

Studies on conductive polymer blends

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Blends of silicon rubber and conductive grade of carbon black which varied from 15 PHR to 25 PHR alongwith other ingredients are reported. The electrical and mechanical properties like density, open porosity, hardness, conductivity, etc., of the blends are studied and also compared to the composites made out of conductex-975-Ultra and furnace black. A comparative electrical conductivity study of the composites reveals that the electrical conductivity of the composites made out of conductex-975-Ultra is higher than that of the composites made out of furnace black.

The conductivity of metals is due to the high mobility of electrons present in them. But physicists believe that conductivity in plastics may well be an evidence of a fractional charge. Numerous research papers¹⁻⁴ and review articles⁵⁻⁸ have been published on conductive polymers in the present past.

The first and the stimulating development in this field occurred in 1977, when it was discovered⁹⁻¹¹ that the electrical conductivity of polyacetylene (PA) (which is an insulator like other pure polymers) increases manifold from that of an insulator ($10^{-9} \Omega^{-1} \text{cm}^{-1}$) on doping with oxidizing (*p*-doping) or reducing agents (*n*-doping). The concept of doping in conductive polymers has been studied earlier¹². Doping in electrochemistry is basically a process by means of which the conductivity of an organic polymer is enhanced by treatment with minute quantities of reactive ionic species, e.g., iodine, potassium naphthalide, etc. Doping operations are as important as polymerisation reactions, since, they affect not only the electrical conductivity and stability of the organic polymer, but also some of the physical and chemical properties. Some doping operations can be controlled to tailor the conductivity to suit the end uses. The commonly employed dopants are alkali metals or alkali metal amides, organometallic fluorides, alkali carbonions, lewis acids, chlorides of transition metals and iodine vapour.

This paper also deals mainly with doping on conductive (semi) carbon black into silicone rubber, alongwith a crosslinking agent.

Materials and Methods

Conductive grade carbon blacks (furnace black

and Conductex-975-Ultra) were purchased from M/s Columbian Chemical Co. and were used as such. Silicon rubber (grade 350 CP) was purchased from M/s Reliance Silicone India Ltd, and was also used as received. All other chemicals used were of AR grade.

The tensile strength and hardness were determined on Universal testing instrument (INSTRON Model 1122) and SHORE—A hardness tester, respectively. The dielectric studies and conductivity measurements were done using an Impedance Analyzer. The real density was determined by using a simple specific gravity bottle but for the determination of apparent density, a special type of Penetrometer was used. The porosity of porous material was calculated from the value of real and apparent densities.

Formulation

Two different sets of formulations, each comprising one of the two stages of carbon black were formed. Within each set there were three batches, all of which had 90 g of silicon rubber and 2 PHR (1.8 g) of crosslinking agent (dicumylperoxide) as constants. The variable was the conductive grade of carbon black, being 15 PHR, 20 PHR and 25 PHR respectively, for the 3 batches within each set. A separate batch was prepared which was free of carbon black. It had only silicone rubber and dicumyl peroxide, so that, a comparison of mechanical properties studied, for the two sets, could be made with this batch which may be considered as a standard measure for observing any improvement or determination in the basic properties of fused silicone rubber.

The different batches with different combinations are shown in Table 1.

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Table 1—Composition of various batches

Batch No.	Composition*
1	DP (5.4 g; 2 PHR) SR (270 g) FB (40.5 g; 15 PHR)
2	DP (5.4 g; 2 PHR) SR (270 g) FB (54.0 g; 20 PHR)
3	DP (5.4 g; 2 PHR) SR (270 g) FB (67.5 g; 25 PHR)
4	DP (5.4 g; 2 PHR) SR (270 g)
5	DP (5.4 g; 2 PHR) SR (270 g) CU (40.5 g; 15 PHR)
6	DP (5.4 g; 2 PHR) SR (270 g) CU (54.0 g; 20 PHR)
7	DP (8.1 g; 3 PHR) SR (270 g) CU (67.5 g; 25 PHR)

*DP = Dicumyl peroxide; SR = silicone rubber; FB = furnace black; CU = conductex-975-Ultra.

Table 2—Values of various properties studied on batches 1, 2, 3 and 4

Property	Batch No.*			
	1	2	3	4
Real density	1.2230	1.2367	1.2486	1.121
Apparent density	1.18085	1.1931	1.2035	1.0945
Hardness (SHORE-A)	64.7	65.0	67.5	54.5
Tensile strength (kg/cm ²)	52.06	36.00	33.33	42.50
Open porosity	3.446	3.526	3.612	2.364
D.C. conductivity (S/cm)	2.45 × 10 ⁻⁹	4.77 × 10 ⁻⁹	6.460 × 10 ⁻⁸	Nil
A.C. breakdown voltage	4200	3240	2340	Nil

*Batch numbering according to Table 1.

Roll-kneading: The rubber mixing mill

The mixing of rubber along with other ingredients was continuously carried out for ~20 min on this machine. The uncured mix was taken off the rolls in a flat shape which could be conveniently placed in between the two glaze sheets and the mix, in turn, was surrounded by a 2 mm thick, 6" × 6" mould.

Press-moulding: The hydraulic press

The glaze plates, with the mould along with the mix

Table 3—Values of various parameters studied on batches 4, 5, 6 and 7

Property	Batch No.*			
	1	2	3	4
Real density	1.2132	1.2279	1.2378	1.121
Apparent density	1.19618	1.211	1.2260	1.0945
Hardness (SHORE-A)	68.58	64.3	62.42	54.5
Tensile strength (kg/cm ²)	37.52	24.01	22.06	42.50
Open porosity	1.4028	1.376	.9533	2.364
D.C. conductivity (S/cm)	3.938 × 10 ⁻⁵	9.83 × 10 ⁻⁵	1.297 × 10 ⁻³	Nil

*Batch numbering according to Table 1.

placed between the two glaze sheets as described earlier, was ready to be placed in the hydraulic press. The pressure was then increased at the rate of 1 ton every five min, starting with a pressure of 1 ton and a temperature of 175°C, which was increased to 195°C, where it was kept for a couple of min, then the heating was ceased and the water circulation started. When the temperature came down to ~100°C, the plates were removed from the compression machine, and cold water sprayed on the plates while they were still kept under a heavy weight. After the mould had completely cooled off, the plates were opened up and the cured sheet removed from the mould which was now ready for testing.

Results and Discussion

It was observed from Tables 2 and 3 that the real density, as well as the apparent density of the composites, increased with the concentration of the carbon black added to the rubber. The difference in real and apparent densities was larger when furnace black was used for making the composites as compared to the case when the composite was prepared with the addition of conductex-975-Ultra.

The porosity was found to be more in the case of composites made by the addition of furnace black as compared to those prepared from conductex-975-Ultra. The porosity value for the composites made by using furnace black was higher than that of rubber itself. This implies that the furnace black particles were themselves porous. This is supported by the slight increase in the porosity with the concentration of furnace black. On the contrary, the composite's porosities decreased continuously, with the addition of conductex-975-Ultra. This is reasonable because, the conductex particles occupy the spaces between the rubber chains. It is likely that the conductex parti-

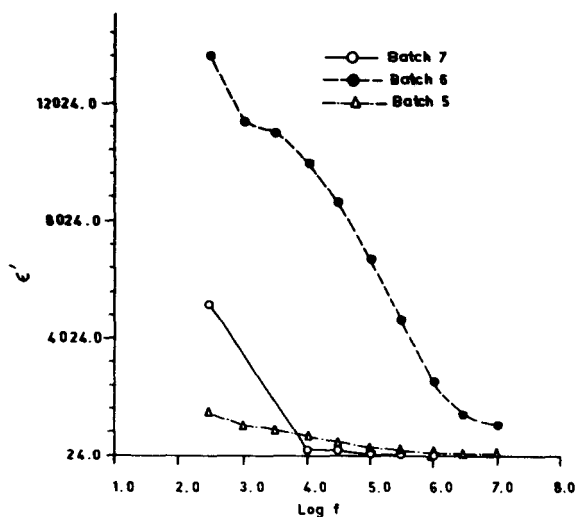


Fig. 1—Plot of log (frequency) vs. dielectric constant (Conductex-975-ultra grade)

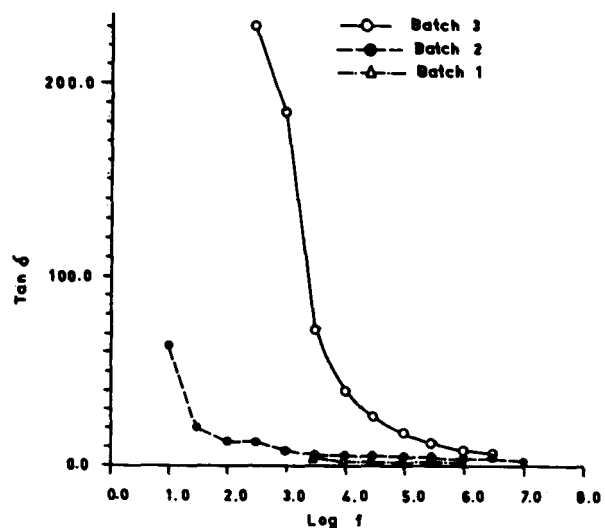


Fig. 3—Plot of log (frequency) vs. loss factor (furnace black grade composite)

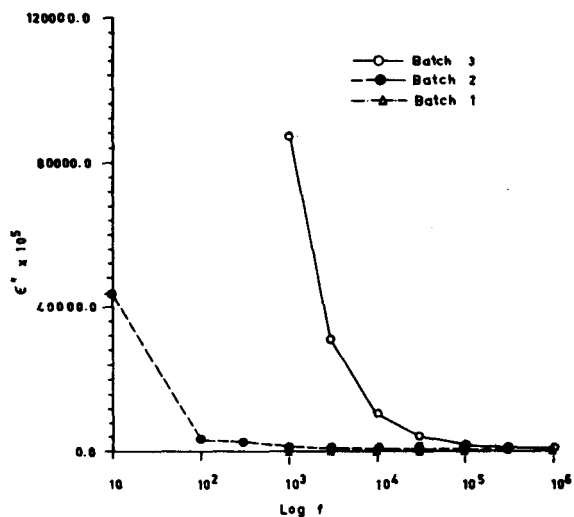


Fig. 2—Plot of log (frequency) vs. dielectric loss (Furnace black grade composite)

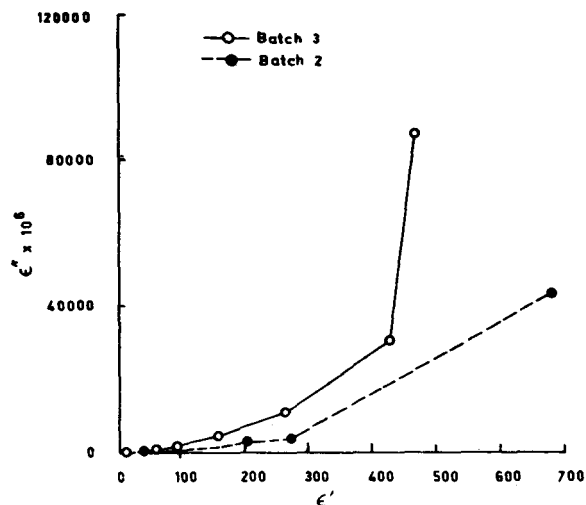


Fig. 4—Plot of dielectric constant vs. dielectric loss (furnace black grade composite)

cles are non-porous, and therefore, the increase in concentration decreases the porosity continuously.

The electrical conductivities of the composites made by using furnace black are too much lower than those of the corresponding composites made out of conductex. Probably one reason for this low conductivity is the increase in porosity due to the porous nature of the particles of furnace black.

The hardness of the composites, prepared by using furnace black, was found to be higher than that of the composites made by using conductex-975-Ultra. It appears that the carbon/rubber bonds are predominant in the former case, whereas, carbon/carbon bonds are dominant in the latter case. This is evidenced by the values of D.C. electrical conductivity which are very much higher in the case of rubber/con-

ductex composites, when compared to those of the rubber/furnace black composites.

It can be observed that in case of highly conducting samples, the A.C. Conductivity remains almost constant with the frequency. Figure 1 shows the characteristic of log F (frequency) versus dielectric constant (E) of the conducting composite, with the different batches of carbon in different proportions. In the composites with high concentrations of carbon, the dielectric constant characteristics are completely distinguishable from Debye behaviour.

In most of the cases as shown in Fig. 2, the dielectric loss decrease gradually with the increase in frequency. In context of the dielectric constant with frequency, the loss factor has also been studied against log F as shown in Fig. 3. It can be observed from the figure

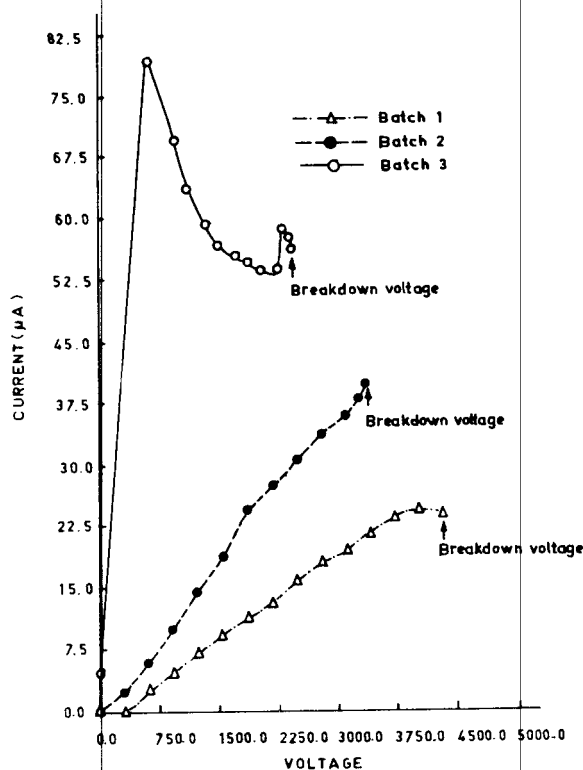


Fig. 5—Plot of voltage vs. current (Furnace black grade composite)

that as the carbon/carbon bonds increases in the polymeric matrix, the loss factor also increases.

The Cole-Cole plots of conducting rubber, with different grades and concentrations of carbon (Fig. 4) show the system is practically a non-existing case of Debye response. Most charge carrier systems show a strong dispersion in the samples; at the same time, there is a strong dispersion in the interfacial regions. The Cole-Cole plots also indicate that there is a contact effect prevailing in the system.

It is clear from Fig. 5 that I V characteristic increases uniformly and the breakdown voltages are 4200 and 3240 when the carbon content is 15 PHR and 20 PHR respectively. There is a sharp increase in I V characteristic till 600 V, but there is a low decay of the current till it reaches the breakdown voltage at 2340 V when the carbon concentration is 25 PHR. As we increase the carbon content in the silicon rubber, the formation of carbon/rubber bonds and carbon/carbon bonds is promoted. At the same time, the arithmetic average distance between the carbon particles in the rubber mix usually decreases upto tens of millimicrons. The carbon particles are dispersed in some non-random dispersion in which they are bound by the surface forces. The reason for high breakdown voltage is that most of the bonds prevailing, i.e., the rubber-carbon bonds in the composite, are high energy

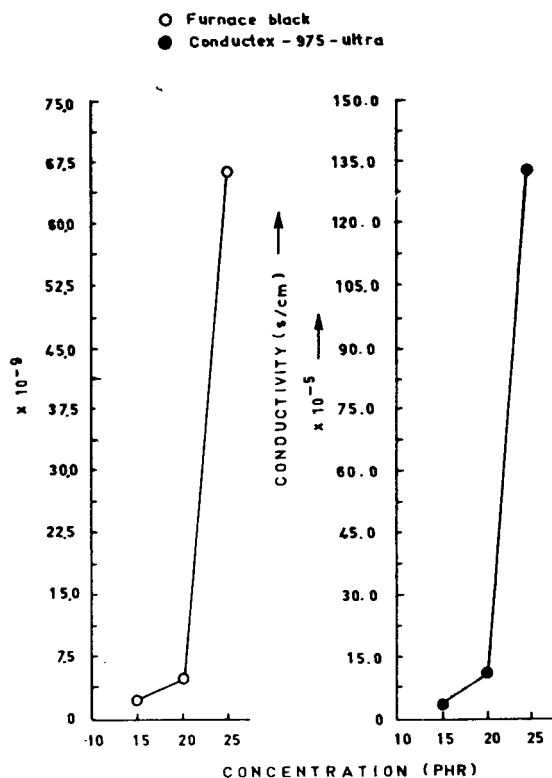


Fig. 6—Plots of concentration vs. D.C. conductivity (Furnace black and conductex-975-ultra grade composites)

bonds and do not contribute to the condition process and hence the increase in the breakdown voltage.

It can be observed from Fig. 6 that the breakdown voltage is inversely proportional to the concentration of carbon in rubber. The conductivity of different batches of furnace black in rubber are of the order of 2.4×10^{-9} s/cm to 6.4×10^{-8} s/cm. This can clearly be attributed to the reason mentioned above. Also as we increase the concentration of conductex-975-Ultra grade of carbon from 15 to 25 PHR in batches 5, 6 and 7 respectively, we observe very high conductivity of the order of 3.94×10^{-5} to 1.29×10^{-3} s/cm in rubber. Although, the concentration of conductex grade of carbon is the same as the furnace black grade of carbon, the carbon/carbon bonds are more prominent in the case of conductex grade (Fig. 7).

Conclusion

From these studies, certain valuable conclusions can be made concerning the electrical conductivities of the composites. The conductex-975-Ultra grade carbon black tends to form more carbon/carbon bonds and hence is more conductive than the furnace black, where, the rubber/carbon bonds are more prominent. The composites made out of conductex-975-Ultra, for at least 15 PHR and above, the electrical conductivity is higher by 10^4 to 10^6 orders as compa-

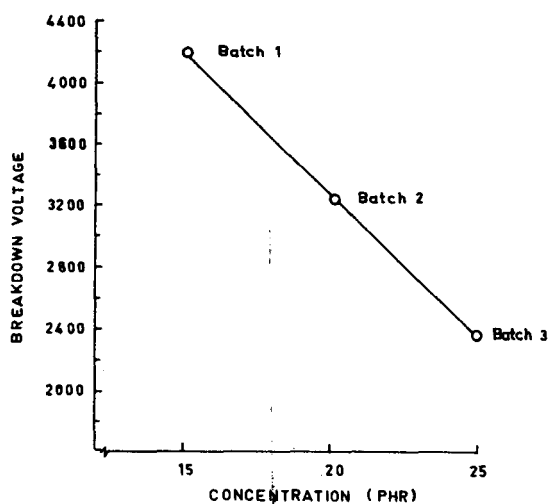


Fig. 7—Plot of concentration vs. breakdown voltage (Furnace black grade composite)

red to those prepared with furnace black. At ~25 per cent by weight of furnace black in the rubber composite, there is no linear dependence of conductivity with frequency and the phenomenon of self-healing breakdown is also observed.

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