A number of investigators$^{(1-4)}$ have reported the effects of pressure on compressibility, crystallization behaviour, and, glass and melting transitions.

Sulphur$^{(5)}$ is the principal vulcanizing agent used with natural rubber as well as the butadiene and isoprene polymers and copolymers.

It was pointed out$^{(6)}$ that SBR vulcanizates increase continuously in tensile strength and decrease continuously in elongation as the sulphur content is increased from 2.5 through 35%.

The D.C. conductivity measurement of poly (paraphenylene) obtained under compaction pressure, were correlated to the structural modifications undergone in the same pressure range$^{(7)}$. It was concluded that pressure could have a double effect on the chain hopping: on one hand, it may favour the phenomenon by approaching the chains, or it could oppose such hopping by increasing the interchain paracrystalline disorder. The balance of these two competing effects leads to a nearly equivalent situation, so that the conductivity does not appreciably change.

The effect of sulphur concentration on the electrical conductivity of SBR vulcanizates was studies in previous work by our group$^{(8)}$. It was found that, the optimum concentration of sulphur, which gives both good mechanical and electrical properties was found to be 2 phr. More than 2 phr gives better swelling resistance composites, but with poor mechanical properties.

The present work aims to elucidate the effect of hydrostatic pressure on the electrical conductivity of conductive SBR loaded with different concentrations of sulphur.

EXPERIMENTAL WORK

The sample properties depend markedly on the method of preparation(9), so, it is important that all samples should pass the same procedure under the same conditions (as described elsewhere(10)). Different concentrations of sulphur were introduced in SBR loaded with 100 phr FEF carbon black according to the formulation illustrate in Table 1. The rubber vulcanization was conducted at 143 ± 2 °C under a pressure of about 40 kg/cm^2 for 20 minutes, to insure stable properties without affecting the electrical one(11,12).

A simple device was used to carry out the measurements of D.C. conductivity, while the samples being under different amounts of pre-compression (hydrostatic pressure). This device is schematically represented in Fig. 1. The test specimen was put in contact with an insulated electrode fitted in a teflon pit. The other face of the specimen was kept in contact with a piston acting as the other electrode. The test specimens had the form of discs of radius 0.5 cm and thickness of about 0.25 cm. In the case of low current measurements, a D.C. Keithly Electrometer type D.C. 616 (U.S.A.) was employed. The power dissipated through the sample was not exceeded the value of 0.1 $Watt/cm^3$, in order to avoid the Joule heating.

RESULTS AND DISCUSSION

Investigations on the electrical properties of rubber composites constitute one of the most convenient methods of studying rubber structure. There are several factors which have appreciable effect on such structure and should be carefully studied. In particular, the influence of hydrostatic pressures one of these factors, the effect of which on the electrical properties of conductive SBR loaded with different concentrations of sulphur in two relevant parts, has been investigated.

1. Current Density - Electric Field Characteristics (J versus E):

Figure 2 represents the dependence of log J (Amp/cm^2) versus E (Volts/cm) at room temperature (about 30 °C). This dependence can readily be fitted to an empirical equation - over a limited values of E up to 400 Volts/cm - of the form

$$J = J_0 \sinh(\omega/2KT) \qquad (1)$$

where $\omega = aeE$, K is the Boltzmann's constant, T (K) is the ambient temperature, e is the effective elective electronic charge, a is the average separation distance between carbon aggregates and J_0 is a fitting parameter which depends on the concentration of sulphur.

An approximate estimated values of the separation distance (a) could be obtained by the iterative method from figure 2. Table 2 illustrates the dependence of the separation distance (a) and J_0 on the concentration of sulphur at zero pre-compression. The fact that the sample S2, which contains 2 phr sulphur, shows the highest characteristic could be ascribed to the optimum value of sulphur. Below this value the process of cross-linking is incomplete while above it there will be excess free sulphur.

The effect of pre-compression on the log J versus E curves for all samples (except S0) is illustrated in Figs. 3-5. The same behaviour of log J vs. E curves was detected for all samples and also obeys equation (1).

The separation distance (a) was found to be highly affected by pre-compression as it is clearly observed from Table 3 (for sample S3).

2. The Temperature Dependence of the Electrical Conductivity:

Styrene-butadiene rubber loaded with different concentrations of sulphur and 100 phr FEF carbon black were prepared and thermally aged at 70 °C for 40 days. This accelerated aging process created the chance for sulphur to continue the process of formulation of the carbon-sulphur carbon bridge(13) especially for higher sulphur concentration (S3). After aging, the obtained structure had fixed conductivity of carbon chains, which were formed during the aging process and lead to reasonable reproducibility in results(14).

Figures 6-9 show the effect of pre-compression on the temperature dependence of the electrical conductivity (σ) of 100 FEF/SBR vulcanizates loaded with different concentrations of sulphur (0, 1, 2 and 5 phr) respectively. The volume changes during processes of pre-compression for all samples did not exceed about 0.24%. On the other hand, the electrical conductivity was calculated using the original dimensions of the sample. The drop in conductivity with temperature, is a characteristic behaviour at high conductive compositions. For samples S2 and S3, a descending branch of conductivity consists of two parts was detected. At low temperature (< 50 °C), the conductivity is slightly dependent on temperature, and the vulcanizates show a metal-like conductivity; the conduction is mainly due to the direct contact between carbon aggregates. At higher temperature, however, there is a marked decrease in conductivity which is mainly due to the breakdown of the structure of carbon black aggregates and the high thermal expansion of rubber host material. At lower concentration of sulphur (< 2 phr), $\sigma(T)$ curves consist of only one part.

The general trend of the $\sigma(T)$ relations in Figs. 6-9 exhibit the high response of S1, S2 and S3 samples to the applied hydrostatic pressure. Actually, the thermally activated part of the conductivity for the sample

S3 has almost vanished at a compression of about 22.56 kg/cm^2. Meanwhile, the conductivity was found to rise owing to both the change in contact resistance between adjacent carbon particles in the rubber, and, softening and molecular orientation. At relatively high pressures (at about 28.82, 6.91 and 37.61 kg/cm^2 for S1, S2 and S3 respectively), the conductivity seems to be independent of temperature owing to the balance between the two previously mentioned competing mechanisms and the direct contact between the carbon particles.

Although vulcanization was conducted at twice the pressure applied during D.C. measurements no symptons of microvoids or other defects were detected even by using optical microscope.

Figure 10 represents the dependence of σ on the applied hydrostatic pressure for S1, S2 and S3 samples (at room temperature); it is obvious that the hydrostatic pressure increases the conductivity for all samples since carbon particles are forced into closer contact by the applied pressure.

Finally, one concluded that, for all vulcanized composites of 100 FEF/SBR loaded with different concentrations of sulphur, the conductivity - measured in the direction of compression - was found to rise with pressure due to the change in contact resistance between adjacent carbon particles in the rubber. The most sensitive sample to pre-compression was found to be S2 (which contains 2 phr of sulphur).

Table 1. The composition of SBR samples containing different concentrations of sulphur. Ingredients are arranged in the sequence of their addition.

Ingredients (phr)[(a)]	S0	S1	S2	S3
SBR	100	100	100	100
Stearic acid	2	2	2	2
FEF black	100	100	100	100
Processing oil	10	10	10	10
MBTS[(b)]	2	2	2	2
PBN[(c)]	1	1	1	1
Zinc oxide	5	5	5	5
Sulphur	-	-	2	5

(a) part per hundred parts by weight of rubber

(b) Dibenthiazyl disulfide

(c) Phenyl-β-naphthylamine

Table 2. The calculated values of the fitting parameters (a) and (J_0) (of equation (1) as a function of sulphur concentration, at zero pre-compression.

Sample	a (cm)	J_0 (Amp/cm^2)
S0	6.78×10^{-5}	5.5×10^{-3}
S1	1.75×10^{-5}	2.5×10^{-4}
S2	6.80×10^{-4}	3.0×10^{-3}
S3	1.03×10^{-5}	1.0×10^{-3}

Table 3. The dependence of the separation distance (a) on the hydrostatic pressure for sample S3 at about 30 °C.

Pressure (kg/cm^2)	a (cm) x 10^{-6}	J_0 (Amp/cm^2)
0	10.3	1.0×10^{-3}
4.5	47.3	1.5×10^{-4}
7.52	40.7	1.7×10^{-3}
10.53	47	2.5×10^{-4}
15.04	38.6	8.0×10^{-4}
22.56	53	2.5×10^{-3}
30.09	58.5	7×10^{-3}
37.61	51.5	2.1×10^{-2}

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FIGURE CAPTIONS

Figure 1: Schematic diagram for the device used to carry out the electrical conductivity measurements, for pre-compressed samples:

(A) Loads
(B) Pan
(C) Screw bolt (for clamping the piston)
(D) Container
(E) Oven
(F) Piston terminal
(G) Screw bolt
(H) Oil seal
(I) Specimen
(J) Teflon gasket
(K) Terminal
(L) Thermometer

Figure 2: Current density (J) versus electric field (E) characteristics for different composites at zero pre-compression and 30 °C.

Figures 3-5:
Dependence of log J versus E curves for S1, S2 and S3 samples on hydrostatic pressure at 30 °C.

Figures 6-9:
Temperature dependence of electrical conductivity (σ) for samples S0, S1, S2 and S3 at different hydrostatic pressure.

Figure 10: Dependence of the electrical conductivity (σ) for samples S0, S1, S2 and S3 on the hydrostatic pressure at 30 °C.

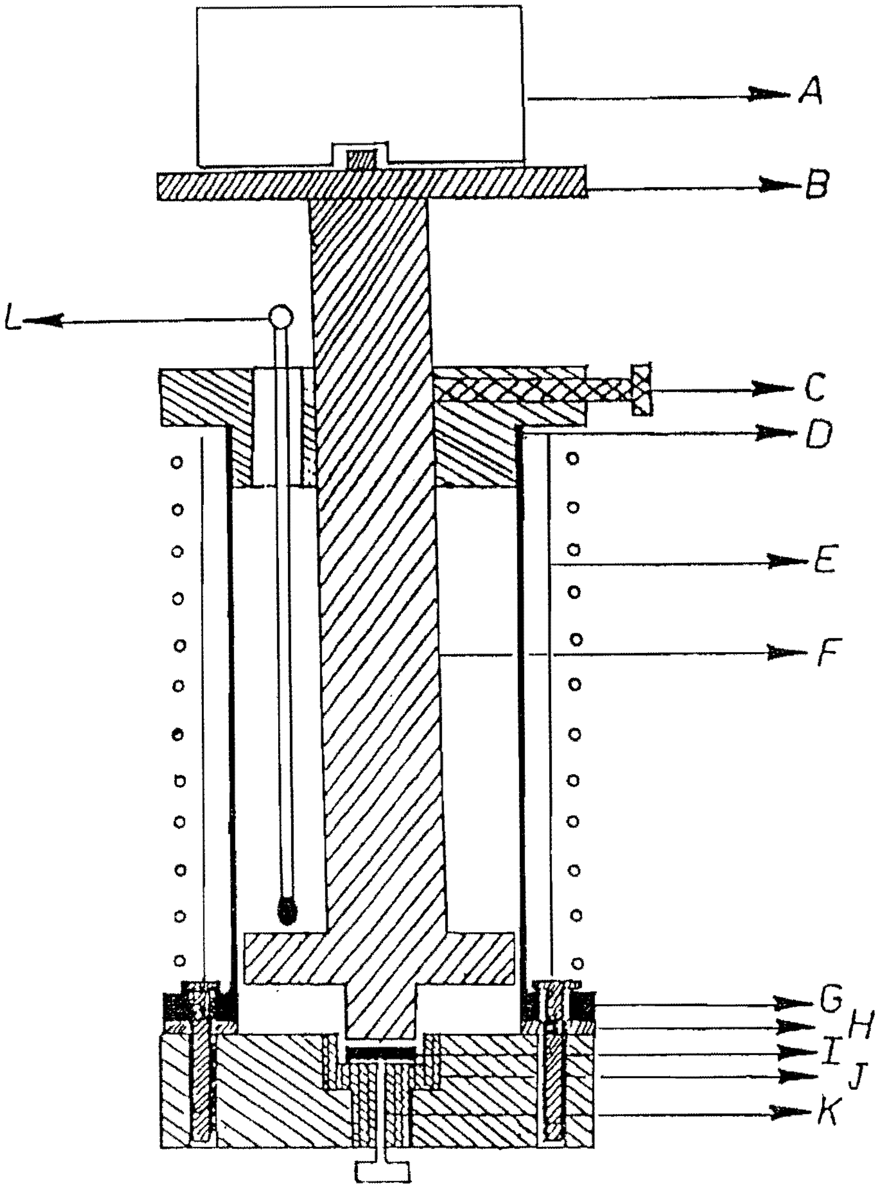

Figure (1) : Schematic diagram for the device used to carry out the electrical condutivity measurements, for pre-compressed samples .

(A)Loads (B)Pan

(C)Screw bolt (for clamping the piston)

(D) Container (E) Oven (F) Piston terminal

(G) Screw bolt (H) Oil seal (I) Specimen

(J)Teflon gasket (K) Terminal (L) Thermometer.

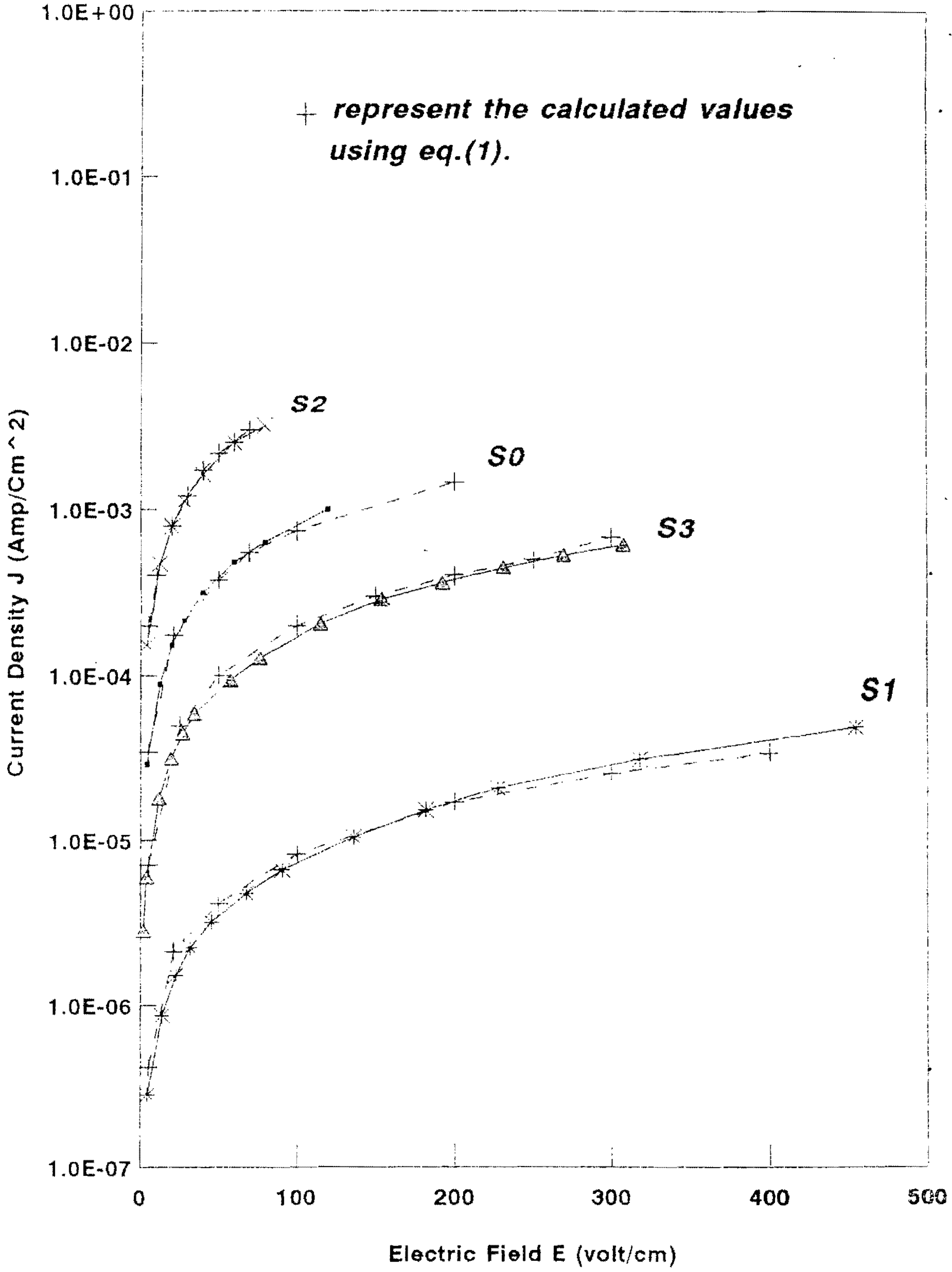

Figure (2) Current density J vs. electric field E curves for different composites at zero pressure.

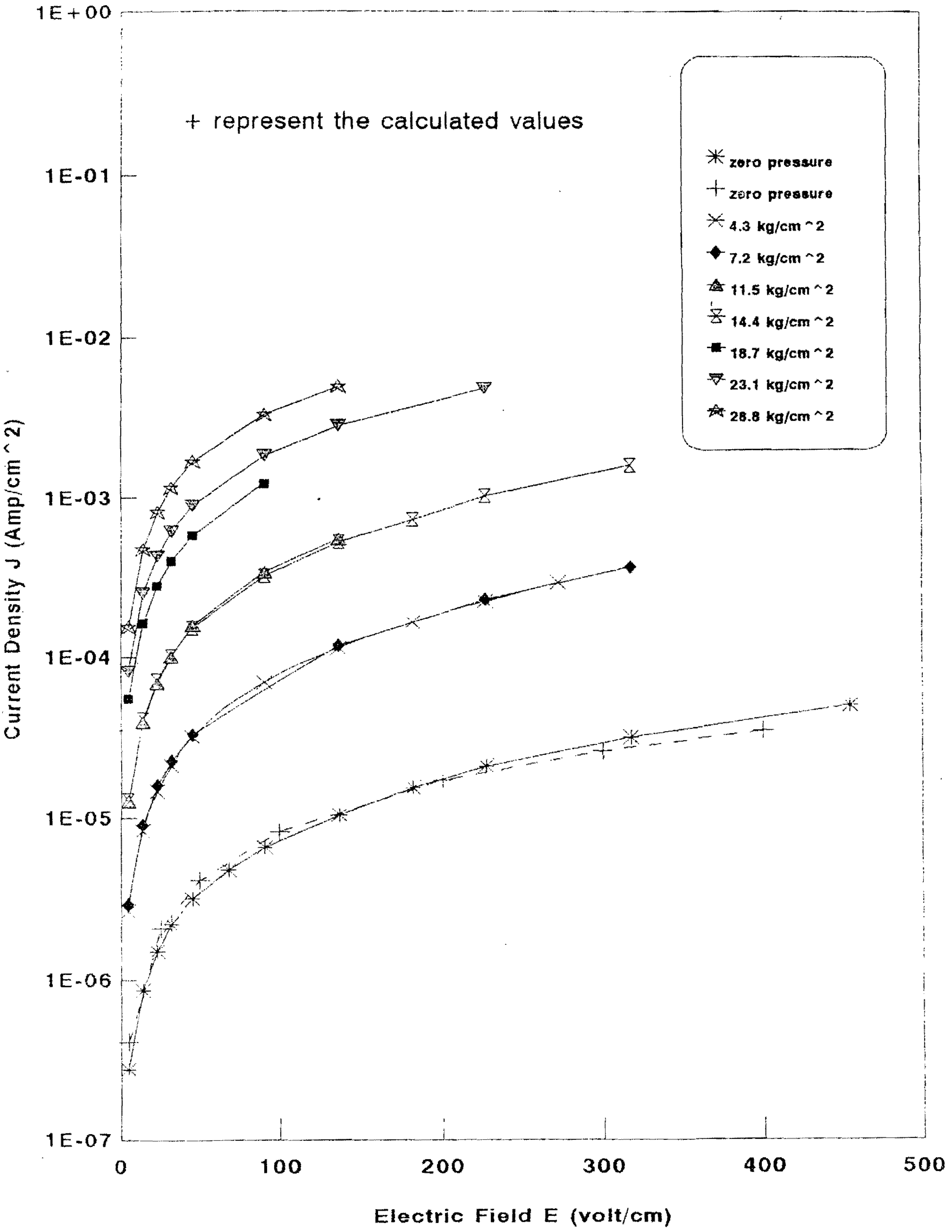

Figure (3) Dependence of log J vs. E curves on hydrostatic pressure for S1.

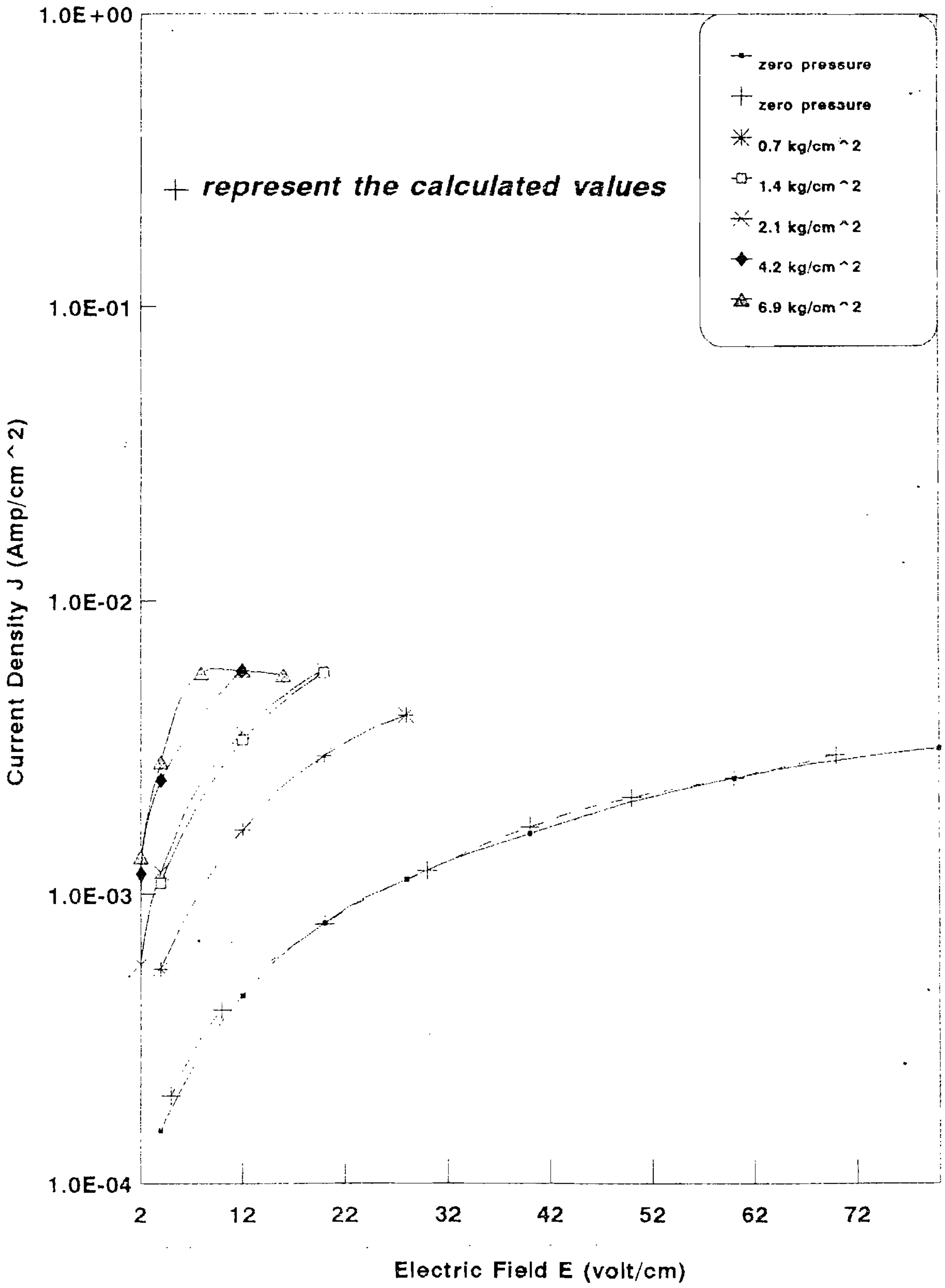

Figure (4) Dependence of log J vs. E curves on hydrostatic pressure for S2.

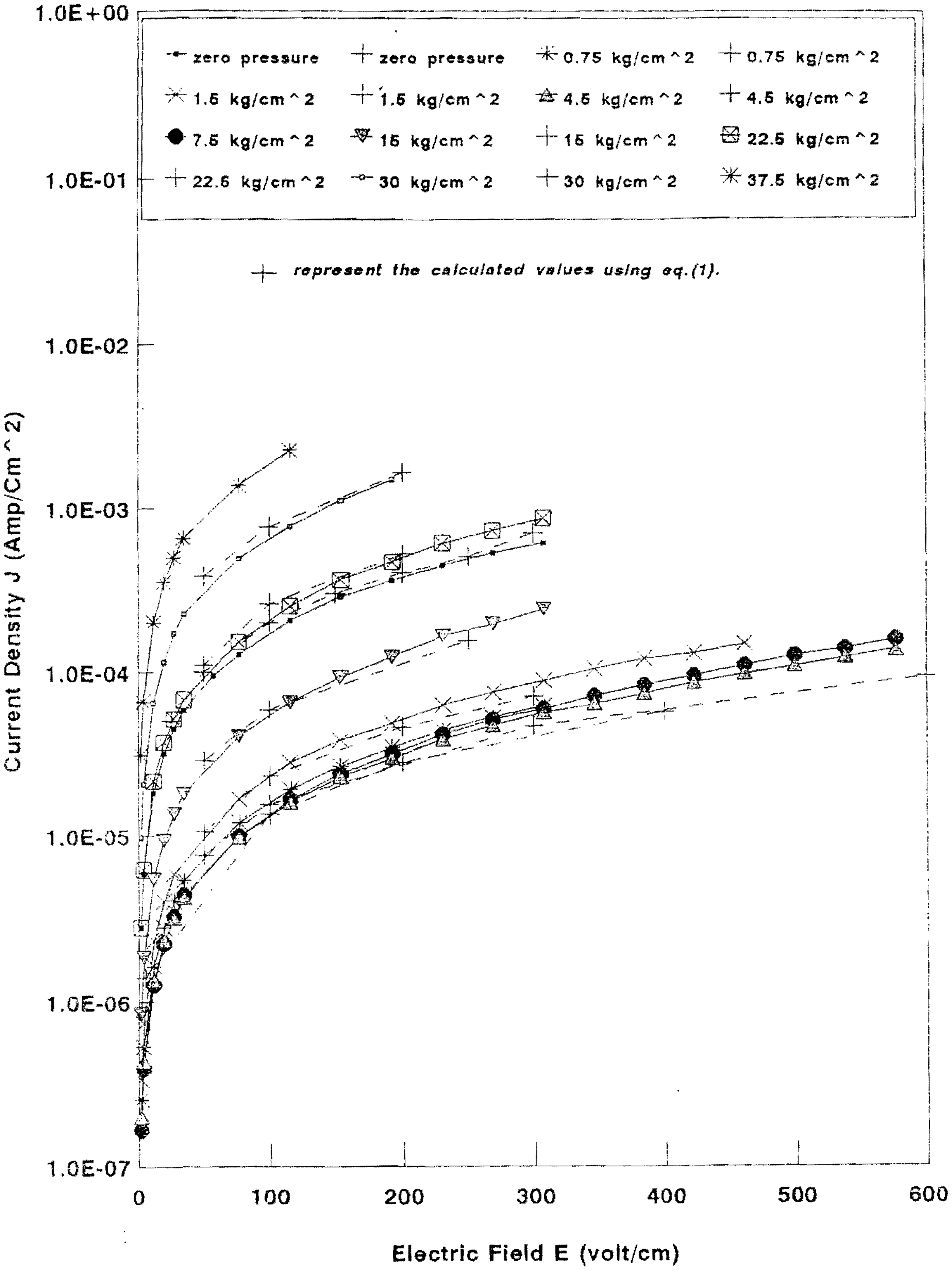

Figure (5) Dependence of log J vs. E curves on hydrostatic pressure for S3.

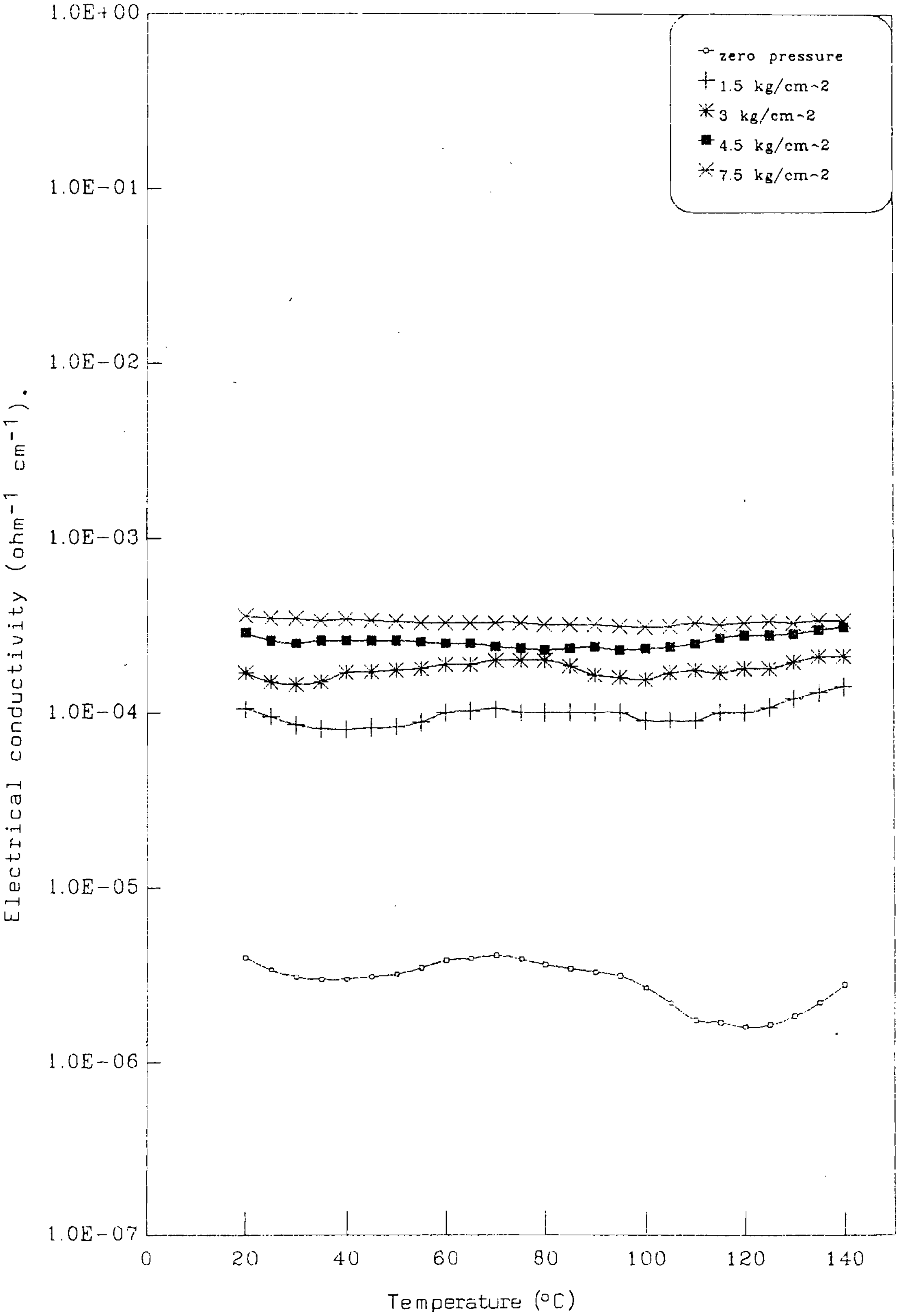

Figure (6) Temperature dependence of electrical conductivity for S0.

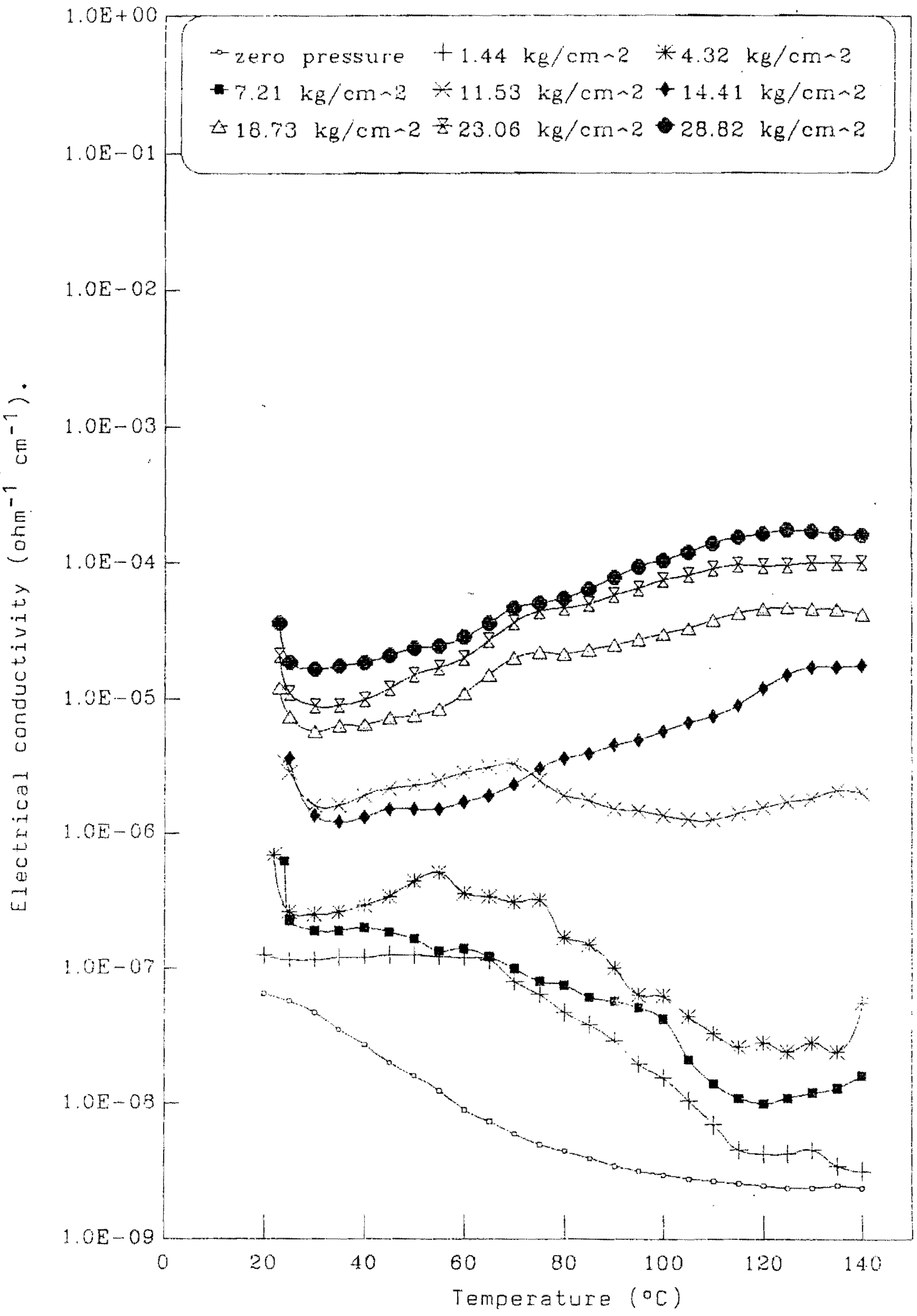

Figure (7) Temperature dependence of electrical conductivity for S1.

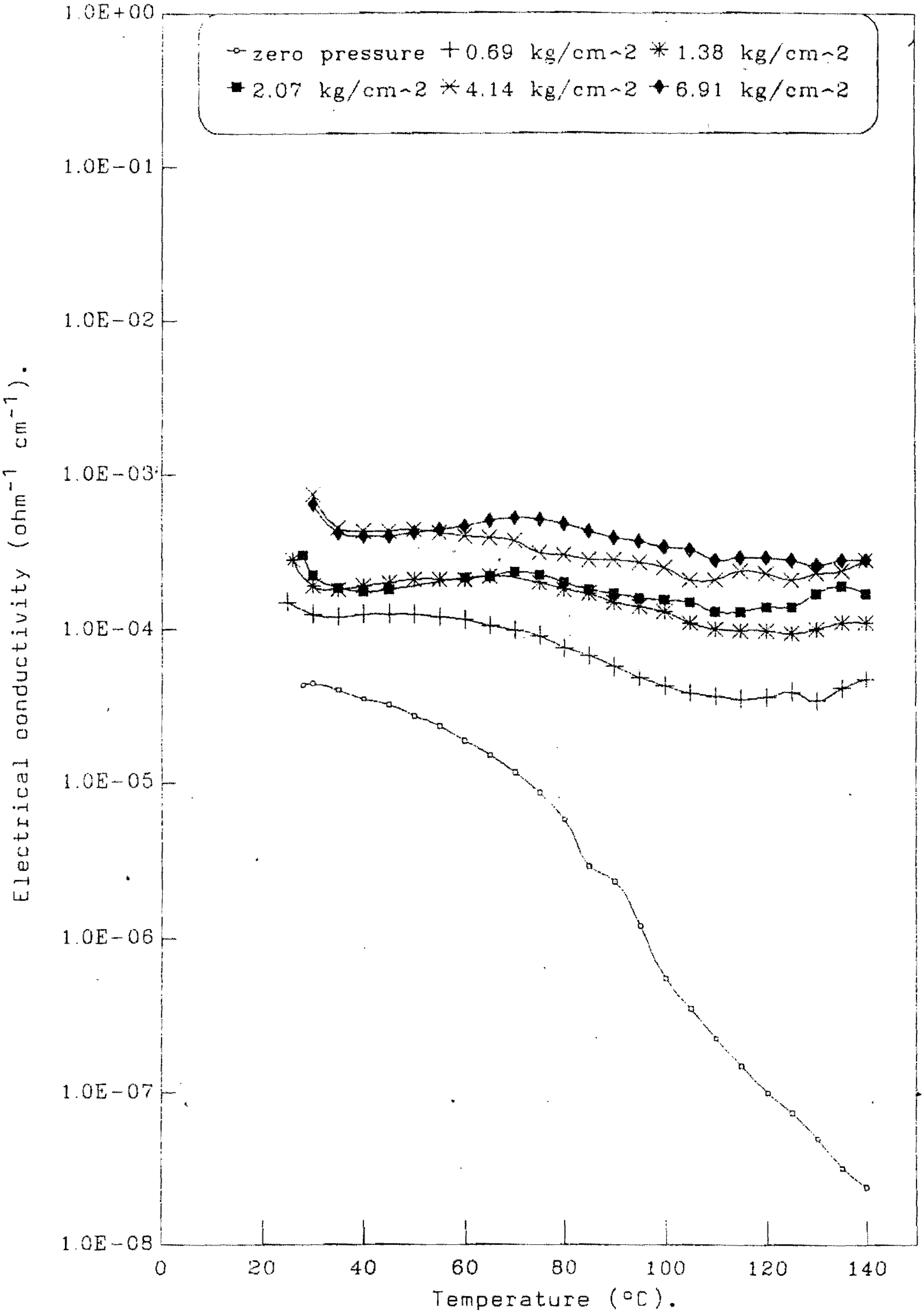

Figure (8) Temperature dependence of electrical conductivity for S2.

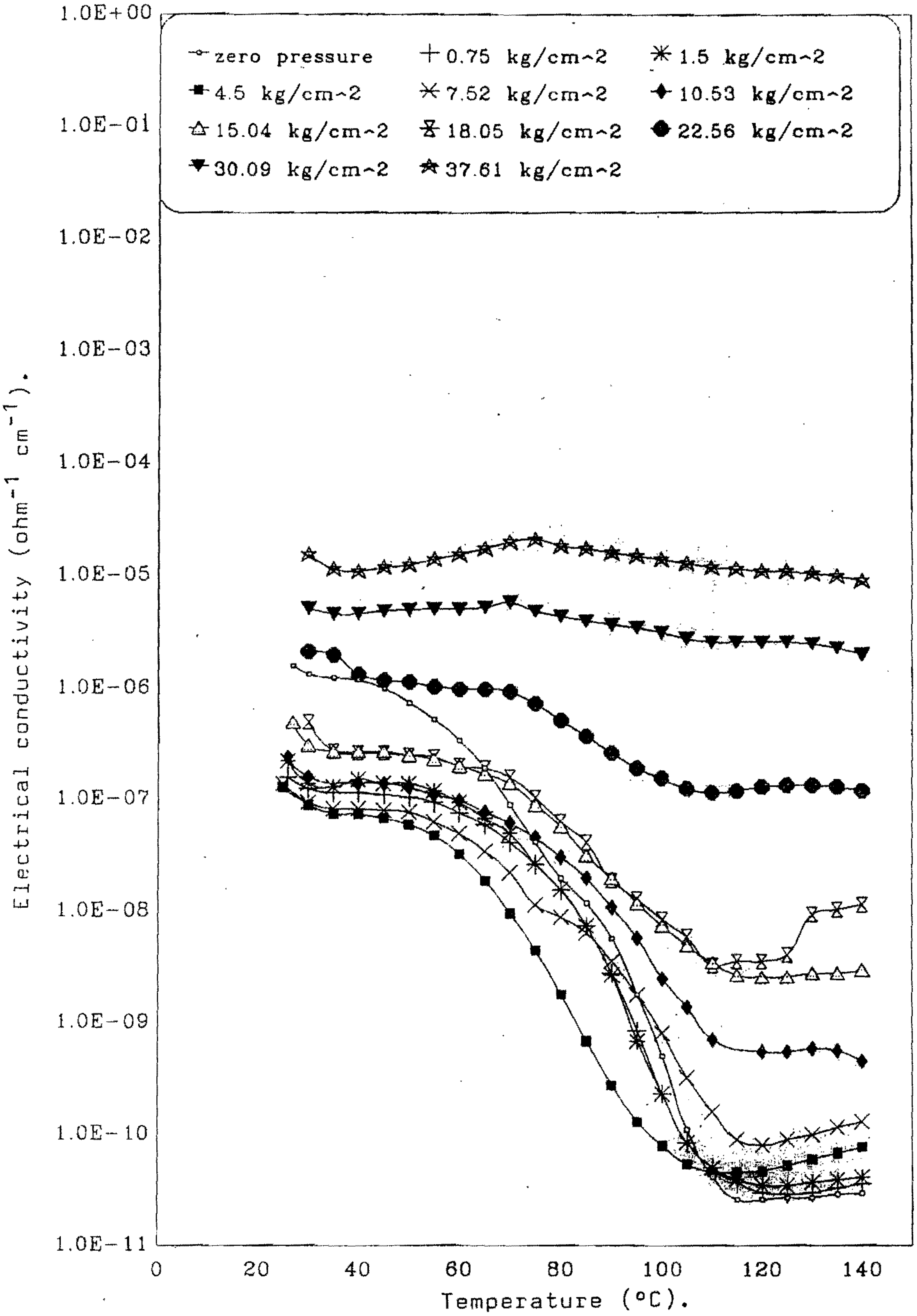

Figure (9) Temperature dependence of electrical conductivity for S3.

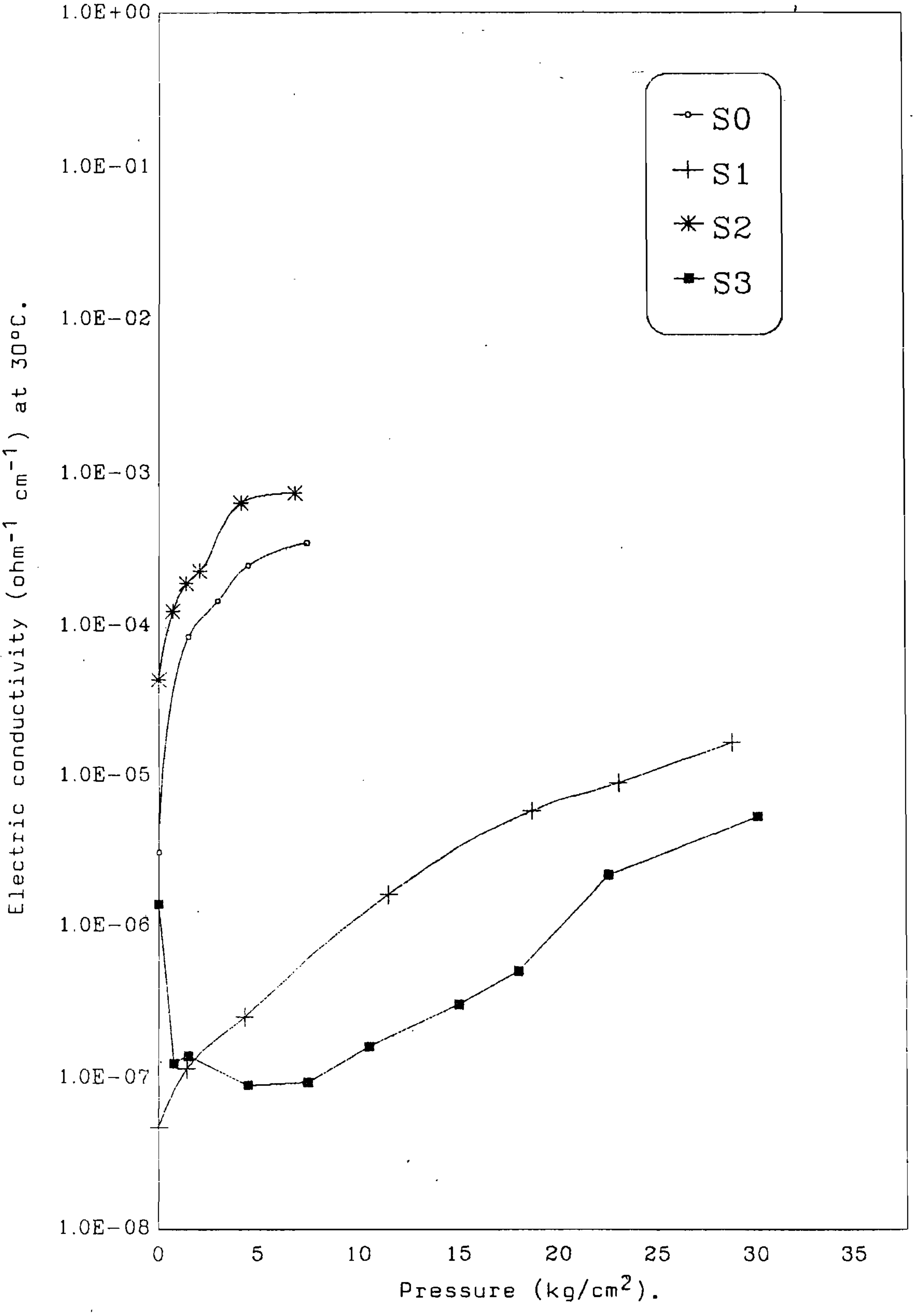

Figure (10) Dependence of the electrical conductivity on the hydrostatic pressure (at 30 C).