Characterization of the Interfacial Surface Energy for Composite Electrical Conduction Measurements using Two Full Range Percolation Threshold Models

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Two full concentration range percolation threshold models were evaluated for three different carbon fillers in both Nylon 6,6 and Lexan. A new Modified Landauer Model was introduced in this study and compared with a Percolation Threshold Model recently published by this author. These models were then utilized to address how to best characterize the interfacial surface energy, γ_{pf}, for composite electrical conduction measurements using Clingerman's data. Three different models used for calculating the interfacial surface energies, γ_{pf}, were evaluated in this study. It was found that solid measurements used in calculating the Fowkes equation for the interfacial surface energy gave the most consistent correlations. A linear correlation was found between the Fowkes Interfacial surface energy and the β constant designated as the insulation surface interaction magnitude from the new Percolation Threshold Model. In addition, three concurrent mathematical conditions were found to occur at the same concentration for both the new percolation threshold models yielding S-shaped curves in this study. These conditions include the concentration at the Inflection Point, the concentration at the maximum slope and the maximum extrapolated percolation threshold concentration calculated at the same concentration.

Introduction

Miyaska, *et al.,* [**1**] appear to be essentially the first to present evidence of a thermodynamic influence on the percolation threshold in electrical conductivity measurements with carbon fillers as indicated in **Fig. 1** and **Fig. 2**. The polymers used in Fig. 1 and Fig. 2 were: LPE – Linear Polyethylene, PP – Polypropylene, BPE – Branched Polyethylene, PS – Polystyrene, Nylon 6, PMMA – Polymethelmethacrylate, NR – Natural Rubber and SBR – Styrene-Butadiene Rubber. As indicated in **Fig. 2** the surface tension of the polymers were shown to have a significant relationship with the percolation threshold concentration as indicated in **Fig. 1**.

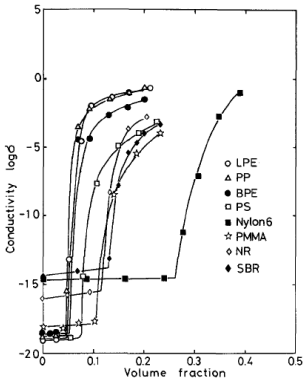

Fig.1. Electrical Conductivity of Carbon Filled Polymer Composites as a Function of Volume Fraction Carbon (σ is in Ω^{-1} cm^{-2}) (From Miyaska, *et al.,* [**1**] with permission).

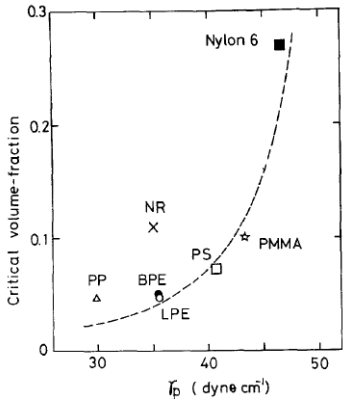

Fig. 2. Plot of the Critical Carbon Content vs Surface Tension of the Polymer (From Miyaska, *et al.,* [**1**] with permission).

Several review authors [**2-11**] have found that many models have been proposed to characterize the percolation threshold as indicated by the sharp increase in the S shaped curves described adequately with the data of Miyaska *et al.,* [**1**] for several carbon filled composites as indicated in **Fig. 1**.

Lux [**12**] points out that in general there appear to be predominantly three different types of models to describe the percolation threshold including:

1. Models describing the concentration curve up to the percolation threshold. These models generally attempt to describe the concentration up to where the percolation threshold just begins.

2. Other models describe the concentration curve from the percolation threshold and upward from the concentration at the percolation threshold.
3. In addition, there have been some attempts to describe the whole concentration curve. However, many of these models often have separate models for the region up to the percolation threshold and another for the region above the percolation threshold.

In addition, there appear to be primarily two different types of models that cover the whole concentration range for the S-Shaped curves found in trying to analyze the electrical conductivity of carbon filled composites. These classes include:

1. Models that appear to address the whole concentration range.
2. Models that actually do cover the whole concentration range.

For example the percolation threshold model developed by Clingerman [**13,14**] appears to address the whole concentration range as indicated in **Fig. 3**. The model indicated in **Fig. 3** was a modification of an earlier model developed by Mamunya, *et al.*, [**15,16**]. The model developed by Clingerman [**13,14**] can be described as follows:

$$(\sigma/\sigma_p) = (\sigma_F/\sigma_p)^{G(\varphi)} \quad (1)$$

Note that equation (1) can also be rewritten as

$$\text{Log } \sigma - \text{Log } \sigma_p = (\text{Log } \sigma_F - \text{Log } \sigma_p)G(\varphi) \quad (2)$$

where

$$G(\varphi) = [(\varphi-\varphi_c)/(F-\varphi_c)]^{k(\varphi)} \quad (3)$$

$$k(\varphi) = K\varphi_c/(\varphi-\varphi_c)^n \quad (4)$$

σ_p = Conductivity of neat polymer

σ_F = The maximum conductivity in the case of ultimate filling when $\varphi = F$

σ_c = Conductivity of the mixture at the percolation threshold where $\varphi = \varphi_c$

F = Maximum packing fraction of the filler

φ = Volume fraction of filler

φ_c = Volume fraction of filler at the percolation threshold

n = An exponent determining the power of conductivity increase = 0.70

$$K = A + B\gamma_{pf} \quad (5)$$

A & B = Constants

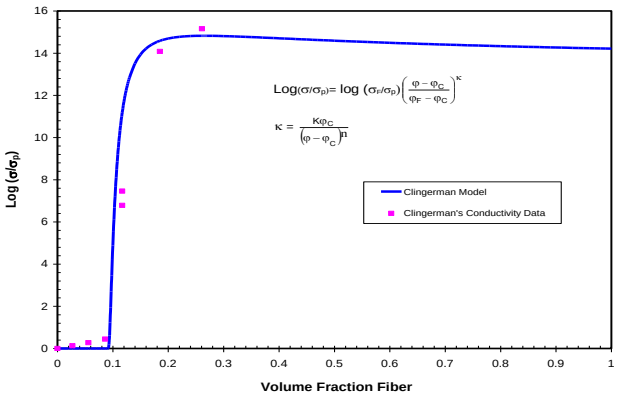

Fig. 3. Clingerman's Model addressing Clingerman's Electrical Conductivity Data [**13**] for a Pitch Based Carbon Fiber in Nylon 6,6 (with Permission).

Clingerman also used a modification of Fowkes [**17**] equation to evaluate the value for the interfacial surface tension, γ_{pf}, as

$$\gamma_{pf} = \gamma_p + \gamma_f - 2(\gamma_p^p\gamma_f^p)^{0.5} - 2(\gamma_p^d\gamma_f^d)^{0.5} \quad (6)$$

where

γ_p = Polymer surface tension

γ_f = Filler surface tension

γ_{pf} = Interfacial surface tension

γ_p^d = Dispersive component of the polymer surface tension

γ_f^d = Dispersive component of the filler surface tension

γ_p^p = Polar component of the polymer surface tension

γ_f^p = Polar component of the filler surface tension

The results in **Fig. 3** were generated from the data in Clingerman's thesis [**13**] for blends of carbon fiber in nylon 6,6. The information utilized from this thesis to generate this plot were as follows $\text{Log}(\sigma_F/\sigma_p) = 12.386$, $\gamma_{PF} = 6.39$, $K = 0.11 + 0.03\gamma_{PF} = 0.302$, $\varphi_c = 0.09$ and $\varphi_F - \varphi_c = 0.132 - 0.09 = 0.042$.

In general, the results in Fig. 3 do appear to describe the data satisfactorily. However, note the following sub-equation, $E(\varphi)$, from equation (4)

$$E(\varphi) = (\varphi-\varphi_c)^n \quad (7)$$

If $\varphi < \varphi_c$ then $E(\varphi)$ is defined if n is an integer. However, if n is a fraction (n = 0.70) and $\varphi < \varphi_c$ then the sign of $E(\varphi)$ is undefined and the Excel program in the computer simply describes the complete calculation as a zero. Therefore, equation (4) becomes undefined below the volume fraction of the percolation threshold even though the plot in Fig. 3 appears to be acceptable.

However, the Original Landauer Model [**18**] and the Landauer model modified by this author do effectively define S-shaped curves where the whole concentration curves are well defined for electrical conductivity measurements as indicated in **Fig. 4**. The electrical conductivity data in Figure 4 are also from Clingerman's thesis [**13**] for blends of carbon fiber in nylon 6,6. Since it is clear that the Original Landauer model [**18**] as indicated in Fig. 4 did not effectively fit the electrical conductivity data in this instance, it was been dropped from further consideration in this study.

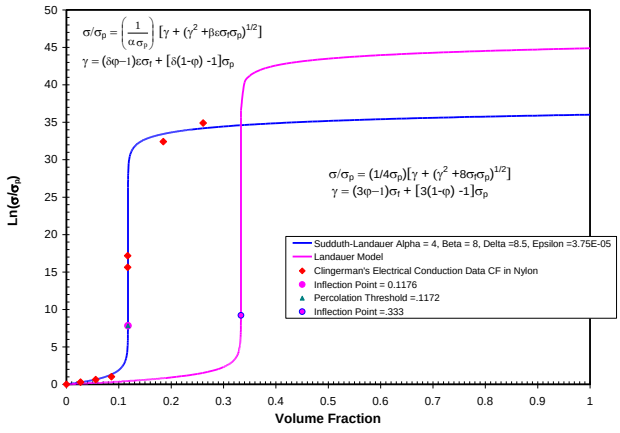

Fig. 4. Clingerman's Electrical Conductivity Data [**13**] for Pitch Based Carbon Fiber in Nylon 6,6 applied to the Modified Landauer Model and the Original Landauer Model (with Permission).

Another model that also addresses the whole concentration range for electrical conductivity measurements is the Sudduth Percolation Threshold model [**2**] as indicated in **Fig. 5**. Note that the model in **Fig. 5** also yielded an excellent fit of Clingerman's electrical conductivity data for blends of carbon fiber in nylon 6,6.

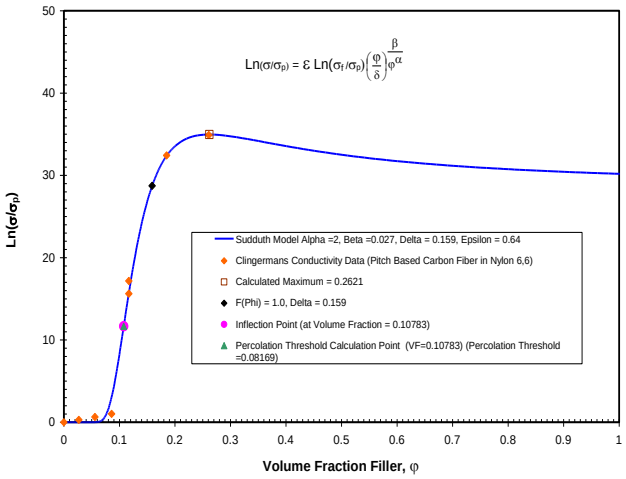

Fig. 5. Sudduth Percolation Threshold Model addressing Clingerman's Electrical Conductivity Data [**13**] for a Pitch Based Carbon Fiber in Nylon 6,6 (with Permission).

The next sections of this study will utilize both the Sudduth Percolation Threshold Model and the Sudduth Modified Landauer Model to characterize data from three different carbon fillers in both Nylon 6,6 and Lexan. These results will then be used to identify how best to characterize the interfacial surface energy, γ_{pf}, for composite electrical conduction measurements using the data from Clingerman's thesis [**13**].

Analysis utilizing the Sudduth Modified Landauer Percolation Threshold Model

Landauer's [**18**] original percolation threshold model has been modified by this author to yield the following new version of this model:

$$\sigma/\sigma_p = \left(\frac{1}{\alpha\,\sigma_p}\right)[\gamma + (\gamma^2 + \beta\varepsilon\sigma_f\sigma_p)^{1/2}] \qquad (8)$$

$$\gamma = (\delta\varphi - 1)\varepsilon\sigma_f + [\delta(1-\varphi) - 1]\sigma_p \qquad (9)$$

where

σ = Conductivity of composite at volume fraction φ
σ_p = Conductivity of the base polymer or matrix
σ_f = Conductivity of the filler particles
φ = Volume fraction of filler
α = Constant
β = Constant
δ = Constant
ε = Efficiency of the filler
γ = Intermediate function of φ , σ_p , σ_f

The additional constants added to the Landauer model to obtain the Sudduth modified Landauer model were generated by simply making the numbers in the original Landauer model to be constants. Consequently, the original Landauer model can be obtained from the Sudduth modified Landauer model when α = 4.0, β = 8.0, δ = 3.0 and ε =1.0. It should be noted that the special limits of the Orginal Landauer model (α = 4.0, β = 8.0, δ = 3.0, ε = 1.0) would include: when φ = 0 then $\sigma = \sigma_p$ and when φ = 1 then $\sigma = \sigma_f$.

The results in **Figs. 6-8** have been generated utilizing the Modified Landauer model to address Clingerman's electrical conductivity data. In **Fig. 6** Clingerman's data for a carbon black Ketjenblack EC-600JD in both Nylon 6,6 and Lexan has been addressed. In **Fig. 7** Clingerman's data for a pitch based carbon fiber Thermograph DKD X in both Nylon 6,6 and Lexan has been addressed. And finally, in **Fig. 8** Clingerman's data for specialty graphite Thermocarb TM CF-300 in Nylon 6,6 and Lexan has been addressed.

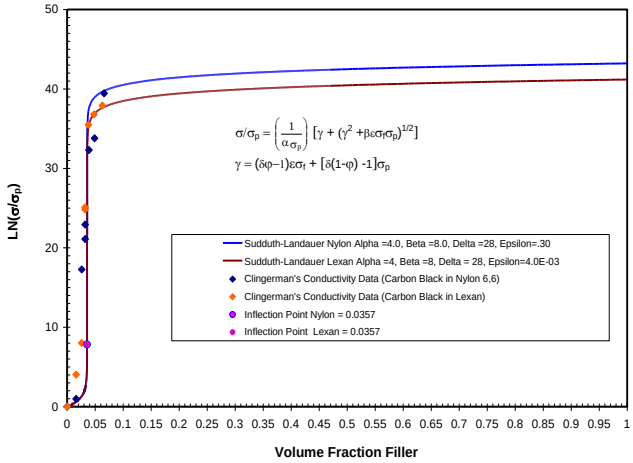

Fig. 6. Modified Landauer Model addressing Clingerman's Electrical Conductivity Data [**13**] for a Carbon Black in Nylon 6,6 and Lexan (with Permission).

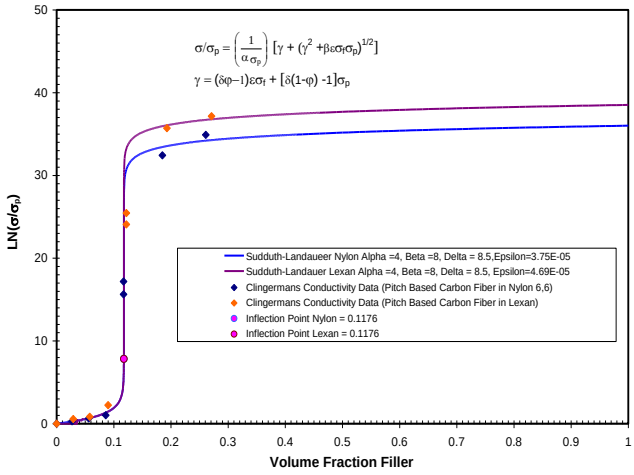

Fig. 7. Modified Landauer Model addressing Clingerman's Electrical Conductivity Data [**13**] for a Pitch Based Carbon Fiber in Nylon 6,6 and Lexan (with Permission).

Table 1. Modified Landauer Model Calculation Results for Carbon Fillers in Nylon 6,6 and Lexan (Using the Data of Clingerman [**13**] with Permission).

	Carbon Black in Nylon 6,6 Ketjenblack EC-600JD	Carbon Black in Lexan Ketjenblack EC-600JD	Pitch Based Carbon Fiber in Nylon 6,6 Thermograph DKD X	Pitch Based Carbon Fiber in Lexan Thermograph DKD X	Specialty Graphite in Nylon 6,6 Thermocarb TM CF-300	Specialty Graphite in Lexan Thermocarb TM CF-300
	Modified Landauer PT Model	Modified Landauer PT Model	Modified Landauer PT Model	Modified Landauer PT Model	Modified Landauer PT Model	Modified Landauer PT Model
Constant, α	4.0000	4.0000	4.0000	4.0000	4.0000	4.0000
Constant, β	8.0000	8.0000	8.0000	8.0000	8.0000	8.0000
Constant, δ	28.0000	28.0000	8.5000	8.5000	7.5000	7.5000
Efficiency Constant, ε	3.00E-01	4.00E-03	3.75E-05	4.69E-05	2.00E-08	1.00E-07
Ratio $1/\delta$	0.0357	0.0357	0.1176	0.1176	0.1333	0.1333
Percolation Threshold, φ_{ciMax}	0.0356	0.0356	0.1172	0.1172	0.1310	0.1310
Inflection Point, φ_{iP}	0.0357	0.0357	0.1176	0.1176	0.1330	0.1330
Maximum Conductivity, φ_{max}	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
Conductivity Ratio, σ_f / σ_p	1.4383E+18	1.4300E+19	3.0891E+19	3.0477E+20	1.4502E+21	1.4299E+22
Ln (σ_f / σ_p)	41.81	44.11	44.88	47.17	48.73	51.01

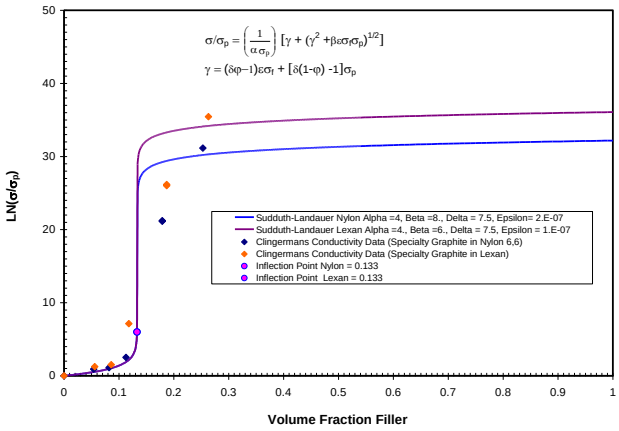

Fig. 8. Modified Landauer Model addressing Clingerman's Electrical Conductivity Data [**13**] for a Specialty Graphite in Nylon 6,6 and Lexan (with Permission).

A summary of the results in **Fig. 6-8** are shown in **Table 1**. The results in this Table yielded the following observations for the Modified Landauer Model:

- The value of δ was found to be the same for each carbon filler independent of whether the polymer used was Nylon 6,6 or Lexan
- The concentration at the inflection point, φ_{ip}, and extrapolated percolation threshold concentration, φ_{ciMax}, both approach a value of $\varphi \cong 1/\delta$ as the ratios of σ_f / σ_p increase when ($\alpha = 4.0$, $\beta = 8.0$).
- The equation constants and calculated results that increased in going from the carbon black to the specialty graphite in both Nylon 6,6 and Lexan included:
  - $1/\delta$ = Conductivity Percolation Threshold Upper Limit
  - φ_{ip} = Concentration at the inflection Point
  - φ_{ciMax} = Maximum Percolation Threshold Concentration
  - $Ln(\sigma_f/\sigma_p)$ = Ln(Maximum possible Conductivity Ratio)
- There is not a well defined maximum where the first derivative is equal to zero for the Modified Landauer Percolation Threshold Model.
- Three concurrent mathematical conditions found to occur at the same concentration included: the concentration at the Inflection Point, φ_{ip}, the concentration at the maximum slope, φ_{ip}, and the maximum extrapolated percolation threshold concentration, φ_{ciMax}, calculated at the same concentration, φ_{ip}.

In general, an inflection point must necessarily occur in S-shaped curves typically characteristic of electrical conductivity measurements of composites for models that cover the whole concentration Range. The concentration at this inflection point, φ_{ip}, for these S-shaped curves occurs when the second derivative is equal to zero or when $\frac{d^2 Ln(\sigma/\sigma_p)}{d\varphi^2} = 0$. For reference the first and second derivatives for the Sudduth Modified Landauer model have been generated in Appendix I. The maximum initial slope of the curve will also occur at the same concentration as the inflection point. In addition, a line through the concentration for the maximum slope also

yields the extrapolated maximum percolation threshold concentration, φ_{ciMax}, on the concentration axis.

The percolation threshold concentration is typically calculated by extrapolating a straight line at the initial maximum slope on the S-shaped conductivity curve back to the intercept on the concentration axis. As derived in Appendix II, the locus of points yielding these possible equations for the percolation threshold concentrations, φ_{ci}, are:

$$\varphi_{ci} = \varphi - \frac{Ln(\sigma/\sigma_p)}{dLn(\sigma/\sigma_p)/d\varphi} \quad (10)$$

or

$$\varphi_{ci} = \varphi - \frac{(\sigma/\sigma_p)Ln(\sigma/\sigma_p)}{d(\sigma/\sigma_p)/d\varphi} \quad (11)$$

Since both equations 10 and 11 are equivalent, it was found to be more convenient to use equation (11) to plot the locus of points for percolation Threshold using the Modified Landauer model to obtain the maximum percolation threshold concentrations as developed in Appendix II.

The results in **Figs. 6-8** indicate that the Sudduth Modified Landauer Model typically does an acceptable job of generally fitting Percolation Threshold data for electrical conductivity measurements for composites

Analysis utilizing the Sudduth Percolation Threshold Model

The previously published percolation threshold model developed by this author [**2**] was obtained from a refinement of Clingerman's model and yielded the following equation:

$$(\sigma/\sigma_p) = (\sigma_f/\sigma_p)^{\varepsilon F(\varphi)} \quad (12)$$

Equation (12) can then be rewritten as

$$Ln(\sigma/\sigma_p) = \varepsilon\, Ln(\sigma_f/\sigma_p)\, F(\varphi) \quad (13)$$

where

$$F(\varphi) = \left(\frac{\varphi}{\delta}\right)^{\frac{\beta}{\varphi^{\alpha}}} \quad (14)$$

Note that several constants in the function G(φ) from equations (1)-(4) were redefined as:

$$\alpha = n,\ \beta = K\varphi_c,\ \delta = F - \varphi_c$$

These constants were not only redefined they were also given the following new meanings in the new percolation threshold model:

α = Insulation Position Property

β = Insulation Surface Interaction Magnitude

δ = Conductivity Percolation Threshold Upper Limit

ε = Efficiency of Conductivity Conversion

σ_p = Conductivity of the base polymer or matrix

σ_f = Conductivity of the base filler

This new percolation threshold model as indicated in Fig. 5 was applied to the same data for the pitch based carbon fiber in nylon 6,6 from Clingerman's thesis [13] as shown previously in Fig. 3.

The results in **Figs. 9-11** have been generated utilizing the Sudduth Percolation Threshold Model to address Clingerman's electrical conductivity data. In **Fig. 9** Clingerman's data a carbon black Ketjenblack EC-600JD in both Nylon 6,6 and Lexan has been addressed. In **Fig. 10** Clingerman's data for a pitch based carbon fiber Thermograph DKD X in both Nylon 6,6 and Lexan has been addressed. And finally, in **Fig. 11** Clingerman's data for specialty graphite Thermocarb TM CF-300 in Nylon 6,6 and Lexan has been addressed.

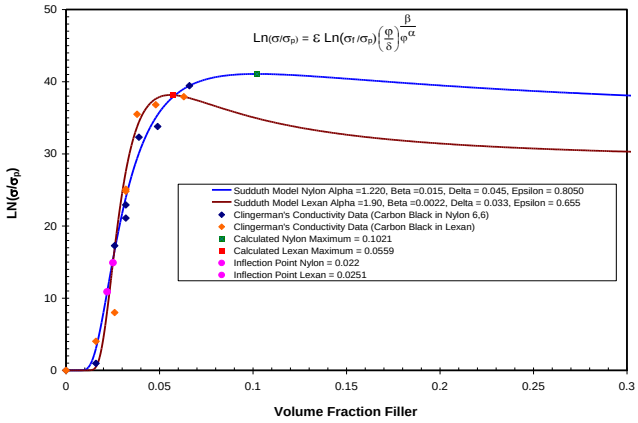

Fig. 9. Sudduth Percolation Threshold Model addressing Clingerman's Electrical Conductivity Data [**13**] for a Carbon Black in Nylon 6,6 and Lexan (with Permission).

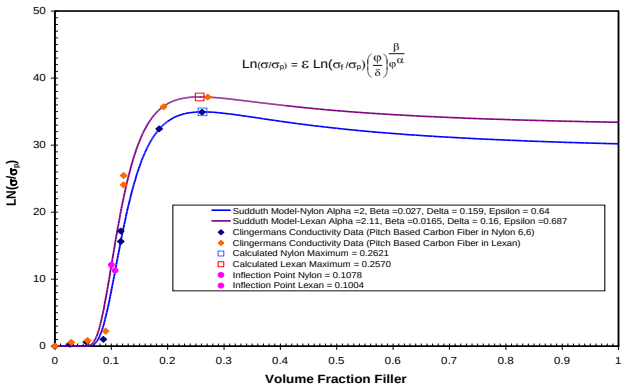

Fig. 10. Sudduth Percolation Threshold Model addressing Clingerman's Electrical Conductivity Data [**13**] for a Pitch Based Carbon Fiber in Nylon 6,6 and Lexan (with Permission).

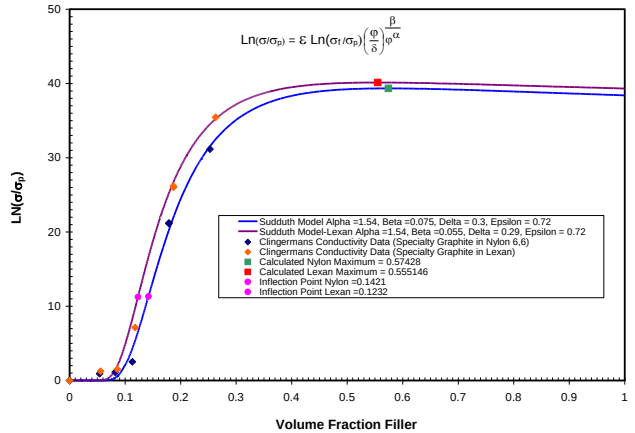

Fig. 11. Sudduth Percolation Threshold Model addressing Clingerman's Electrical Conductivity Data [**13**] for a Specialty Graphite in Nylon 6,6 and Lexan (with Permission).

Table 2. Sudduth Percolation Threshold Model Calculation Results for Carbon Fillers in Nylon 6,6 and Lexan (Using Clingerman's Data with Permission).

	Carbon Black in Nylon 6,6 Ketjenblack EC-600JD	Carbon Black in Lexan Ketjenblack EC-600JD	Pitch Based Carbon Fiber in Nylon 6,6 Thermograph DKD X	Pitch Based Carbon Fiber in Lexan Thermograph DKD X	Specialty Graphite in Nylon 6,6 Thermocarb TM CF-300	Specialty Graphite in Lexan Thermocarb TM CF-300
	Sudduth PT Model	Sudduth PT Model	Sudduth PT Model	Sudduth PT Model	Sudduth PT Model	Sudduth PT Model
Insulation Position Property, α	1.2200	1.9000	2.0000	2.1000	1.5400	1.5400
Insulation Surface Interaction Magnitude, β	0.0150	0.0022	0.0270	0.0165	0.0750	0.0550
Conductivity Percolation Threshold Upper Limit, δ	0.0450	0.0330	0.1590	0.1600	0.3000	0.2900
Efficiency of Conductivity Conversion, ε	0.8050	0.6550	0.6400	0.6870	0.7200	0.7200
Volume Fraction at Percolation Threshold, φ_{ciMax}	0.0145	0.0183	0.0817	0.0764	0.0985	0.0848
Volume Fraction at Inflection Point, φ_{IP}	0.0220	0.0242	0.1078	0.1004	0.1421	0.1232
Volume Fraction at Maximum Conductivity, φ_{max}	0.1021	0.0559	0.2621	0.2576	0.5743	0.5551
Max Conductivity Ratio, σ_f / σ_p	1.4383E+18	1.4300E+19	3.0891E+19	3.0477E+20	1.4502E+21	1.4300E+22
Ln(Max Conductivity Ratio), Ln (σ_f / σ_p)	41.8100	44.1068	44.8770	47.1661	48.7260	51.0145

A summary of the results in **Figs. 9-11** are shown in **Table 2**. The results in this Table yielded the following observations for the Sudduth Percolation Threshold Model:

- A well defined concentration at maximum conductivity, φ_{Max}, was found for the Sudduth Percolation Threshold Model where the first derivative was equal to zero. The concentration at maximum conductivity, φ_{Max}, was found to be nearly identical for each carbon filler independent of whether the polymer used was Nylon 6,6 or Lexan
- The concentration at the inflection point, φ_{ip}, and extrapolated percolation threshold concentration, φ_{ciMax}, both tended to approach a Maximum value of $\varphi \cong \delta$
- The equation constants and calculated results that increased in going from the carbon black to the specialty graphite in both Nylon 6,6 and Lexan included:
  - β = Insulation Surface Interaction Magnitude
  - δ = Conductivity Percolation Threshold Upper Limit
  - φ_{ciMax} = Maximum Percolation Threshold Concentration
  - φ_{ip} = Concentration at the inflection Point
  - φ_{Max} = Concentration at Maximum Conductivity
  - $Ln(\sigma_f/\sigma_p)$ = Ln(Maximum possible Conductivity Ratio)
- Three concurrent mathematical conditions that occurred at the same concentration included: the concentration at the Inflection Point, φ_{ip}, the concentration at the maximum slope, φ_{ip}, and the maximum extrapolated percolation threshold concentration, φ_{ciMax}, calculated at the same concentration, φ_{ip}.

The volume fraction at the inflection point, φ_{ip} , in Fig. 5 was generated by setting second derivative of equation (13) equal to zero. The second derivative of equation (13) has been generated in Appendix III as indicated by equation (C-6). The location of the inflection point as indicated in the appendix must be solved by trial and error using the following equations.

$$\left(\frac{z^2}{(\varphi)^{\alpha}}\right) - z(\alpha + 1) - \alpha = 0 \qquad (15)$$

where

$$z = \left(1 - \alpha Ln\left(\frac{\varphi}{\delta}\right)\right) \qquad (16)$$

The volume fraction of the inflection point indicated in Fig. 5 has also been included for reference in **Table 2**. The maximum extrapolated percolation threshold concentration, φ_{ciMax}, is also calculated at the volume fraction of the inflection point, φ_{ip}. In general, the projected intercept or the projected percolation threshold, φ_{ci}, on the concentration axis has been generated in appendix II and yielded the following equation:

$$\varphi_{ci} = \varphi - \frac{Ln(\sigma/\sigma_p)}{dLn(\sigma/\sigma_p)/d\varphi} \qquad \text{B-3}$$

Substituting the appropriate values from Appendix III into equation B-3 yields

$$\varphi_{ci} = \varphi - \left(\frac{1}{\beta}\right)\left(\frac{\varphi^{\alpha+1}}{1 - \alpha Ln\left(\frac{\varphi}{\delta}\right)}\right) \qquad (17)$$

The results in **Fig. 12** were generated using equation 17 to yield the maximum percolation Threshold volume fraction of φ_{ciMax} = 0.08169 utilizing an analysis of the data shown in **Fig. 5**. The volume fraction for the percolation threshold, φ_{ciMax}, from **Fig. 12** has also been included in **Table 2**.

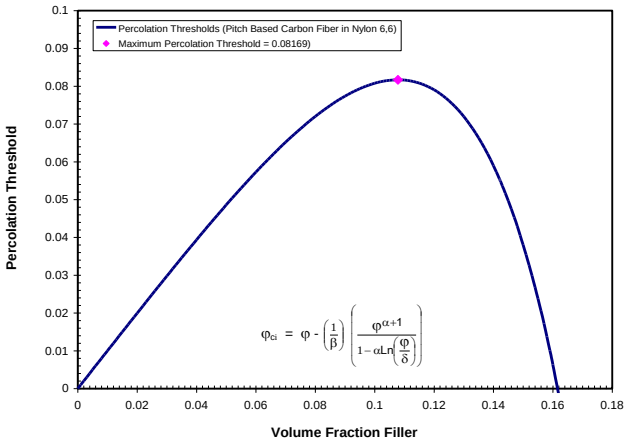

Fig. 12. Sudduth Percolation Threshold Plot addressing Clingerman's Electrical Conductivity Data [**13**] for a Pitch Based Carbon Fiber in Nylon 6,6.

At this point it is useful to note that F(φ) described by equation (14) can also be separated into a conductive component and an insulation component.

$$F(\varphi) = \left(\frac{\varphi}{\delta}\right)\frac{\beta}{\varphi^{\alpha}} \quad (14)$$

The conductive component can be described as

$$F_{Conductivity}(\varphi) = \left(\frac{\varphi}{\delta}\right) \quad (18)$$

And the insulation component can be described as

$$F_{Insulation}(\varphi) = \frac{\beta}{(\varphi)^{\alpha}} \quad (19)$$

These three functions are plotted in **Fig. 13** with the constants α, β, δ and ε set at the same values as the results plotted in Fig. 5. Note in **Fig. 13** that the conductivity component, $F_{Conductivity}(\varphi)$, is a straight line with slope (1/δ) that increases linearly with concentration of the filler while the insulation component, $F_{Insulation}(\varphi)$, decreases exponentially with an increase in filler concentration. Note that as long as the concentration of filler is less than δ then the conductivity component will be a fraction less than 1. This means that as long as the insulation component, $F_{Insulation}(\varphi)$, is a large number as well as an exponent for the conductive component, $F_{Conductivity}(\varphi)$, that the combination described as function F(φ) will generate a very small number essentially approaching zero. However, once the concentration exceeds the value of δ then the conductivity component, $F_{Conductivity}(\varphi)$, will no longer be a fraction less than 1 and the conductive component will continue to increase significantly while the insulation component will more rapidly approach zero forcing the combination of the two to cause the function F(φ) to approach the value of one.

Note that the function F(φ) described by equation (14) also has several interesting but important limits. If α > 0, β > 0 and δ > 0 then the function F(φ) has the following limits:

$$\varphi \rightarrow 0 \text{ then } F(\varphi) \rightarrow 0 \text{ and } (\sigma/\sigma_p) = 1.0 \text{ and } \sigma = \sigma_p \quad (20)$$

$$\varphi = \delta \text{ then } F(\varphi) = 1.0 \text{ and } Ln(\sigma/\sigma_p) = \varepsilon\, Ln(\sigma_f/\sigma_p) \quad (21)$$

$$\varphi = \varphi_{max} = \delta e^{(1/\alpha)} \text{ then } F_{max}(\varphi) = \left(e^{1/\alpha}\right)^{\beta/e\delta^{\alpha}} \geq 1 \quad (22)$$

$$\varphi \rightarrow \infty \text{ then } F(\varphi) \rightarrow 1.0 \text{ and } Ln(\sigma/\sigma_p) = \varepsilon\, Ln(\sigma_f/\sigma_p) \quad (23)$$

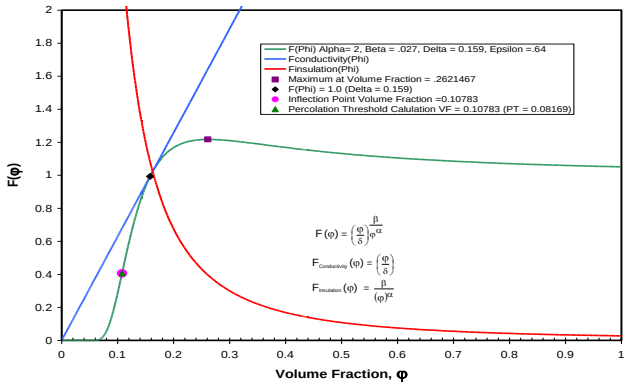

Fig. 13. Sudduth F(φ) Model addressing Clingerman's Electrical Conductivity Data [**13**] for a Pitch Based Carbon Fiber in Nylon 6,6.

Evaluation of the Predicted Maximum Packing Fraction Based on the Shape of Carbon Fillers Using the New Percolation Threshold Model

The volume fraction for which equation (13) yields the maximum conductivity can be easily generated from the first derivative indicated as equation (C-3) in the Appendix III. Setting this equation to zero and solving yields a maximum volume fraction at:

$$\varphi_{max} = \delta e^{(1/\alpha)} \quad (24)$$

The volume fraction at the maximum, φ_{max}, calculated from the results in Fig. 5 yielded a value of $\varphi_{max} = 0.2621$. This volume fraction at the maximum has been included in Table 2 along with the other calculated values from Fig. 5.

The surface to volume ratio of each particle in a composite has been identified previously [**19,20**] to be the most important consideration when generating its maximum random packing fraction as indicated in **Fig. 14** and **Fig. 15**. Typically, the larger the surface to volume ratio for a particle as described by its "sphericity" as indicated in **Fig. 14** then the lower the volume fraction for the maximum random packing fraction. Consequently, a more general model has been developed [**19,20**] that addresses the random packing fraction of fibers as well as discs as shown in **Fig. 15** using the "sphericity" as described in **Fig. 14**. Also note that **Fig. 15** also includes data from German [**21**] and Milewski [**22**] who actually physically measured values of the maximum random packing fraction for several fibers and discs of different aspect ratios. Once the volume fraction of a particle exceeds its maximum random packing fraction then Flory [**23**] points out that the particles with high aspect ratios like fibers must necessarily begin to orient to allow more fibers to contribute to the packing fraction. Consequently, after the maximum random packing fraction has been reached, then the overall packing fraction often begins to drop until the oriented fibers get close enough to each other to begin to allow an increase the packing fraction again.

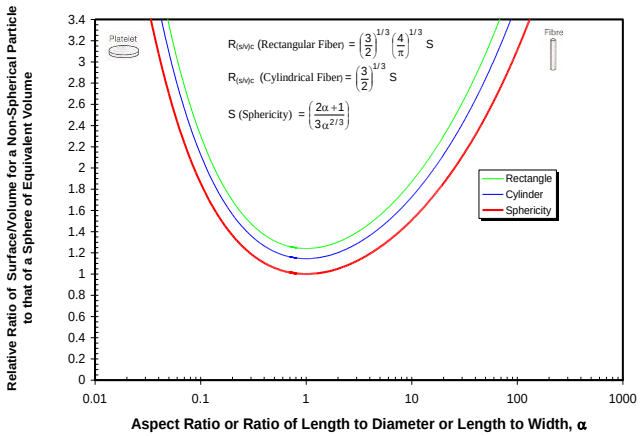

Fig. 14. Relative Ratio of Surface to Volume Fraction for a Non-Spherical Particle to that of a Sphere of Equivalent Volume as a Function of Aspect Ratio [**19**].

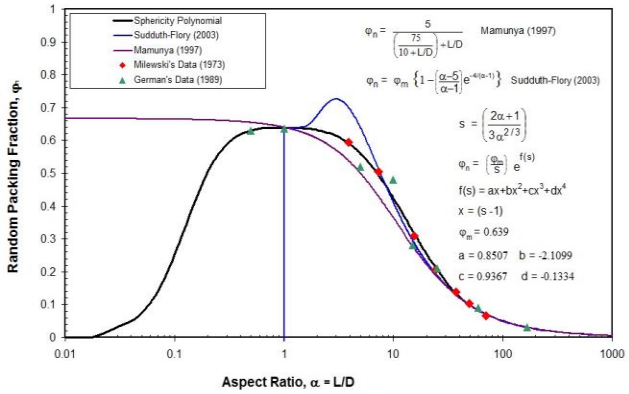

Fig. 15. Theoretical and Measured Random Packing Fractions for Cylindrical Fibers Modeled as a Function of Sphericity but Plotted as a Function of Aspect Ratio [**19**].

While several models have been addressed in the literature to predict the maximum random packing fraction of different particle shapes as a function of aspect ratio [**15,19,23-26**] only two of these models [**15,19**] have been included in **Fig. 15**.

It is interesting that the volume fractions yielding maximum conductivity as calculated by equation (24) and summarized in Table 2 appear to yield nearly identical values for the same carbon filler with two different polymers as the matrix.

A comparison of these calculated maximums to the maximum random of the packing fraction for the same fillers based on their aspect ratios is shown in **Table 3**. The results in **Table 3** have been addressed in two ways. First the aspect ratio of the fillers have been calculated from their calculated concentrations giving the maximum conductivities. The second approach was to use the measured aspect ratio measured for the carbon fillers and then using the models in **Fig. 15** to calculate their estimated random packing fraction.

For reference, Clingerman measured an aspect ratio of 16 for the carbon fiber and an aspect ratio for the speciality carbon to be approximately 3. In general, there was an excellent relative agreement within experimental error in comparing the measured concentration for the maximum conductivity and the maximum random packing fraction for both the specialty carbon and the carbon fiber.

Unfortunately, Clingerman was not able to measure an aspect ratio for the carbon black.

However, the masters thesis of Geraedts [**27**] did provide a strong indication as indicated in **Table 4** that the carbon black Ketjenblack EC-600JD does appear to have a larger surface to volume ratio than the other carbon blacks evaluated by Geraedits [**27**]. There is a further indication in Geraedits thesis that this carbon black can separate into different disk like plates with a very high surface to volume ratio. Consequently, this carbon black then would be expected to have the very low random packing fraction as was found.

Table 4. Characteristics of Some Carbon Black Powders (From Geraedts [**27**] with Permission).

Carbon Black	Manufacturer	BET (m^2/g)	Particle Diameter (nm)	Application
Printex 30	Degussa	80	27	Printing Inks
Printex XE-2	Degussa	950	30	Electrical Conductive Coatings and Plastics
Ketjenblack EC 600JD	Akzo Nobel	1250	30	Electrical Conductive Coatings and Plastics

Table 3. Maximum Random Packing Fractions and Predicted Aspect Ratios.

	Carbon Black in Nylon 6,6 Ketjenblack EC-600JD	Carbon Black in Lexan Ketjenblack EC-600JD	Pitch Based Carbon Fiber in Nylon 6,6 Thermograph DKD X	Pitch Based Carbon Fiber in Lexan Thermograph DKD X	Specialty Graphite in Nylon 6,6 Thermocarb TM CF-300	Specialty Graphite in Lexan Thermocarb TM CF-300
	Sudduth PT Model	Sudduth PT Model	Sudduth PT Model	Sudduth PT Model	Sudduth PT Model	Sudduth PT Model
Volume Fraction at Maximum Conductivity, φ_{max}	0.1021	0.0559	0.2621	0.2576	0.5743	0.5551
Sudduth Aspect Ratio, Length/Diameter --- Fiber	48.17	85.77	19.40	19.79	4.51	5.18
Mamunya Aspect Ratio, Length/Diameter --- Fiber	47.67	88.70	16.21	23.36	2.89	3.42
Sudduth Aspect Ratio, Diameter/Length --- Disc	16.85					
Clingerman Measured Average Aspect Ratio			16	16	3	3
Sudduth Fraction--- Fiber			0.3084	0.3084	0.6134	0.6134
Mamunya Fraction --- Fiber			0.2648	0.2648	0.5702	0.5702

In any case it was some what surprising that the concentration for maximum conductivity indicated by equation (25) resulting from the Sudduth Percolation Threshold model also appears to yield values close to the maximum random packing fraction for each type of particle being evaluated.

Evaluation of the Interfacial Surface Energy of Additional Carbon Fillers in both Nylon 6,6 and Lexan Using the New Percolation Threshold Model

As indicated earlier both Mamunya [**15,16**] and Clingerman [**10,13,14**] have suggested that their value of $K\varphi_c$ should have some functional relationship with the interaction surface energy, γ_{pf}. Since the value of β in the model developed by this author has been modified directly from the value of $K\varphi_c$ as originally proposed by Mamuny and Clingerman, then there would be some expectation that the value of β should directly relate to the value of the interaction surface energy, γ_{pf}, as well. This proposition was then addressed using the very useful surface energy data generated in Clingerman's thesis [**13**].

Table 5. Clingerman's Measurements of Surface Energy of Carbon Fillers and Polymers.

Material Name	Common Name	Materials State	Polar Component mJ/m^2	Dispersive Component mJ/m^2	Total Surface Energy mJ/m^2
Zytel 101 NC010	Nylon 6,6	Solid	2.42	42.21	44.64
Zytel 101 NC010	Nylon 6,6	Melt	17.24	28.68	45.92
Lexan HF 1110-111N	Polycarbonate	Solid	1.97	38.26	40.23
Lexan HF 1110-111N	Polycarbonate	Melt	8.55	29.50	38.05
Ketjenblack EC-600JD	Carbon Black	Powder	2.18	19.59	21.77
Thermograph DKD X	Carbon Fiber	Powder	3.99	20.01	24.00
Thermocarb TM CF-300	Synthetic Graphite	Powder	5.47	16.76	22.23

Clingerman [**13**] evaluated the surface energies of the different components of the carbon fillers as well as the polymers separately as summarized in **Table 5**. In addition, the three different approaches to calculating the interaction surface energies evaluated in this study have been summarized in **Table 6**. The first approach indicated in **Table 6** is the classic approach originally proposed by Fowkes [**17**]. The second approach indicated in Table 6 was the one proposed by Mamunya [**15,16**]. The third approach in **Table 6** was originally proposed by Owens, and Wendt [**29**] but utilized more recently by Clingerman *et al.*, [**13,14**].

Table 6. Equations for Calculating the Interfacial Surface Energy.

Equation	Author
$\gamma_{pf} = \gamma_p + \gamma_f - 2(\gamma_p^d \gamma_f^d)^{0.5}$	Fowkes[17] (1964)
$\gamma_{pf} = \gamma_p + \gamma_f - 2(\gamma_p \gamma_f)^{0.5}$	Mamunya[15,16] (1997&1999)
$\gamma_{pf} = \gamma_p + \gamma_f - 2(\gamma_p^d \gamma_f^d)^{0.5} - 2(\gamma_p^p \gamma_f^p)^{0.5}$	Owens and Wendt[28] (1997) & Clingerman[13,14] (2001 & 2003)

where
γ_p = Polymer surface tension
γ_f = Filler surface tension
γ_{pf} = Interfacial surface tension
γ_p^d = Dispersive component of the polymer surface tension
γ_f^d = Dispersive component of the filler surface tension
γ_p^p = Polar component of the polymer surface tension
γ_f^p = Polar component of the filler surface tension

The results calculated in **Table 7** have utilized the equations in Table 6 as well as the data generated by Clingerman [**13**] indicated in Table 5. The results in **Table 7** clearly show that the most consistent correlations were obtained between the Fowkes [**17**] interaction surface energies and both the Insulation Surface Interaction Magnitude, β, and the calculated concentration at maximum conductivity, φ_{max}.

Table 7. Surface energy calculations.

Composites	State	Beta Values	Maximum Volume Fraction	Ln(Cond Ratio), $Ln(\sigma_f/\sigma_p)$	Fowkes mJ/m^2	Mamunya mJ/m^2	Owens and Wendt mJ/m^2
Carbon Black in Nylon 6,6	Solid	0.015	0.1021	41.81	8.8985	4.0622	4.3047
Carbon Fiber in Nylon 6,6	Solid	0.027	0.2621	44.88	10.5152	3.1767	4.3005
Synthetic Carbon in Nylon 6,6	Solid	0.075	0.5743	48.73	13.6745	3.8669	6.3979
Carbon Black in Lexan	Solid	0.0022	0.0559	44.11	7.2455	2.8119	3.1008
Carbon Fiber in Lexan	Solid	0.0165	0.257	47.17	8.8917	2.0844	3.2844
Synthetic Carbon in Lexan	Solid	0.055	0.5551	51.02	11.8147	2.6499	5.2493
Carbon Black in Nylon 6,6	Melt	0.015	0.1021	41.81	20.2836	4.4546	8.0226
Carbon Fiber in Nylon 6,6	Melt	0.027	0.2621	44.88	22.0081	3.5248	5.4205
Synthetic Carbon in Nylon 6,6	Melt	0.075	0.5743	48.73	24.3013	4.2500	4.8794
Carbon Black in Lexon	Melt	0.0022	0.0559	44.11	11.7407	2.2579	3.1061
Carbon Fiber in Lexan	Melt	0.0165	0.257	47.17	13.4580	1.6116	1.7765
Synthetic Carbon in Lexan	Melt	0.055	0.5551	51.02	15.8089	2.1129	2.1314

The results for both the melt evaluations and the solid evaluations indicated in **Table 7** have been plotted in **Fig. 16** and **Fig. 17** respectively. The results for the melt calculations in Figure 16 show two different straight lines for Nylon 6,6 and Lexan with the Fowkes interfacial surface energy as a function of β. However, the plot of the Fowkes interaction surface energies for both the solid calculations for both Nylon 6,6 and Lexan yielded an effective combined straight line with insulation surface interaction magnitude, β.

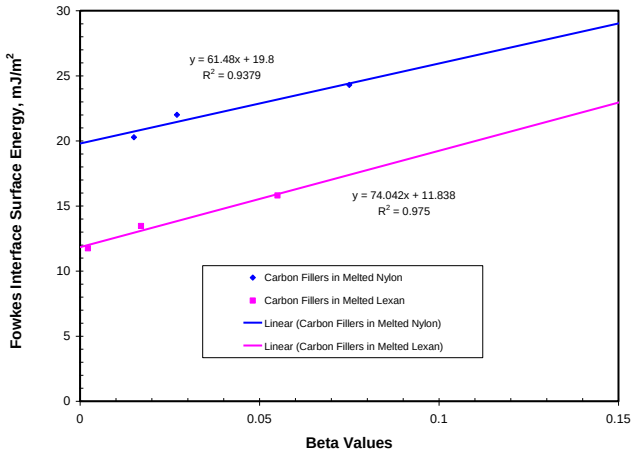

Fig. 16. Fowkes Interfacial Surface Energy vs Beta Values for Carbon Fillers in Melted Nylon and Lexan.

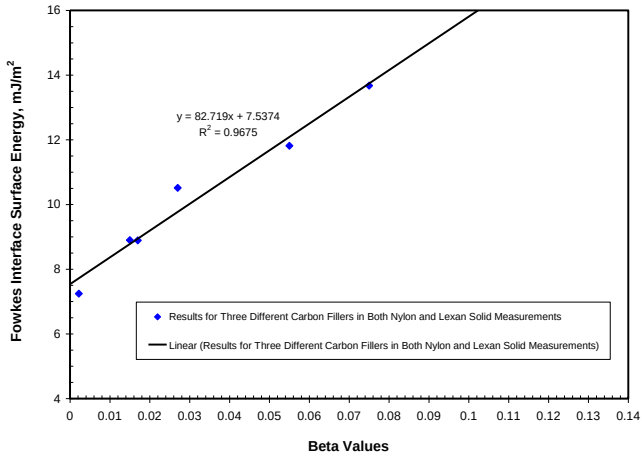

Fig. 17. Fowkes Interfacial Surface Energy vs Beta Values for Carbon Fillers in Solid Nylon 6,6 and Lexan.

Also note from the results in **Table 7** that there appears to be a strong direct correlation between the insulation surface interaction magnitude, β, and the concentration at the maximum conductivity, φ_{max}, as indicated in **Fig. 18**.

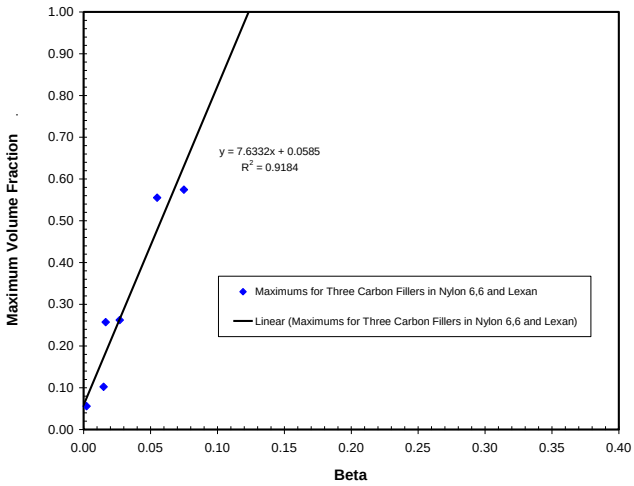

Fig. 18. Maximums for the Sudduth Percolation Threshold Model for Three Carbon Fillers in Nylon 6,6 and Lexan vs Beta Constants.

Table 8. Comparison of Maximum Percolation Threshold, φ_{ciMax}, Vs Fowkes Interfacial Surface Energy, γ_{pf}.

Composites	State	Sudduth PT Model Maximum Percolation Threshold, φ_{ciMax}	Sudduth-Landauer Maximum Percolation Threshold, φ_{ciMax}	Fowkes mJ/m^2, γ_{pf}
Carbon Black in Nylon 6,6	Solid	0.0145	0.0356	8.8985
Carbon Fiber in Nylon 6,6	Solid	0.0817	0.1172	10.5152
Synthetic Carbon in Nylon 6,6	Solid	0.0985	0.131	13.6745
Carbon Black in Lexan	Solid	0.0183	0.0356	7.2455
Carbon Fiber in Lexan	Solid	0.0764	0.1172	8.8917
Synthetic Carbon in Lexan	Solid	0.0848	0.131	11.8147

The results in **Table 8** as shown in **Fig. 19** and **Fig. 20** indicate that for the models addressed in this study a relationship does appear to exist between the maximum percolation thresholds, φ_{ciMax}, and the Fowkes interaction surface energies, γ_{pf}, as originally implicated by Miyaska, *et al.*, [**1**]. However, the relationships indicated in **Fig. 19** and **Fig. 20** do not appear to be linear.

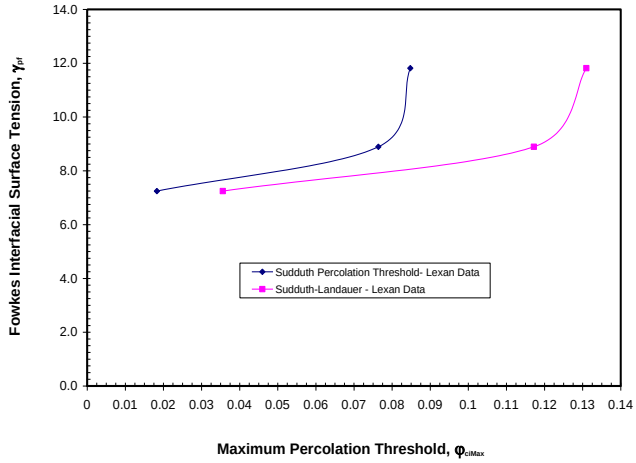

Fig. 19. Fowkes Interfacial Surface Energy, γ_{pf} Vs Maximum Percolation Threshold, φ_{ciMax}, in Lexan.

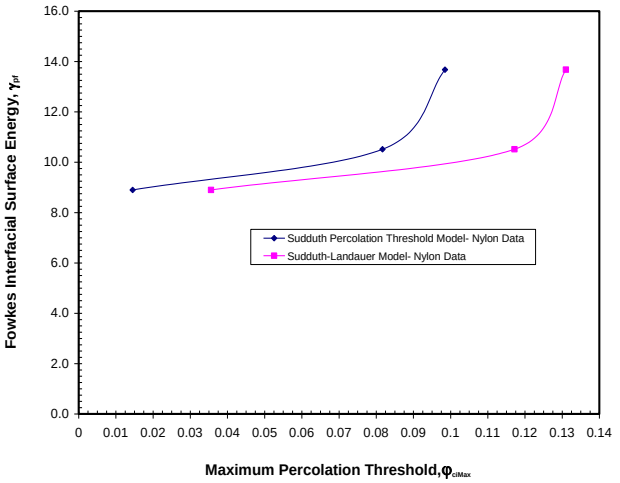

Fig. 20. Fowkes Interfacial Surface Energy, γ_{pf} Vs Maximum Percolation Threshold, φ_{ciMax}, in Nylon 6,6.

Finally, it appears to be conclusive that the insulation surface interaction magnitude, β, from the new percolation threshold model developed by this author does appear to have a strong primarily linear relationship to Fowkes interaction surface energies, γ_{pf} , for solid surface energy measurements

Conclusions

Of the three different approaches used in calculating the interaction surface energies only the interfacial surface energies calculated using Fowkes equation gave the most consistent results. In addition, the solid evaluations used in calculating the Fowkes interaction surface energies, γ_{pf}, gave just one consistent linear correlation with the β constant from the Percolation Threshold Model previously published by this author. This correlation worked well for all the data evaluated for both Nylon 6,6 and Lexan.

It was found that the previously published percolation threshold model fit the data extremely well over the whole concentration range for all six sets of data sets evaluated. The electrical conductivity data evaluated in this study included composites prepared from both Nylon 6,6 and Lexan and formulated with a carbon black, a pitch based carbon fiber, and a specialty graphite.

The new Landauer model modified introduced in this study was also able to give a reasonably good fit of all the data addressed in this study over the whole concentration range.

A direct linear correlation was also found between the calculated concentration at the maximum conductivity, φ_{max}, with the insulation surface interaction magnitude, β.

The Maximum Percolation Threshold concentration, φ_{ciMax}, did increase with an increase in the Fowkes interfacial Surface Energy, γ_{pf}, for both the new Percolation Threshold Model developed by this author and the Modified-Landauer Model. However, the correlations were not linear.

Three concurrent mathematical conditions were found to occur at the same concentration for percolation threshold S-shaped curves. These conditions include the Inflection Point, the maximum slope and the maximum extrapolated percolation threshold concentration calculated at the same concentration.

One extraordinary characteristic of the Sudduth Percolation Threshold model is that it is possible to evaluate as separate equations both the conducting filler component and the insulating matrix component. In general it was found that the conductivity component, $F_{Conductivity}$ (φ), is a straight line with slope ($1/\delta$) that increases linearly with concentration of the filler while the insulation component, $F_{Insulation}$ (φ), decreases exponentially with an increase in filler concentration.

In general, the percolation threshold models addressed in this study introduced several new quantities that are expected enhance the understanding of the percolation threshold process.

This study also confirmed that the concentration, φ_{max}, at maximum conductivity from the S-shaped percolation threshold curve for electrical conduction measurements is most likely the maximum random packing fraction for the conductive particle in the formulation.

Appendix I

Landauer percolation threshold model:

$$\sigma/\sigma_p = (1/4\sigma_p)[\gamma + (\gamma^2 + 8\sigma_f\sigma_p)^{1/2}] \quad \text{A-1}$$

$$\gamma = (3\varphi - 1)\sigma_f + [3(1-\varphi) - 1]\sigma_p \quad \text{A-2}$$

$$\frac{d(\sigma/\sigma_p)}{d\varphi} = \left(\frac{3\sigma_f - 3\sigma_p}{4\sigma_p}\right)[1 + \gamma(\gamma^2 + 8\sigma_f\sigma_p)^{-1/2}] \quad \text{A-3}$$

$$\frac{d^2(\sigma/\sigma_p)}{d\varphi^2} = (\sigma_f - \sigma_p)^2\left(\frac{18\sigma_f}{(\gamma^2 + 8\sigma_f\sigma_p)^{3/2}}\right) \quad \text{A-4}$$

$$Ln(\sigma/\sigma_p) = Ln\{(1/4\sigma_p)[1 + (\gamma^2 + 8\sigma_f\sigma_p)^{1/2}]\} \quad \text{A-5}$$

The first derivative gives

$$\frac{dLn(\sigma/\sigma_p)}{d\varphi} = \left(\frac{1}{(\sigma/\sigma_p)}\right)\frac{d(\sigma/\sigma_p)}{d\varphi} \quad \text{A-6}$$

The second derivative gives

$$\frac{d^2Ln(\sigma/\sigma_p)}{d\varphi^2} = -\left(\frac{1}{(\sigma/\sigma_p)^2}\right)\left(\frac{d(\sigma/\sigma_p)}{d\varphi}\right)^2 + \left(\frac{1}{(\sigma/\sigma_p)}\right)\frac{d^2(\sigma/\sigma_p)}{d\varphi^2} \quad \text{A-7}$$

Appendix II

A straight line through the point at φ will have the following equation

$$Ln(\sigma/\sigma_p)(\varphi) = (Slope(\varphi))\varphi + Intercept(\varphi) \quad \text{B-1}$$

When $Ln(\sigma/\sigma_p)(\varphi) = 0$,

Then the Projected Percolation Threshold, φ_{ci}, on the concentration axis can be calculated at each point as

$$\varphi_{ci} = -\frac{Intercept(\varphi)}{(Slope(\varphi))} = \frac{(Slope(\varphi))\varphi - Ln(\sigma/\sigma_p)(\varphi)}{(Slope(\varphi))} = \varphi - \frac{Ln(\sigma/\sigma_p)(\varphi)}{(Slope\ (\varphi))} \quad \text{B-2}$$

Hence

$$\varphi_{ci} = \varphi - \frac{Ln(\sigma/\sigma_p)}{dLn(\sigma/\sigma_p)/d\varphi} \quad \text{B-3}$$

or

$$\varphi_{ci} = \varphi - \frac{(\sigma/\sigma_p)Ln(\sigma/\sigma_p)}{d(\sigma/\sigma_p)/d\varphi} \quad \text{B-4}$$

Where

σ = Conductivity of composite at volume fraction φ

σ_p = Conductivity of the base polymer or matrix

φ = Volume fraction of filler

φ_{ci} = Projected Percolation Threshold on the concentration axis

φ_{ciMax} = Maximum Projected Percolation Threshold on the concentration axis

Appendix III

Sudduth Percolation Threshold Model

$$Ln(\sigma/\sigma_p) = \varepsilon\, Ln(\sigma_F/\sigma_p)\left(\frac{\varphi}{\delta}\right)^{\frac{\beta}{\alpha}} \quad \text{C-1}$$

The first derivative yields

$$\frac{dLn(\sigma/\sigma_p)}{d\varphi} = \varepsilon\, Ln(\sigma_F/\sigma_p)\left(\frac{\beta}{(\varphi)^{\alpha+1}}\right)\left(\frac{\varphi}{\delta}\right)^{\frac{\beta}{\alpha}}\left(1 - \alpha Ln\left(\frac{\varphi}{\delta}\right)\right) \quad \text{C-2}$$

$$\frac{dLn(\sigma/\sigma_p)}{d\varphi} = Ln(\sigma/\sigma_p)\left(\frac{\beta}{(\varphi)^{\alpha+1}}\right)\left(1 - \alpha Ln\left(\frac{\varphi}{\delta}\right)\right) \quad \text{C-3}$$

Let

$$z = \left(1 - \alpha Ln\left(\frac{\varphi}{\delta}\right)\right) \quad \text{C-4}$$

The second derivative yields

$$\frac{d^2 Ln(\sigma/\sigma_p)}{d\varphi^2} = \varepsilon Ln(\sigma_F/\sigma_p)\left(\frac{\beta}{(\varphi)^{\alpha+2}}\right)\left(\frac{\varphi}{\delta}\right)^{\kappa}\left(z^2\left(\frac{\beta}{(\varphi)^{\alpha}}\right) - z(\alpha+1) - \alpha\right) \quad \text{C-5}$$

$$\frac{d^2 Ln(\sigma/\sigma_p)}{d\varphi^2} = Ln(\sigma/\sigma_p)\left(\frac{\beta}{(\varphi)^{\alpha+2}}\right)\left(z^2\left(\frac{\beta}{(\varphi)^{\alpha}}\right) - z(\alpha+1) - \alpha\right) \quad \text{C-6}$$

Keywords

Electrical conductivity, carbon black, nylon 6,6, lexan, carbon filled composite, percolation threshold.

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