Applications and Uses for the Bruggeman Mixing Formula (Effective Medium Approximation)

The symmetrical Bruggeman formula (effective medium approximation, EMA) in (2) works well with certain types of random composite materials. The MG mixing formula does not usually work well with such random mixtures.

An example of this application for the Bruggeman formula is found in the paper Chung et al, "Electrical permittivity and conductivity of carbon black-polyvinyl chloride composites," J. Appl. Phys., Oct. 1982.

The various components of PVC were dry blended with different types of carbon black, and in various volume fractions. Each specimen was formed into a puck, heated & pressed, cooled, and then top & bottom was coated w/ gold. A network analyzer was used to measure the ac conductivity & permittivity.

Certain types of carbon black are comprised of spherical particles. Others aggregate into chain-like structures with different aspect ratios.

For time-harmonic fields, the complex permittivity $\epsilon_r = \epsilon_r' - j\epsilon_r''$ can be used in the Bruggeman formula for sufficiently low frequencies such that the particles & their spacings are electrically small, which is certainly the case for these carbon black particles.

Using Bruggeman formula (2) for complex permittivity & for PVC $\epsilon_p = 3.0$ & $\sigma_p = 50\times10^{-9}$ S/m & for carbon black $\epsilon_c = 0$ (?) & σ_c varies from 0.1 to 1000/Ω·cm &

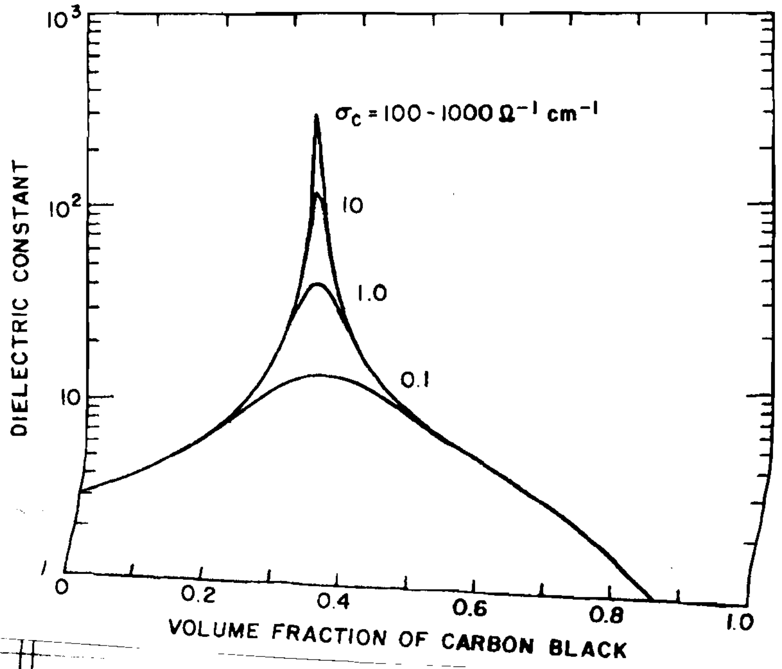


FIG. 1(b). The corresponding predicted bulk dielectric constants of carbon black-PVC composites under the same assumption used in calculating the volumetric conductivity.

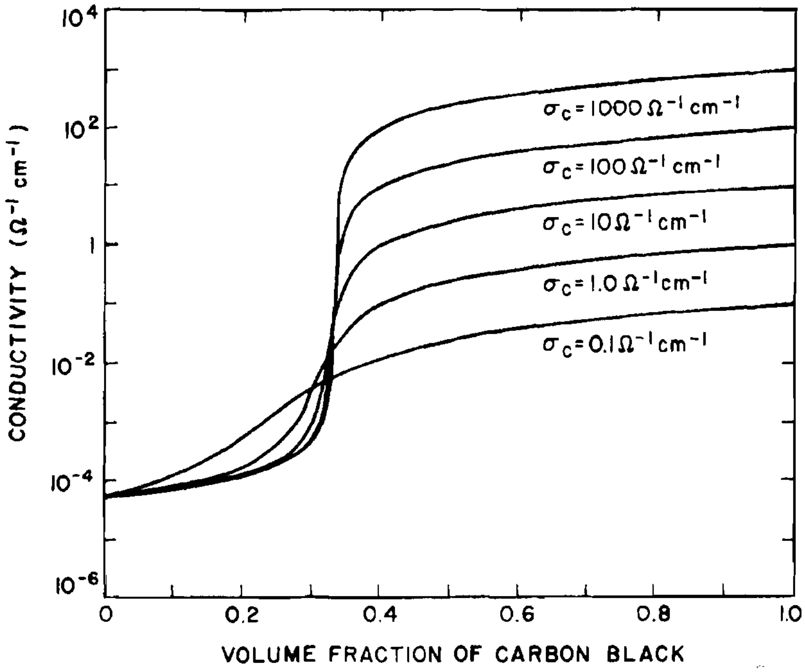


FIG. 1(a). Volumetric conductivity of carbon black-PVC composites as a function of carbon black loading at 915 MHz predicted by Bruggeman's effective medium theory. The parameters used for the calculation are the measured $\epsilon_p = 3.0$, $\sigma_p = 50 \times 10^{-6}\ \Omega^{-1}\ \mathrm{cm}^{-1}$; ϵ_c is assumed to be zero while σ_c is assumed to possess values of 0.1 to 1000 Ω^{-1} cm^{-1}.

The rapid variation in ϵ_{eff} & σ_{eff} near $f \approx 0.33$ is called the percolation threshold.

What is happening near percolation? A very small change in the volume fraction of carbon black is producing a huge change in σ_{eff} and ϵ_{eff}. Why? Carbon black particles are starting to form interconnections throughout the space.

Is this percolation really happening? Fig 1 just Bruggeman formula.

Here are results for an SRF-S carbon black (spherical particles) and PVC system:

4/8

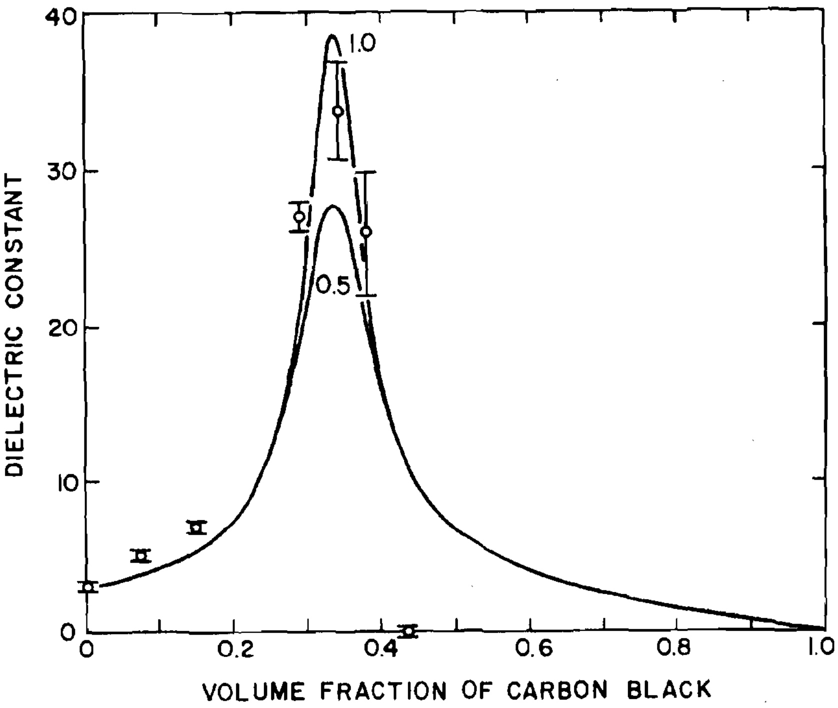


FIG. 9. A comparison of the percolation behavior between the theoretical and experimental dielectric constant results for the spherical carbon black system. The unfilled circles represent the experimental data for PVC/SRF-S System, and the continuous curves represent the prediction of Eq. (2) with $\sigma_c = 0.5$ and $1.0\ \Omega^{-1}\,\mathrm{cm}^{-1}$, respectively.

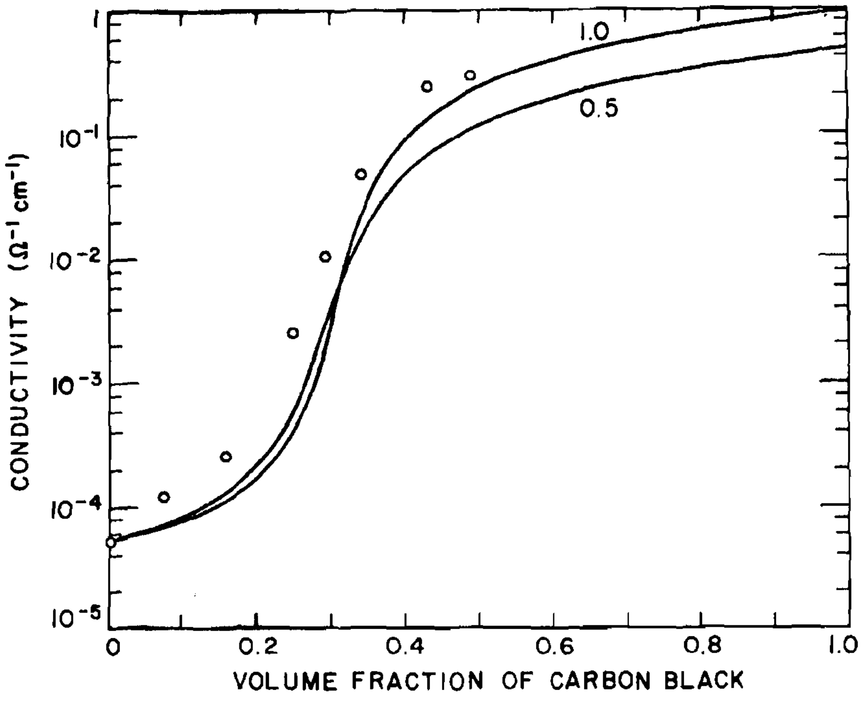


FIG. 11. A comparison between experimental data and theoretical predication on composite conductivity. The legend is the same as in Fig. 9. The solid lines represent the prediction of Eq. (2) with $\sigma_c = 0.5$ and $1.0\ \Omega^{-1}\,\mathrm{cm}^{-1}$, respectively. The conductivities of PVC/SRF-S and PVC/Mogul-L system are extremely similar to those predicted in Fig. 1 for $\sigma_c = 1.0\ \Omega^{-1}\,\mathrm{cm}^{-1}$.

These results show that the symmetrical Bruggeman formula does an excellent job of predicting effective ε_{eff} + σ_{eff} for this SRF-S/PVC system. And, yes, percolation is really occurring.

However, not all carbon blacks have a spherical morphology, and consequently there percolation threshold changes. Longer chain (higher aspect ratio) particles can have a significantly lower percolation threshold. (Carbon nanotubes can be as low as ~ 0.5% volume fraction, for example.)

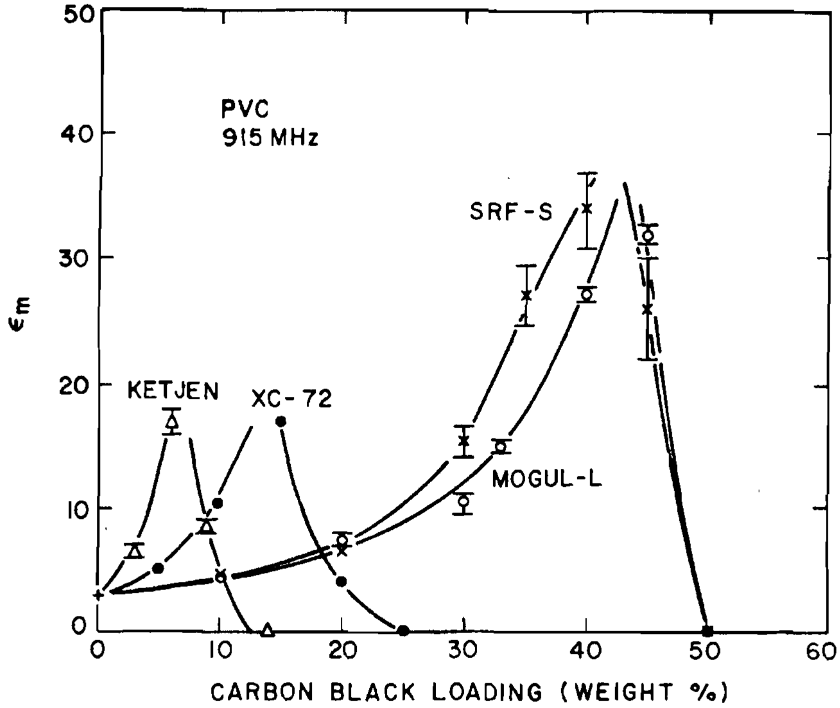


FIG. 8. Carbon black-PVC composite dielectic constants at 915 MHz as a function of wt. % loading. Ketjen Black shows percolation at around 8%, both SRF-S and Mogul-L show percolation at 40% while XC-72 shows percolation at intermediate loading of ~15%.

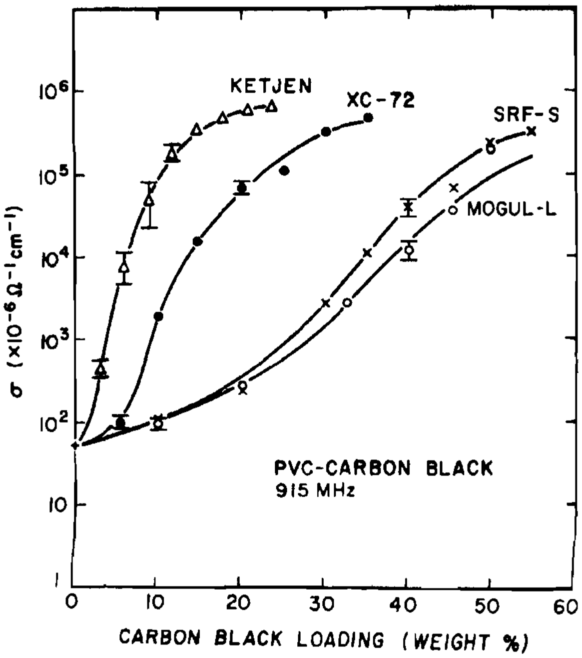


FIG. 10. PVC carbon composite conductivities at 915 MHz as a function of wt. % loadings. *Similar to the dielectric constants, the percolation in conductivity depends on the packing efficiency and thus its structure.*

Would need to use another mixing formula to predict the effective medium parameters for these systems w/ non-spherical carbon black particles. Or maybe fit curve w/ "unified mixing formula" of Sihvola.

What about using the Maxwell Garnett formula to predict the effective media properties of the carbon black/PVC system? Even for spherical particles.

Consider these results for Bruggeman, Coherent potential, and MG formulas:

■ Solve the Bruggeman formula for ϵeff.

```
Solve[(1 - f) * (ϵe - ϵeff) / (ϵe + 2 * ϵeff) + f * (ϵi - ϵeff) / (ϵi + 2 * ϵeff) == 0, ϵeff]
```

$$\left\{\left\{\epsilon\mathrm{eff}\to\frac{1}{4}\left(2\,\epsilon\mathrm{e}-3\,\mathrm{f}\,\epsilon\mathrm{e}-\epsilon\mathrm{i}+3\,\mathrm{f}\,\epsilon\mathrm{i}-\sqrt{8\,\epsilon\mathrm{e}\,\epsilon\mathrm{i}+(2\,\epsilon\mathrm{e}-3\,\mathrm{f}\,\epsilon\mathrm{e}-\epsilon\mathrm{i}+3\,\mathrm{f}\,\epsilon\mathrm{i})^2}\right)\right\},\right.$$
$$\left.\left\{\epsilon\mathrm{eff}\to\frac{1}{4}\left(2\,\epsilon\mathrm{e}-3\,\mathrm{f}\,\epsilon\mathrm{e}-\epsilon\mathrm{i}+3\,\mathrm{f}\,\epsilon\mathrm{i}+\sqrt{8\,\epsilon\mathrm{e}\,\epsilon\mathrm{i}+(2\,\epsilon\mathrm{e}-3\,\mathrm{f}\,\epsilon\mathrm{e}-\epsilon\mathrm{i}+3\,\mathrm{f}\,\epsilon\mathrm{i})^2}\right)\right\}\right\}$$

■ Solve the Coherent potential formula for ϵeff.

```
Solve[ϵeff == ϵe + f * (ϵi - ϵe) * 3 * ϵeff / (3 * ϵeff + (1 - f) * (ϵi - ϵe)), ϵeff]
```

$$\left\{\left\{\epsilon\mathrm{eff}\to\frac{1}{6}\left(4\,\epsilon\mathrm{e}-4\,\mathrm{f}\,\epsilon\mathrm{e}-\epsilon\mathrm{i}+4\,\mathrm{f}\,\epsilon\mathrm{i}-\sqrt{(-4\,\epsilon\mathrm{e}+4\,\mathrm{f}\,\epsilon\mathrm{e}+\epsilon\mathrm{i}-4\,\mathrm{f}\,\epsilon\mathrm{i})^2-12\left(\epsilon\mathrm{e}^2-\mathrm{f}\,\epsilon\mathrm{e}^2-\epsilon\mathrm{e}\,\epsilon\mathrm{i}+\mathrm{f}\,\epsilon\mathrm{e}\,\epsilon\mathrm{i}\right)}\right)\right\},\left\{\epsilon\mathrm{eff}\to\right.\right.$$
$$\left.\left.\frac{1}{6}\left(4\,\epsilon\mathrm{e}-4\,\mathrm{f}\,\epsilon\mathrm{e}-\epsilon\mathrm{i}+4\,\mathrm{f}\,\epsilon\mathrm{i}+\sqrt{(-4\,\epsilon\mathrm{e}+4\,\mathrm{f}\,\epsilon\mathrm{e}+\epsilon\mathrm{i}-4\,\mathrm{f}\,\epsilon\mathrm{i})^2-12\left(\epsilon\mathrm{e}^2-\mathrm{f}\,\epsilon\mathrm{e}^2-\epsilon\mathrm{e}\,\epsilon\mathrm{i}+\mathrm{f}\,\epsilon\mathrm{e}\,\epsilon\mathrm{i}\right)}\right)\right\}\right\}$$

■ Mixing Formulas for Bruggeman, Maxwell Garnett, and Coherent potential.

$$\epsilon\mathrm{effBG}[\mathrm{f\_},\epsilon\mathrm{e\_},\epsilon\mathrm{i\_}]:=\frac{1}{4}\left(2\,\epsilon\mathrm{e}-3\,\mathrm{f}\,\epsilon\mathrm{e}-\epsilon\mathrm{i}+3\,\mathrm{f}\,\epsilon\mathrm{i}+\sqrt{8\,\epsilon\mathrm{e}\,\epsilon\mathrm{i}+(2\,\epsilon\mathrm{e}-3\,\mathrm{f}\,\epsilon\mathrm{e}-\epsilon\mathrm{i}+3\,\mathrm{f}\,\epsilon\mathrm{i})^2}\right)$$

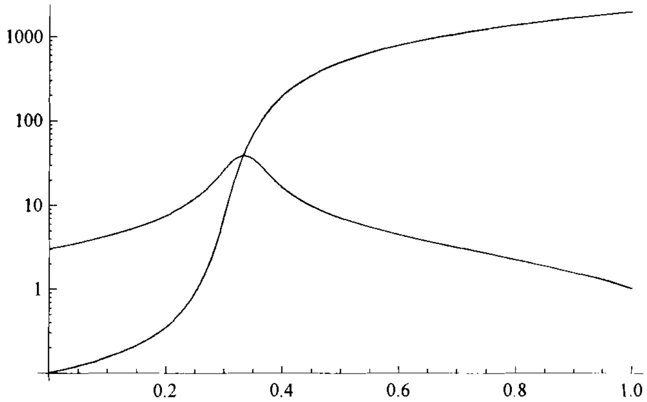
```
ϵeffMG[f_, ϵe_, ϵi_] := ϵe + 3 * f * ϵe * (ϵi - ϵe) / (ϵi + 2 * ϵe - f * (ϵi - ϵe))
ϵeffCP[f_, ϵe_, ϵi_] :=
```

$$\frac{1}{6}\left(4\,\epsilon\mathrm{e}-4\,\mathrm{f}\,\epsilon\mathrm{e}-\epsilon\mathrm{i}+4\,\mathrm{f}\,\epsilon\mathrm{i}+\sqrt{(-4\,\epsilon\mathrm{e}+4\,\mathrm{f}\,\epsilon\mathrm{e}+\epsilon\mathrm{i}-4\,\mathrm{f}\,\epsilon\mathrm{i})^2-12\left(\epsilon\mathrm{e}^2-\mathrm{f}\,\epsilon\mathrm{e}^2-\epsilon\mathrm{e}\,\epsilon\mathrm{i}+\mathrm{f}\,\epsilon\mathrm{e}\,\epsilon\mathrm{i}\right)}\right)$$

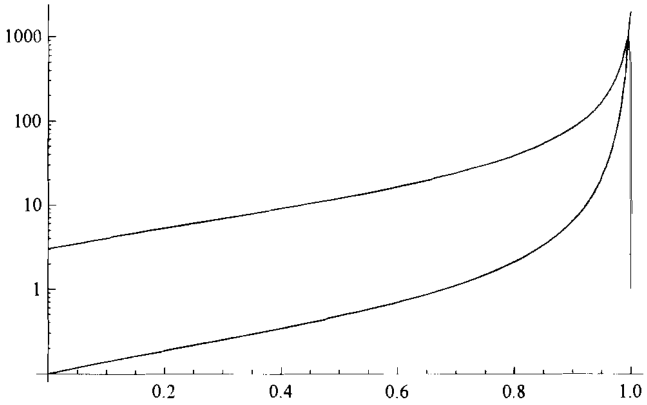
- **Plot relative effective permittivity for carbon black particles in PVC host, following the paper of Chung, Sabo, and Pica, J. Appl. Phys., Oct. 1982.**

```
ω = 2. * Pi * 915. * 10^6 ;
ϵ0 = 8.854 * 10^-12 ;
ϵrPVC = 3. - I * 50. * 10^-4 / (ω * ϵ0) ;
ϵrCB = 1. - I * 100. / (ω * ϵ0) ;
```

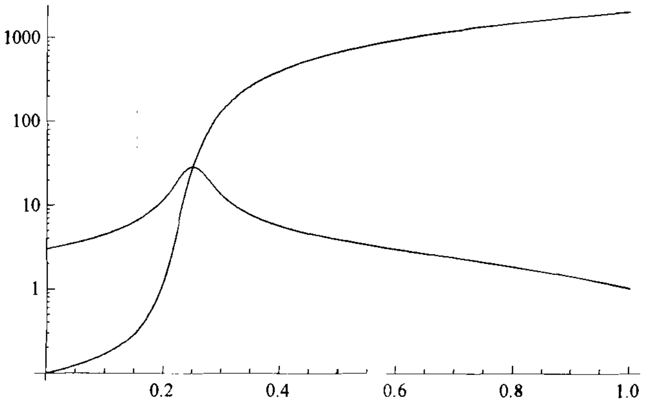
```
LogPlot[{Re[ϵeffBG[f, ϵrPVC, ϵrCB]], -Im[ϵeffBG[f, ϵrPVC, ϵrCB]]}, {f, 0, 1}]
```



```
LogPlot[{Re[ϵeffMG[f, ϵrPVC, ϵrCB]], -Im[ϵeffMG[f, ϵrPVC, ϵrCB]]}, {f, 0, 1}]
```



```
LogPlot[{Re[ϵeffCP[f, ϵrPVC, ϵrCB]], -Im[ϵeffCP[f, ϵrPVC, ϵrCB]]}, {f, 0, 1}]
```



The MG formula has a percolation threshold of 100% volume fraction. It can't possibly accurately predict behavior of the carbon black/PVC model.

This is just one plot of results from MG. Does MG always have percolation threshold of 100%? (Yes, it models particles in a lattice. The particles never touch in this system until 100% v.f. not realistic, of course.)

Hybrid Mixtures

In some of our research, we've found it helpful to use both the Bruggeman & MG formulas. This research was presented at the Metamaterials 2009 conference.

There we were interested in extending the range of effective surface impedance of films that could be achieved by varying the volume fraction of carbon in a lossy film and simultaneously printing regular patterns of conductive shapes onto the film.

At that Metamaterials 2009 presentation we showed that it was possible to simultaneously increase ϵ_r' + ϵ_r'' for films using this process.