# Quantified non-destructive dispersion assessment via macrodispersion and AC/DC ratio analyses for hybrid polycarbonate/graphite nanoplatelet/carbon nanotube composites

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ABSTRACT

New quantitative image analysis methods are presented for non-destructive characterization of nanocomposite macrodispersion. The first method employs spherical contact distribution functions allowing macrodispersion analysis for micrographs with thick sections or films previously requiring modification for analysis. Additionally, a promising quantitative approach utilizing the AC/DC conductivity ratio was demonstrated for the study of dispersion within hybrid polycarbonate/carbon nanotube/graphite nanoplatelet nanocomposites. For the first time, a mechanism for the correlation between the AC/DC ratio and nanofiller dispersion level is theorized. Furthermore, it is demonstrated that the AC/DC ratio method has the potential to be used with metrics for quality assurance and performance assessment of nanocomposites.

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## 1. Introduction

The dispersion of nanofiller within polymer matrices is one of the key challenges associated with polymer nanocomposites and their acceptance into mainstream product. Recently, much effort is being focused on the ability to quantitatively characterize the dispersion of polymer nanocomposites, with emphasis on industry friendly methods. Currently, several different methods are being used for the dispersion characterization of polymer nanocomposites, with no standards being in place at this time [1]. Most commonly, dispersion characterization is performed qualitatively through a high resolution morphology investigation accompanied by bulk material property testing used to verify observed dispersion states. Quantitative methods have been published and normally fall under two categories: nanodispersion investigations via TEM [2–5] or SEM [6–11] and macrodispersion studies through optical microscopy [12–17]. Previously, we studied a quantified macrodispersion analysis approach applying stereological principles to estimate the volume agglomeration state from the 2D optical image measurements [18–20]. Macrodispersion characterization offers an industry friendly method for dispersion analysis due to it requiring relatively inexpensive equipment and it being a bulk analysis. However, no macrodispersion approach published thus far is appropriate for use with investigations of micrographs with overlapping agglomerates, a situation commonly found with thicker films or sections.

Recently, a process presented for the analysis of TEM images of polycarbonate (PC)/carbon nanotube (CNT) nanocomposites that employed spherical contact distribution functions (SCDF) to quantify dispersion parameters was reported [2]. Using this process, correlations were found between the nanocomposite electrical properties and dispersion features. Never before have SCDFs been applied to macrodispersion studies with optical analyses of agglomeration states. This SCDF method is useful for studying systems where the identification of single agglomerates or inclusions is impossible or inappropriate, which is often the case with studying thicker nanocomposite sections or films [21]. For some nanocomposite characterization, it may be impractical to prepare thin samples for dispersion analysis, especially for quality assessment purposes. Therefore, the application of the SCDF method is promising for broadening the application and industry friendliness of macrodispersion analyses of polymer nanocomposites.

Of special interest for polymer nanocomposite dispersion characterizations are processes that are non-destructive to the test specimen [22]. Non-destructive dispersion characterization provides opportunity for in-part testing and quality assurance, which is a necessity for industry adoption of polymer nanocomposite technology. Few groups have developed non-destructive dispersion characterization methods. Atomic force microscopy (AFM) is a non-destructive method that has been used to study nanofiller distribution and edge to edge associations [23,24]. Other approaches include X-ray computed micro-tomography [25] and a

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photoluminescence approach using defect-derived luminescence emissions [26]. Most of these approaches require the use of expensive equipment, confined space, and therefore very small samples making them inappropriate for industry assessment use. Hence, more realistic factory friendly processes need to be introduced before in-part quality and performance type assessment of polymer nanocomposites becomes practical.

The testing of nanocomposite electrical properties to help characterize the dispersion of a nanocomposite system is not a new concept. Some of its benefits are that it is a bulk analysis (unlike morphology investigation with SEM or TEM), the equipment is relatively inexpensive, and the characterization process has the potential to be non-destructive. Low percolation thresholds have been used in literature as an indicator of good dispersion within a nanocomposite system [1]. However, it is possible to achieve percolation with both a poorly dispersed or well dispersed system. Conductive pathways through the nanocomposite indicating percolation may be formed through individualized or agglomerated nanofiller; the conductive pathways are not selective. Hence, using the percolation threshold as a dispersion indicator is ambiguous [27–29]. Therefore, special considerations or new tools need to be developed before electrical property characterization can be made a standalone, useful tool in terms of dispersion characterization.

Polymer nanocomposites with different types of nanofiller embedded within the polymer matrix, often called hybrid nanocomposites, have shown great potential in achieving good electrical properties at lower filler loading compared with single nanofiller systems [30]. This is due to the synergistic behavior between different nanofillers such as CNT, graphite nanoplatelets (GNP), and carbon black [27,31–33]. Previous studies from our group have found synergy with CNT and GNP in conductive polymer composites leading to lower percolation thresholds compared to single filler systems [34,35]. However, adding different types of nanofiller adds complexity to the characterization of the nanocomposite microstructure and is mostly unstudied. Thus, the understanding of dispersion and its effects in hybrid polymer nanocomposites, which is a general key challenge, is critical to the development and quality control of functional hybrid polymer nanocomposites.

Recently, we reported on a non-destructive, quantitative dispersion characterization tool with studying polyetherimide/carbon nanofibre composites [29]. This method uses the bulk AC and DC electrical properties of nanocomposite samples to characterize the dispersion properties. It was found that a better dispersed nanocomposite had a lower AC/DC ratio compared to a worse dispersed composite. In the previous work, no mechanism was presented for the different AC/DC electrical property behavior for the differently dispersed nanocomposites. Additionally, this process has never been investigated with other polymers or nanofillers. Due to this process only requiring electrical property characterization equipment and yielding quantitative results, it is a prime candidate for industry friendly characterization of more complex, hybrid nanofiller polymer nanocomposites.

In this paper, we study PC/CNT/GNP hybrid nanocomposite systems above the percolation threshold. We characterize the nanocomposites with the AC/DC conductivity ratio tool and macrodispersion analyses via SCDFs. This is the first reported work using SCDFs to characterize nanocomposite macrodispersion and is necessary for studying optical images with overlapping agglomeration. In this case, because we are studying films, employing the SCDF method for macrodispersion analysis allows us to characterize the nanocomposite dispersion without sectioning or altering the composite, which is beneficial for industry. Additionally, we discuss a possible mechanism behind the differences in the nanocomposite AC versus DC conductivity that makes this a potentially viable and valuable industry and research tool. The studied results show that this quantitative electrical property method of analysis for hybrid polymer nanocomposites may be feasible for use with metrics for dispersion/property assessments.

## 2. Theoretical background

### 2.1. Spherical contact distribution functions

The macrodispersion study performed in this work stems from the process successfully used to study TEM images of PC/CNT nanocomposites by Pegel et al. [2]. Following binarization of the optical images, which are projections of the microstructure on a plane, the images are treated as a realization of a random closed set (RCS). The RCS under study, $\Xi$, will be the union of the black pixels in the image [2]. $\Xi$ is then put through a dilation process that will measure $A_A(r)$ which is the area fraction as a function of the radius of dilation [2,21]. Once the data is processed, instead of assuming the features in $\Xi$ to be random segments, as done by Pegel, we assume them to be random discs which allows us to use the following equation

$$\widehat{H}_s(r) = 1 - \exp\left\{-\lambda\pi r(2m_R^{(1)} + r)\right\} \quad \text{for } r \geqslant 0 \tag{1}$$

where $\widehat{H}_s(r)$, $\lambda$, $r$, and $m_R^{(1)}$ are the empirical SCDF, intensity (number of agglomerates per area), radius of dilation, and mean agglomerate radius, or first moment of the agglomerate radius distribution function respectively. With Eq. (1), we are able to determine $\lambda$ and $m_R^{(1)}$ via a best fit method enabling us to find

$$m_R^{(2)} = -\ln(1 - A_A)/\lambda\pi \tag{2}$$

where $m_R^{(2)}$, $A_A$, are the agglomerate radius variance, or second moment of the radius distribution function, and area fraction at zero radius [21]. Using these equations we are able to collect the several different parameters that may be used to correlate the hybrid nanocomposite macrodispersion and AC/DC ratio properties.

The films we are studying obviously have a volume, and exhibit a thickness of about 20–30 μm. The previously mentioned equations for the SCDF are from special 2D Boolean models [21]. Using 3D models will result in inaccuracies due to it requiring a solution of ill-posed problems. Therefore, similar to what has been done with previous works, we restrict our investigation to the second order characteristics (dispersion, distribution) to the 2D planar case and assume the data obtained will reflect what is in the volume of the composite [2]. A discussion on the use of the SCDF methods compared to a traditional method for macrodispersion analysis of optical micrographs can be found in Section 4.4.

### 2.2. AC/DC ratio

For this work, we are employing the 'equivalent circuit model,' treating the composite system as a conductor–dielectric mixture [36–38]. In this model, the AC dielectric response considers the conductors (CNT/GNP) to be pure resistors, while the dielectric matrix (PC) is considered as a perfect capacitor, which is called an RC model. This model assumes implicitly the conductivities of the two components to be different; one being high conductivity $\sigma_1$, and the other being low conductivity $\sigma_2$ where $\sigma_1 \gg \sigma_2$. Now, the bulk conductivity of the binary system around the percolation threshold can be defined as

$$\Sigma(p, \omega) \propto \sigma_1 |\Delta p|^t \Phi_\pm(h|\Delta p|^{-(s+t)}) \tag{3}$$

where $\Delta p \equiv p - p_c$ with $p$ being a bond occupation probability number (which will be thought of as the nanofiller loading throughout the paper) and $p_c$ being the percolation threshold [36]. Additionally,