Title: Computer vision and machine learning for assessing dispersion quality in carbon nanotube / resin systems

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Abstract

The addition of nanomaterials to polymeric resins can enhance a range of bulk material properties, but the nanofiller effectiveness varies strongly on the dispersion quality. The ability to independently, objectively, and quickly assess the dispersion quality of nano-loaded resins based on microscopy is desirable, but current techniques are often subjective and time-consuming. For this paper, we utilize a dispersion metric based on the use of image segmentation on optical microscope images. We then show that by training a computer vision model on a dataset of segmented microscopy images, the model can then quickly and accurately assess the dispersion of nanoparticles in a material. We apply this process to microscope images of carbon nanotube-loaded commercial resins. Our results indicate that this machine-learning methodology can match the accuracy and repeatability of current methods. In principle, this same machine-learning approach can be applied to a broad range of nanomaterials and matrices, allowing for rapid and quantitative analysis of microscope images for in-line quality control.

Keywords: Nanotube, dispersion, machine learning, microscopy, resin, computer vision, artificial intelligence

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1. Introduction

Carbon nanotubes (CNTs) and other nanofillers have found numerous applications in commercial products as additives for improving bulk composite properties.[1-3] These include mechanical reinforcement, often in thermoplastic or thermoset structural materials and coatings.[4-7] CNTs are also used to enhance electrical properties of a range of resins by forming interconnected, percolated networks.[8, 9] CNTs are frequently mixed into target resins using high-shear mixing or sonication for thermosets or twin-screw extrusion in the case of thermoplastics.[10-12]

These property enhancements are highly dependent on the quality of the dispersion of the filler within the matrix.[1, 9] For instance, the percolation threshold of randomly dispersed particles within a matrix is inversely proportional to the aspect ratio of the filler.[13, 14] Individual CNTs (with an aspect ratio of 1000 or more) are more effective than CNT bundles or agglomerates with low aspect ratios.[15] Confusingly, percolation can sometimes be enhanced by loose agglomeration of CNTs, allowing the CNTs to form a network based on interparticle interaction rather than random placement.[16-18] This interplay between particle separation and particle interaction has led to numerous theoretical and experimental studies of percolation and dispersion quality.[8, 19-21] Processing techniques like shear mixing are directly tied to these dispersion quality metrics.[22-24]

Unfortunately, dispersion is often a subjective measurement based on human assessment of optical or electron microscope images.[25-27] There have been attempts to develop a more quantitative interpretation of these images, relying on factors such as number of agglomerates, size of agglomerates, average interparticle distance, and concentration.[14, 26, 28, 29] These values are hard to keep consistent with microscopy, causing an inconsistent evaluation of dispersion quality. Quantitative analysis of microscope images is often carried out using human-guided software like ImageJ.[14, 28] Such techniques are ill-suited to scalable, objective, rapid quality control.

One promising approach to image processing is the use of image segmentation, which has been shown to be highly effective in identifying and segmenting various objects and features within an image. For instance, computer vision segmentation methods have been used to analyze cell images with high accuracy,[30] allowing for cell counting and tracking.[31] Here we utilize image segmentation to analyze dispersion quality; however, human-guided pre-processing is currently needed prior to image segmentation for nanomaterial matrices.

Recent advancements in machine learning (ML) have led to a rapid expansion of its applications, particularly in the field of computer vision. One notable category in this domain is ML-guided image segmentation [32-34]. This approach can analyze large datasets quickly and efficiently. This is especially critical when dealing with high-resolution images, where manual annotation can be time-consuming and prone to errors [35, 36]. The use of machine learning algorithms for image segmentation, followed by conventional methods of labeling can significantly reduce the time and cost associated with data annotation, allowing for more efficient and accurate analysis of large datasets [33, 34].

Here we show a machine learning approach to rapidly assess CNT/resin dispersion quality based on microscope images. We first outline a quantitative assessment method for determining quantitative dispersion quality. Conventional methods for calculating this method are time consuming and require subjective human judgments on every image. The machine learning approach is able to attain the same level of accuracy, with increased repeatability and increased speed.

2. Methods

2.1. Sample preparation and Optical Microscopy

For our samples, we started by preparing carbon nanotube-loaded resins with varying resin types and carbon nanotube grades. (Resin and CNT details are proprietary.) Next, we carefully placed a small drop of the mixture onto a microscope slide and used a second microscope slide to cover the sample. Shearing was carried out on the microscope slide itself with a shear rate of ~ 70/sec.

The slide was placed on the microscope stage and focused at 11.2x (162x) zoom in order to capture the nanoparticle agglomerates in the resin solution. The image was saved as a .tif file with a 1280x960 pixel size. A reference image of the microscope without a sample was saved to identify the background for creating our training dataset.

2.2. Conventional Image Segmentation

In order to calculate the dispersion metric, we used image segmentation techniques to identify and isolate the carbon nanotubes in the nano-filled resin. Image segmentation is a powerful tool that allows us to divide an image into multiple segments or regions, each of which corresponds to a different object or background. In this case, we used image segmentation to identify the carbon nanotube agglomerates in the sample image, and to remove the background of the resin.

First, we retrieved a sample image and a background image from the methods described above. We then applied adaptive histogram equalization to both images, which enhanced their contrast and improved their visual quality. To ensure that we accurately removed the background from the sample image, we used a histogram shift to match the intensity values of the sample image background to those of the background image.

Next, we subtracted the two images from each other, creating a binary image that contained only the carbon nanotubes and the background of the resin solution. Using the watershed method from the scikit-image python library, we split this binary image into a topographic elevation map, which allowed us to identify and label the distinct regions in the image. Each region was outputted as a binary image in the python console, with the carbon nanotubes represented by the color white and the background represented by the color black. A human user then selects the binary image that represented the optical microscope image as accurately as possible.

2.3. Machine Learning: Training and Validation

We then used machine learning techniques to improve the repeatability and speed of the conventional image segmentation method, while maintaining the accuracy of the dispersion quality result.

We utilized 32 microscope images of nanotube-loaded resins from a commercial partner and used conventional segmentation methods on these images to create a corresponding binary image for training and validating the computer vision model.

Out of the 32 microscope images, 22 were used for training, while 10 were used for validation. A training sample is a pair of corresponding microscope and binary images used for updating the model's parameters, and a validation sample is a pair of microscope and binary images used for assessing the model's performance.

The model architecture itself utilizes MobileNet, a convolutional neural network with 28 layers that is adept at recognizing patterns with the Adam optimizer to change the weights and biases. It also includes data augmentation to the training samples, including a horizontal flip to 50% of augments, an application of either random contrast, gamma, or brightness to 50% of augments, and either an elastic transform or grid distortion to 50% of augments. Data augmentation was applied to 90% of training samples per epoch. Data augmentation improves the generalization of the model, expanding the opportunity for other microscopes and nanomaterials. The model was trained for 80 epochs with 2 steps per epoch and 11 training samples per step.

The loss function used in this case was binary cross entropy, defined by the following equation

$$Loss = \sum_{i=1}^{2} t_i \, log_2(p_i)$$

where t_i is the truth label and p_i is the binary Softmax probability for the i^{th}class. In this model, there are two classes: background, or nanotube. The binary Softmax probability is defined as

$$S(y)_i = p_i = \frac{\exp{(y_i)}}{\sum_{j=1}^{2} \exp{(y_j)}}$$

where y is an input vector, y_i is the outputted logit from the final layer in the MobileNet model, and $\sum_{j=1}^{2} \exp{(y_j)}$ is the sum of exponentials of all output logits in the vector. After the computer vision model is trained, users input a microscope image, and the final emitting output is a binary image that has been segmented in its respective two classes.

2.4. Dispersion Assessment

After the formation of a binary image from a microscope image, the dispersion quality could be assessed quickly using SciPy and scikit-image python libraries. First, the binary image was labeled using the ndi.label function from the SciPy library, grouping connected carbon nanotube agglomerates together. This function scans the binary image and identifies connected agglomerate based on neighboring like-pixels, then assigns a unique integer label to each agglomerate.

Then, the scikit-image python library was used to calculate properties for each agglomerate. For each image, all agglomerate labels properties were calculated, and averaged. The final average perimeter pixels divided by total particle pixels for each image was recorded as the dispersion quality.

3. Results

Figure 1 displays 24 microscope images with four grades of carbon nanotubes in three different resin mixtures. Each sample has two microscope images taken, one with an applied shear and one without. These optical images feature a wide range of dispersion quality, and the machine-learning model developed below was used to calculate the dispersion metric, denoted by the yellow bars in **Figure 1**.

In this study, we utilize a specific quantitative metric of dispersion quality: The dispersion quality is defined as "particle perimeter pixels per total particle pixels," averaged over all distinct particles. This allows for a dispersion metric that varies from 0 to 1. Note that there may be other, better metrics for calculating dispersion quality based on microscope images, but we utilize this method to demonstrate the machine learning approach.

Figure 2 illustrates a conventional method for calculating this dispersion quality metric, which is contingent on distinguishing particles. First, microscope images are used as input. Then the image is converted to grayscale, and the contrast is expanded using a method called adaptive histogram equalization (AHE). The values of the greyscale image are then expanded into an elevation map of pixel intensity. This elevation map needs to be collapsed into a binary image by selecting a threshold grayscale value; pixels above this value are identified as particle and pixels below this value are identified as resin. However, a human user must cycle through possible threshold values and identify the correct cutoff; this is based largely on subjective assessments of the resulting binary images. This image is then labeled into individual “particles,” which may actually be agglomerates of particles. Once the image is labeled, a dispersion metric can be computed. This method is accurate with a trained user but can be time-consuming and subjective because of the cut-off selection. The ability to carry out this process in an objective, repeatable, rapid fashion would be highly beneficial.

We seek to improve this method using a computer vision model utilizing machine learning methods: The time for assessing each image can be radically reduced and subjectivity decreased. The model would not mechanically pick a cutoff and compute a binary from the grayscale; instead, the model would transition straight from the original microscope image to a binary image based on prior training data for a wide variety of realistic microscope deformations and distortions This could be especially useful in manufacturing settings to decrease energy consumption while maintaining dispersion quality and material properties.

In order to train the computer vision model, we utilize a suite of microscope images of CNT dispersions in various target matrices from a commercial partner (**Figure S1**). From these microscope images, binary images in **Figure S2** are then generated via the conventional method.[37] A training sample is a pair of microscope and respective binary image used for training the model. The training process itself is then initiated. The machine learning model is generated by running the training samples for 80 epochs (the number of times all training images in the dataset are passed through the neural network), using data augmentation with a MobileNet architecture. At the end of each step (two steps per epoch), the cross-entropy loss is calculated and minimized using the Adam optimizer. For each epoch, the MobileNet architecture identifies patterns in the training data to create the model.

To determine whether the model is overfitting based on the training images, a range of microscope images and their human-selected binary images are used to test the model (**Figure S3**). A validation sample is a pair of microscope and respective binary images used for testing the model, but the validation samples have no direct feedback to changing parameters. All calculations performed for the training samples are also calculated for the validation samples.

Figure S4 shows a quantitative score of the accuracy and loss of this model as a function of epoch. As epochs (the number of times the training samples from Figure S1-S2 are passed through the neural network) increase to 80, the training and validation accuracy increases, with a stable value of ~0.87. Accuracy is calculated by the number of correct predictions over the total number of predictions. The accuracy stabilizes after less than 10 epochs, but more epochs are trained because data augmentation allows the model to be generalized for more microscope techniques and nanomaterials. As the model is trained over many epochs, the loss value is minimized using the Adam optimizer. After 80 epochs, the training loss is calculated to be 0.0971, and the validation loss (calculated by cross entropy for the validation samples from **Figure S3**) was calculated to be 0.6069.

An example of the model's ability to create binary images that mimic the conventional method can be seen in **Figure S5**. In this figure, three validation samples were verified using the trained computer vision model. The predicted binary images from the machine learning model appears to match the input image more than the binary images found by the conventional image segmentation method. Machine learning utilizes a large number of samples and can be robust against noise, selecting only the most relevant features.

As a simple test of the model, a straightforward binary input image with an easily calculated dispersion metric was used on both the conventional and the computer vision model (**Figure S6**). The conventional method and the computer vision model both computed a dispersion quality of 0.025.

We then apply this method to new sample images to showcase how valuable this approach is. **Figure 3** shows a comparison of a low-quality dispersion from the conventional method and the computer vision model. Here, the conventional method computes a dispersion quality of 0.23, and the computer vision model computes a dispersion quality of 0.16. The computer vision model binary image visibly appears to match the microscope image more closely than the conventional method, explaining the difference in dispersion quality.

Figure 4 is a high-quality dispersion that is analyzed using both the conventional method and the computer vision model. The binary images and labeled images are shown for the conventional method and computer vision model. Notably, the computer vision model appears to have many more agglomerates visible in the binary and labeled images, which is due to the model picking up tighter contrast differences from the training data. This is an important point: Because the computer vision model has been trained by a range of images, the model can often outperform the conventional method for any given image. The dispersion qualities are calculated to be 0.57 and 0.59 respectively.

Figure 5 shows the computer vision model's application to microscopy images that show a given CNT-loaded resin progressing through a series of shear mixing passes. Notably, the microscope images have a different background contrast, but the model classifies the carbon nanotubes very effectively because of the generalization from data augmentation. The dispersion quality appears to improve for the first three shear mixing passes (0.43, 0.61, 0.65). After the fourth progression, the model illustrates a slightly lower dispersion quality of 0.58, which indicates that shearing is yielding diminishing returns after three passes. This sort of analysis has immediate relevance for process manufacturing optimization, allowing an engineer to decrease energy consumption and increase throughput while maintaining dispersion quality and material properties.

Finally, this method was then applied to the images shown in **Figure 1**, allowing for a dispersion quality score (marked as yellow bars in **Figure 1**). (This data is also depicted in bar graph form in **Figure S7**.) Resin 1 and CNT grade 4 with shear appears to have the highest dispersion quality and the mixture of Resin 1 and Resin 2 with no shear for CNT Grade 1 appears to have the lowest dispersion quality.

4. Conclusions

These results are emblematic of the advantages afforded by a machine learning approach: It does not vary from user to user, it is rapid, and it can be applied to a wide array of microscopy images. Although our results in the current paper are largely built around CNT-resin optical microscopy images, a similar approach could be carried out for CNT-polymer SEM images or for other carbon nanomaterials (such as graphene) as well. In each case, the quality of the machine learning approach is determined by the training data and can be assessed by a simple test run. We anticipate that machine learning approaches will become widespread in both industry and in academia as a means to increase the reliability of objectivity of nanomaterial dispersion assessment. The success of this machine-learning approach suggests that the methodology holds promise for predicting material properties on the basis of microscopy as well.

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References

1. Grady, B.P., *Carbon nanotube-polymer composites: manufacture, properties, and applications*. 2011: John Wiley & Sons.
2. Mittal, G., et al., *A review on carbon nanotubes and graphene as fillers in reinforced polymer nanocomposites.* Journal of Industrial and Engineering Chemistry, 2015. **21**: p. 11-25.
3. Crowley, A.G., T.Q. Tran, and M.J. Green, *Using nanomaterials to enhance the additive manufacturing of polymeric resins.* Nano Futures, 2022. **6**(4): p. 042502.
4. Kumar, A., K. Sharma, and A.R. Dixit, *A review on the mechanical properties of polymer composites reinforced by carbon nanotubes and graphene.* Carbon Letters, 2021. **31**(2): p. 149-165.
5. Nyholm, N. and N. Espallargas, *Functionalized carbon nanostructures as lubricant additives – A review.* Carbon, 2023. **201**: p. 1200-1228.
6. Arshad, M.U., et al., *Mechanics – Microstructure relations in 1D, 2D and mixed dimensional carbon nanomaterials.* Carbon, 2023. **204**: p. 162-190.
7. Sarmah, A., et al., *Additive manufacturing of nanotube-loaded thermosets via direct ink writing and radio-frequency heating and curing.* Carbon, 2022. **200**: p. 307-316.
8. Kyrylyuk, A.V. and P. van der Schoot, *Continuum percolation of carbon nanotubes in polymeric and colloidal media.* Proceedings of the National Academy of Sciences, 2008. **105**(24): p. 8221-8226.

9. Bauhofer, W. and J.Z. Kovacs, *A review and analysis of electrical percolation in carbon nanotube polymer composites.* Composites Science and Technology, 2009. **69**(10): p. 1486-1498.
10. Kaushal, A. and V. Singh, *Electromagnetic interference shielding response of multiwall carbon nanotube/polypropylene nanocomposites prepared via melt processing technique.* Polymer Composites, 2021. **42**(3): p. 1148-1154.
11. Shukla, M.K. and K. Sharma, *Improvement in mechanical and thermal properties of epoxy hybrid composites by functionalized graphene and carbon-nanotubes.* Materials Research Express, 2019. **6**(12): p. 125323.
12. Villmow, T., et al., *Influence of twin-screw extrusion conditions on the dispersion of multi-walled carbon nanotubes in a poly(lactic acid) matrix.* Polymer, 2008. **49**(16): p. 3500-3509.
13. Sang, Z., et al., *Dynamic polymer network conductive Nanocomposites: Low percolation threshold and Joule-heating-induced network plasticity.* Chemical Engineering Journal, 2022. **443**: p. 136400.
14. Tanabi, H. and M. Erdal, *Effect of CNTs dispersion on electrical, mechanical and strain sensing properties of CNT/epoxy nanocomposites.* Results in Physics, 2019. **12**: p. 486-503.
15. Green, M.J., *Analysis and measurement of carbon nanotube dispersions: nanodispersion versus macrodispersion.* Polymer International, 2010. **59**(10): p. 1319-1322.
16. Davis, V.A. and M.J. Green, *Controlling and characterizing anisotropic nanomaterial dispersion.* Nanotechnology Commercialization: Manufacturing Processes and Products, 2017: p. 65-99.
17. Vigolo, B., et al., *An experimental approach to the percolation of sticky nanotubes.* Science, 2005. **309**(5736): p. 920-923.
18. Hobbie, E.K. and D. Fry, *Nonequilibrium phase diagram of sticky nanotube suspensions.* Physical review letters, 2006. **97**(3): p. 036101.
19. Simoes, R., et al., *Low percolation transitions in carbon nanotube networks dispersed in a polymer matrix: dielectric properties, simulations and experiments.* Nanotechnology, 2008. **20**(3): p. 035703.
20. Lu, W., T.-W. Chou, and E.T. Thostenson, *A three-dimensional model of electrical percolation thresholds in carbon nanotube-based composites.* Applied Physics Letters, 2010. **96**(22): p. 223106.
21. Du, F., J.E. Fischer, and K.I. Winey, *Effect of nanotube alignment on percolation conductivity in carbon nanotube/polymer composites.* Physical Review B, 2005. **72**(12): p. 121404.
22. Eken, A., et al., *A simulation study on the combined effects of nanotube shape and shear flow on the electrical percolation thresholds of carbon nanotube/polymer composites.* Journal of Applied Physics, 2011. **109**(8): p. 084342.
23. Bałdyga, J., et al., *Dispersion of Nanoparticle Clusters in a Rotor−Stator Mixer.* Industrial & Engineering Chemistry Research, 2008. **47**(10): p. 3652-3663.
24. Rosén, T., et al., *Understanding ion-induced assembly of cellulose nanofibrillar gels through shear-free mixing and in situ scanning-SAXS.* Nanoscale Advances, 2021. **3**(17): p. 4940-4951.

25. Varenne, F., et al., *Evaluation of the size distribution of a multimodal dispersion of polymer nanoparticles by microscopy after different methods of deposition.* Journal of Drug Delivery Science and Technology, 2020. **60**: p. 102047.
26. Urban, D.A., et al., *Taylor Dispersion of Inorganic Nanoparticles and Comparison to Dynamic Light Scattering and Transmission Electron Microscopy.* Colloid and Interface Science Communications, 2018. **22**: p. 29-33.
27. Nguyen, V.S., D. Rouxel, and B. Vincent, *Dispersion of nanoparticles: From organic solvents to polymer solutions.* Ultrasonics Sonochemistry, 2014. **21**(1): p. 149-153.
28. Buford, M.C., R.F. Hamilton, and A. Holian, *A comparison of dispersing media for various engineered carbon nanoparticles.* Particle and Fibre Toxicology, 2007. **4**(1): p. 6.
29. Samoilov, A.N., et al., *Anomalous optical properties of photoactive cholesteric liquid crystal doped with single-walled carbon nanotubes.* Liquid Crystals, 2018. **45**(2): p. 250-261.
30. Moen, E., et al., *Deep learning for cellular image analysis.* Nature Methods, 2019. **16**(12): p. 1233-1246.
31. Scherr, T., et al., *Cell segmentation and tracking using CNN-based distance predictions and a graph-based matching strategy.* PLOS ONE, 2020. **15**(12): p. e0243219.
32. Minaee, S., et al., *Image Segmentation Using Deep Learning: A Survey.* IEEE Transactions on Pattern Analysis and Machine Intelligence, 2022. **44**(7): p. 3523-3542.
33. Liu, X., et al., *A Review of Deep-Learning-Based Medical Image Segmentation Methods.* Sustainability, 2021. **13**(3): p. 1224.
34. Luo, D., et al., *Deep Learning for Automatic Image Segmentation in Stomatology and Its Clinical Application.* Frontiers in Medical Technology, 2021. **3**.
35. Wang, R., et al., *Medical image segmentation using deep learning: A survey.* IET Image Processing, 2022. **16**(5): p. 1243-1267.
36. Rizwan I Haque, I. and J. Neubert, *Deep learning approaches to biomedical image segmentation.* Informatics in Medicine Unlocked, 2020. **18**: p. 100297.
37. Kadam, K., S. Ahirrao, and K. Kotecha, *Efficient Approach towards Detection and Identification of Copy Move and Image Splicing Forgeries Using Mask R-CNN with MobileNet V1.* Computational Intelligence and Neuroscience, 2022. **2022**: p. 1-21.