

# Fluorinated and Engineering Thermoplastics with Carbon Nano Structures for Wire and Cable Claddings

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## Abstract

The wire and cable industry has long understood the benefits of conductive claddings for anti-static, shielding and trace-cable applications. A new entry into the field is carbon nanostructures (CNS). CNS has significant efficiency advantages over carbon black pigments. CNS yields large conductivity gains at low loadings (under 2% by weight) in most melt-processable polymers. Additionally, CNS may offer improvements in tensile strength and flexural modulus values versus conductive carbon blacks.

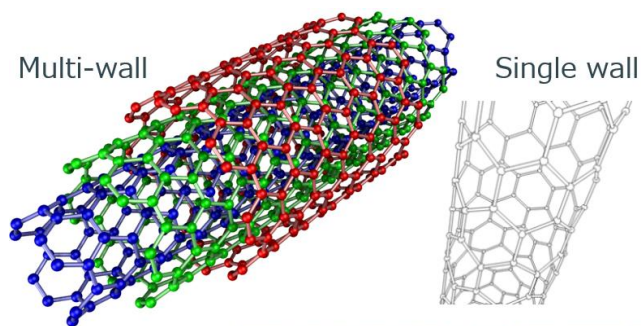
In this paper we discuss the use of CNS with fluoropolymers and PEEK to produce experimental conductive claddings with enhanced durability and resistance to high service temperatures. The experimental materials were compounded on twin-screw extruders, then tested for electrical and physical properties to ensure efficacy.

The compounds produced in these experiments were “ready-to-use” compounds, in which the CNS was incorporated at loading levels typical of end uses in the wire and cable industry. Another approach involves creation of masterbatches at maximum CNS loadings so that end users could adjust CNS contents as required. AGC’s team plans to evaluate the efficacy of the latter method as part of further studies with CNS.

**Keywords:** Trace cables; anti-static; conductive claddings; carbon nano structures; nanotechnology; shielding; fluoropolymers; ETFE; PFA; PEEK

## 1. Introduction

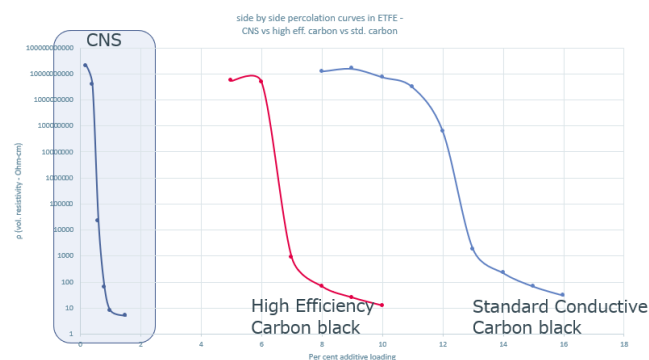
Carbon nanostructures (CNS) are engineered forms of carbon dating back to nineteenth century efforts to develop carbon-based incandescent filaments [1]. The filaments were not recognized as tubular forms of carbon until the advent of transmission electron microscopy and some pioneering work by Russian scientists proved their nature (1952) [2]. Research began in earnest after Iijima’s articles about practical synthesis methods for single- and multi-wall carbon nanotubes [3] and potential applications for same [4].



[https://en.wikipedia.org/wiki/Carbon\\_nanotube](https://en.wikipedia.org/wiki/Carbon_nanotube)

**Figure 1: Carbon Nano-Structures (CNS)**

Carbon nanostructures hold considerable promise as fillers and reinforcement materials for thermoplastics. Firstly, CNS materials are heat and chemical resistant, allowing their use in difficult environments. Secondly, the graphitic structure of CNS induces electrical conductivity at much lower loading levels than conventional pro-conductive fillers (such as conductive carbon blacks – see Figure 2). Lastly, the long chain length and rigid covalent carbon-carbon matrix allows CNS to provide considerable strengthening and stiffening reinforcement to thermoplastic materials.



**Figure 2: Percolation curves - CNS vs. High Efficiency Carbon Black vs. Standard Carbon Black**

## 2. Experimental

Trial compounds were produced, using twin-screw compounding extruders at AGC Chemicals Americas Exton and AGC Chemicals Americas Thorndale. (Conditions used are proprietary to AGC Chemicals Americas.) Raw ingredients (polymers and the CNS filler) were added at the extruder throat using loss-in-weight

feeders. Extruded strands were collected after cooling and tested for volume resistivity, using a Keithley 6917A electrometer.

The compounds were pelletized, then injection-molded into ASTM D638 (Type I) tensile bars and ASTM D790 flex bars for evaluation of physical properties (Instron).

The compounds were tested for viscoelastic properties on an extrusion plastometer (MFR) and capillary rheometer. Results were examined for trends, using MINITAB statistical software.

## 3. Results

### 3.1 Volume Resistivity

CNS proved to be highly efficient in reducing the volume resistivity of PFA- and ETFE-based compounds. Results indicated that the low MFR ETFE achieved volume resistivity under 50 ohm-cm at approximately 1.2% to 1.5% by weight loading.

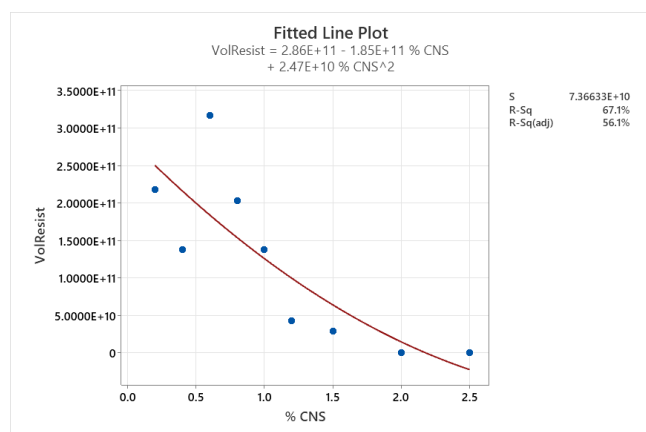


Figure 3: Volume resistivity (ohm-cm) vs. % CNS in low MFR ETFE

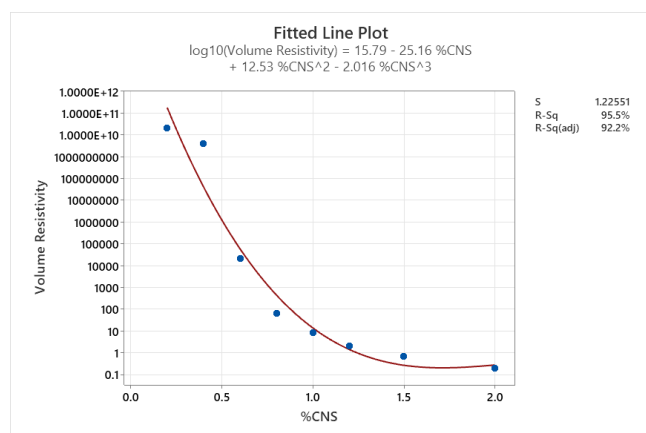


Figure 4: Volume resistivity (ohm-cm) vs. % CNS for medium MFR PFA

Similarly, the medium MFR PFA attained low volume resistivity (under 50 ohm-cm) at 1.0% to 1.2% loading by weight.

### 3.2 Tensile properties

Effects of CNS were pronounced on tensile and elongation properties of resultant ETFE- and PFA-based compounds.

For the low MFR ETFE, tensile strength (measured as peak stress; ASTM D638) was enhanced by approximately 10% through incorporation of 1% of the CNS. Higher CNS loadings resulted in higher gains in tensile strength – up to 45% at 2.5% loadings by weight (Figure 5) – but the gains were offset by substantial decreases in elongations at break (~50% and ~87% for 1% and 2.5% CNS loadings, respectively). See Figure 6.

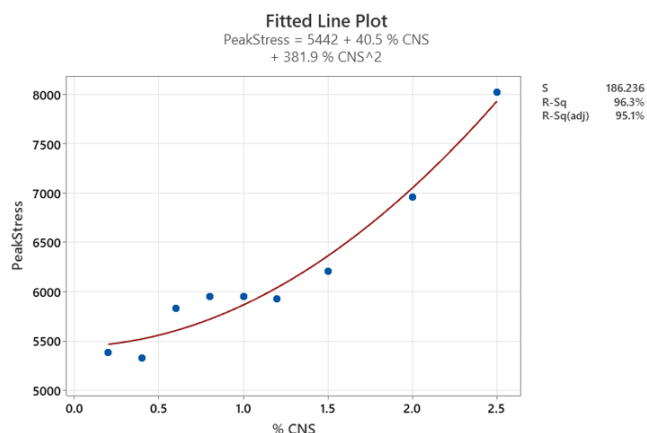


Figure 5: Peak Stress vs. % CNS for low MFR ETFE

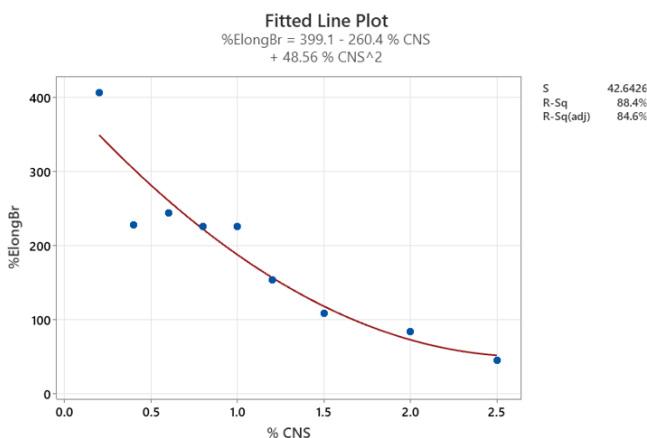


Figure 6: % Elongation at Break vs % CNS for low MFR ETFE

Enhancements in tensile strength were more substantial for medium MFR PFA (~ 54% at 1.0% CNS loading; ~65% at 2.5% CNS), likely due to low tensile strength (for PFA, relative to ETFE) in the base material. See figure 5.

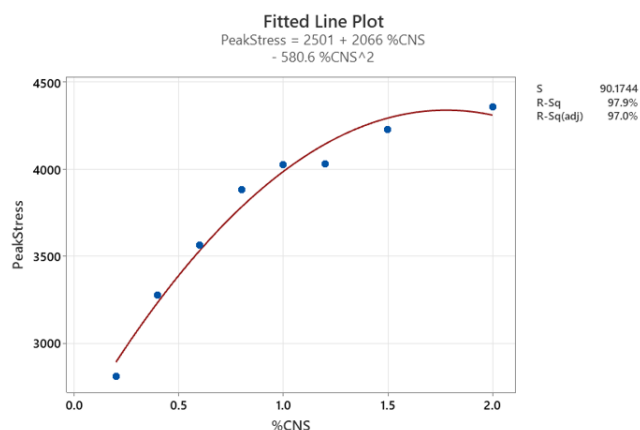


Figure 7: Tensile Strength vs. % CNS for medium MFR PFA

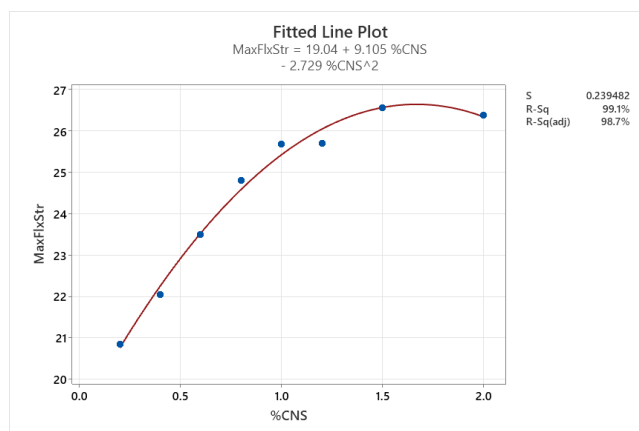


Figure 8: Max. Flexural Stress vs. % CNS for medium MFR PFA

CNS had a much greater effect on elongation at break values for the medium MFR PFA, with ~80% reductions in value observed at 0.4% CNS by weight (Figure 6).

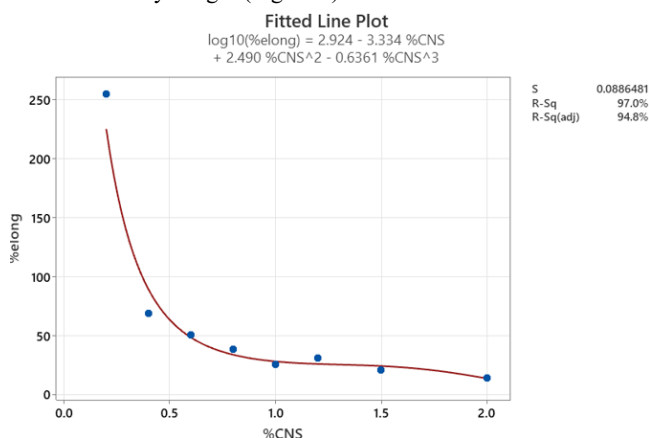


Figure 8: % Elongation at Break vs. % CNS for medium MFR PFA

### 3.3 Flexural properties

CNS loadings also had significant impacts on the flexural strengths (stiffnesses) of the low MFR ETFE and medium MFR PFA. (Figures 7 and 8)

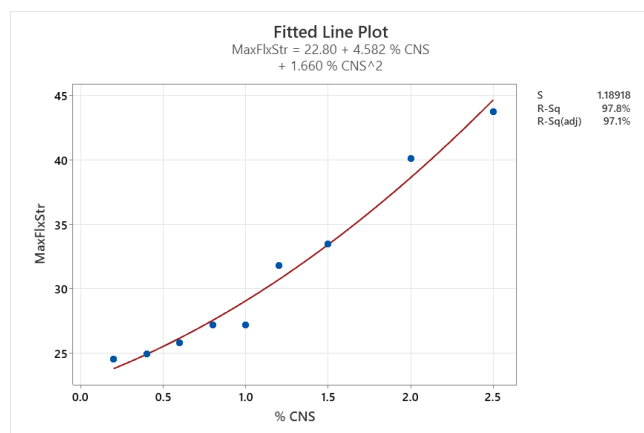


Figure 9: Max. Flexural Stress vs. % CNS for low MFR ETFE

The CNS increased flexural stress of the low MFR ETFE and the medium MFR PFA by about 20% at 1% loading by weight. Additional gains in stiffness were observed for the low MFR ETFE but not for the medium MFR PFA, which showed leveling behavior after 1.2% loading by weight.

### 3.4 Viscoelasticity

Inclusion of CNS yielded substantial reductions in melt indices of the low MFR ETFE and medium MFR PFA, as follows:

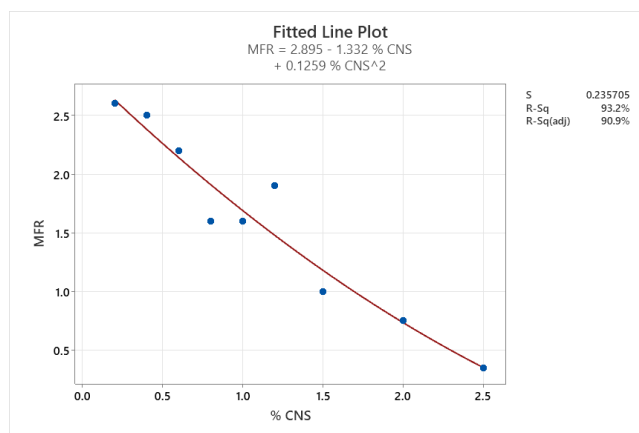


Figure 9: MFR vs. % CNS for low MFR ETFE

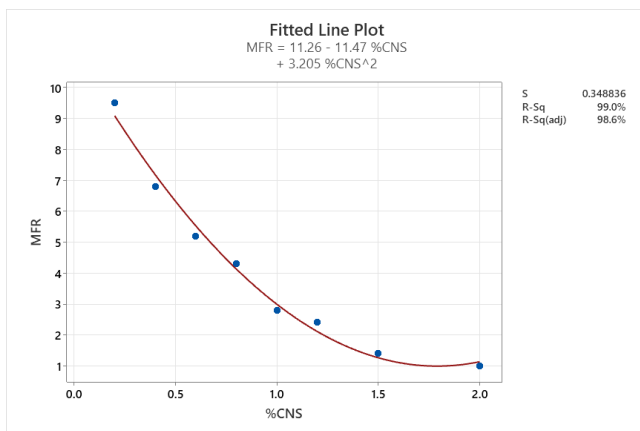


Figure 10: MFR vs. % CNS for medium MFR PFA

Capillary rheometry was performed on the low MFR ETFE CNS compounds to determine the relationship between viscosity and rate of strain. Results were as follows:

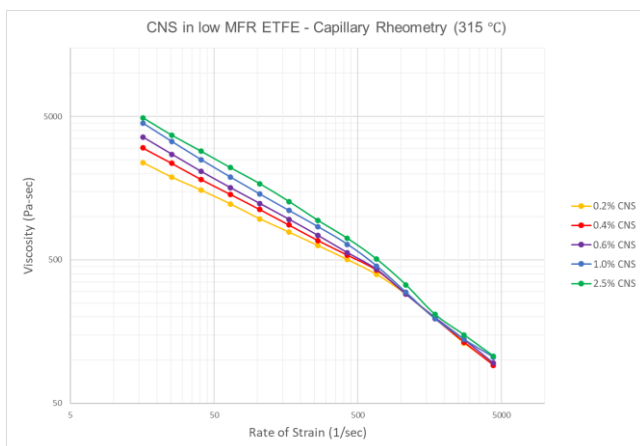


Figure 11: CNS in Low MFR ETFE - Viscosity vs. Rate-of-strain

Results for the CNS ETFE compounds were then compared against those obtained for conductive carbon black compounds based in the low MFR ETFE. The carbon black compounds were much more highly loaded (10%-16%, vs. 0.2%-2.5% for CNS), but performance was similar in terms of volume resistivity. As follows:

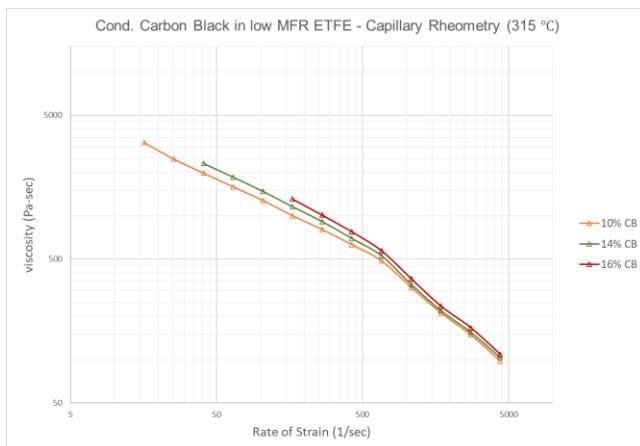


Figure 12: CB in low MFR ETFE - Viscosity vs. Rate-of-strain

A composite version of the capillary rheometry data from the CNS and carbon black compounds in ETFE is as presented, below.

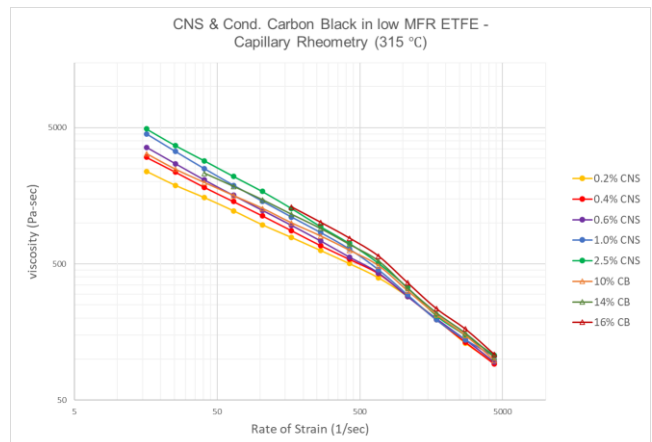


Figure 12: Composite of CNS and CB rheometry data

Some trends were apparent from the rheometry data.

- 1) At typical loadings used for conductive and semi-conductive compounds, CNS and carbon black had similar impact on viscoelastic properties of the ETFE-based compounds (Figure 12)
- 2) CNS has more of a significant impact on viscoelastic properties on a gram-per-gram basis, however.
- 3) CNS and carbon black compounds exhibited shear-thinning behavior at rates-of-strain greater than  $500 \text{ sec}^{-1}$ . This is largely as expected for ETFE-based compounds, as the ETFE is itself shear-thinning in its behavior.

### 3.5 Other effects of CNS

The two polymer base resins responded differently to inclusion of the CNS when bulk density of extruded pellets was measured. In the case of the low MFR ETFE, pellet bulk density decreased with increased loadings of the CNS. As follows:

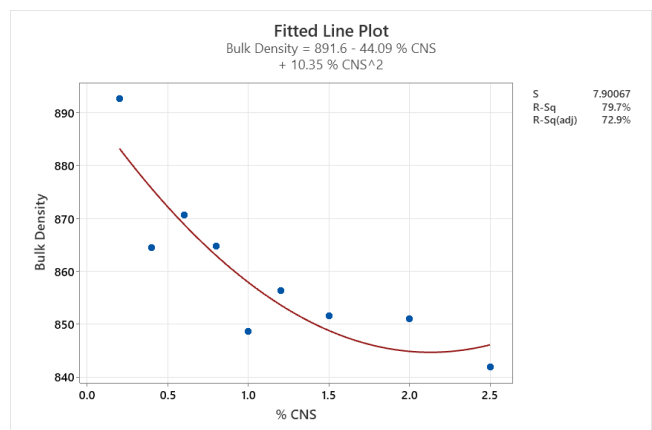


Figure 13: Pellet bulk density vs. % CNS for low MFR ETFE

For the medium MFR PFA, pellet bulk density *increased* with increased loadings of the CNS.

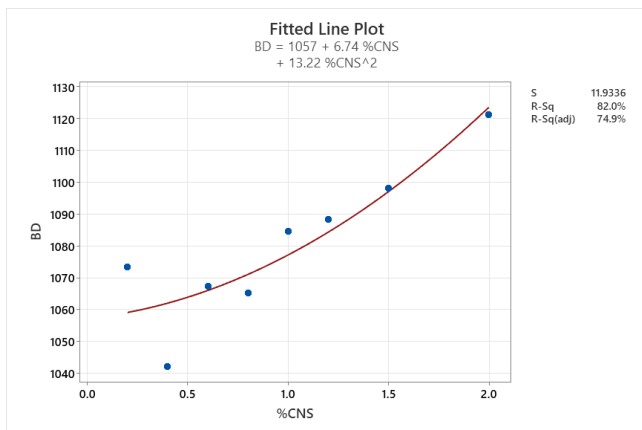


Figure 14: Pellet bulk density vs. % CNS for medium MFR PFA

### 3.6 Further Studies

AGC plans to continue its evaluation of fluoropolymer-based CNS compounds in the future.

- The impact of the CNS on notch sensitivity (Izod impact) of the base resins will need to be studied
- The effects of the CNS on coefficients of thermal expansion will need to be determined.
- Flame retardant status (per UL94) will need to be evaluated relative to the base resins and to filled conductive carbon alternatives.

There are also plans to evaluate concentrate (masterbatch) forms of the ETFE- and PFA-based compounds, along with studies to determine efficacy of the CNS in other engineering plastics (such as modified and unmodified PEEK and PPS).

## 4. Conclusions

Our studies indicated that carbon nanostructures (CNS) have good potential for use in trace or shielding compounds in the wire and cable industry, particularly in those applications where enhanced physical properties are required. That potential is predicated upon suppliers' ability to promote safe use of CNS, increase availability and maintain (if not reduce) production costs.

Users of CNS need to ensure operators are adequately protected from hazards inherent to nano-scale materials. This is not an issue for end users that process wire and cable but is a special concern for compounding operations. Our experiments used a special wetted form of CNS, whereby the material was prevented from becoming airborne through addition of a proprietary high boiling-point liquid.

At present CNS prices are well above highly structured conductive carbon blacks, at approximately \$350-500 USD per kilogram (vs \$30-50 per kilogram for conductive carbon blacks). Despite the cost differential, the greater efficiency of CNS means that conductive formulations can be created with similar (or even superior) cost structures to conventional carbon-filled compounds. CNS has the added advantage of allowing processors to run 'resin-rich', thereby maintaining chemical resistance, natural flame

retardance and other beneficial properties of the base material. AGC intends to explore these additional benefits as part of further studies.

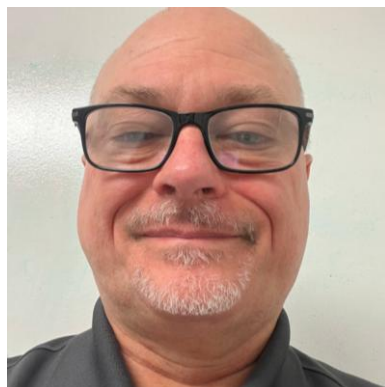
## 5. Acknowledgments

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## 6. References

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## 7. Notes on the Author:



Mike Sanchez works for AGC Chemicals Americas as a Technical Service Engineer for the Fluon+ Melt Processable Compounds group. In addition to providing customers with direct technical support, Mr. Sanchez spends much of his time developing new compounds and concentrates for the wire and cable industry. He holds bachelor's degrees in chemical engineering and chemistry and has over twenty years of experience in the plastics and pigments industries.

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