

Electrical and mechanical tuning of 3D printed photopolymer-MWCNT nanocomposites through in situ dispersion

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ABSTRACT: An electric field-assisted *in situ* dispersion of multiwall carbon nanotubes (MWCNTs) in polymer nanocomposites, fabricated through stereolithography three-dimensional (3D) printing technique, was demonstrated. The introduction of MWCNTs increased the elasticity modulus of the polymer resin by 77%. Furthermore, the use of an electric field for *in situ* MWCNT dispersion helped improving the average elongation at break of the samples with MWCNTs by 32%. The electric field also increased the ultimate tensile strength of the MWCNT reinforced nanocomposites by 42%. An increase of over 20% in the ultimate tensile strength of *in situ* dispersed MWCNT nanocomposites over the pure polymer material was observed. Finally, it was demonstrated that the magnitude and direction of the electrical conductivity of MWCNT nanocomposites can be engineered through the application of *in situ* electric fields during 3D printing. An increase of 50% in the electrical conductivity was observed when MWCNTs were introduced, while the application of the electric field further improved the electrical conductivity by 26%. The presented results demonstrated the feasibility of tuning both electrical and mechanical properties of MWCNT reinforced polymer nanocomposites using *in situ* electrical field-assisted 3D printing. © 2019 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2019**, 136, 47600.

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INTRODUCTION

Polymer matrix nanocomposites have gained an increased amount of interest in recent years due to the highly desirable properties from their fillers and the scalability and manufacturability provided by the use of polymers.¹ Polymer matrix nanocomposites are fabricated by incorporating ceramic, metallic, and/or organic fillers to enable improvements on thermal, electrical, mechanical, and dielectric properties.^{2,3} These polymer-based nanocomposites have been used in a wide variety of applications, ranging from the development of energy storage materials,⁴ piezoelectric pressure sensors,⁵ self-healing materials,⁶ and so forth. As nanocomposites reinforcement, single-wall and multiwall carbon nanotubes (SWCNT and MWCNT) have attracted a great amount of attention from the scientific and engineering community since they were first synthesized over two decades ago. This interest has been due to their exceptional thermal, electrical, and mechanical properties, and therefore potential applications. Despite the outstanding properties shown in individual form,

these properties are not exhibited when used in bulk.⁷ As a result, a great amount of work has been dedicated to the use of MWCNTs as reinforcements or fillers in different composite systems. MWCNT composites have been mostly fabricated using a polymer matrix to improve electrical and mechanical properties.⁸ MWCNT-polymer composites have been mainly produced using traditional techniques such as solution processing,⁹ melt processing,¹⁰ *in situ* polymerization processing,¹¹ and so forth. However, a very limited amount of research has been dedicated to the use of additive manufacturing techniques. Efforts to produce MWCNT-polymer nanocomposites through additive manufacturing commonly use a low percentage of MWCNT due to the tendency of these to agglomerate and therefore become a point of failure for the composite instead of a reinforcement.^{4,5,12} Consequently, methods to inhibit the agglomeration of MWCNTs in polymer solutions need to be implemented.

Several techniques to alleviate the agglomeration of MWCNTs in different solutions have been developed in recent years. Multiple

chemical treatments have been used to introduce different polar groups to the surface of the MWCNTs.¹³ Furthermore, dispersion and distribution control of nanoparticles can be achieved through the use of other approaches. Nanomaterials have been dispersed and aligned using magnetic fields, as well as sound waves to tune the properties of composite materials.^{14,15} With the development of additive manufacturing techniques and the implementation of nanocomposites to these technologies, efforts to align the fillers in these composites have become an area of interest in recent years. Recently, reinforcements of different natures have been aligned in polymer matrices during three-dimensional (3D) printing to achieve a higher degree of control over the enhanced properties of the final structure. For instance, alumina nanowires were aligned during stereolithography (SLA) printing of a composite using shearing force in the fluid through a mechanical oscillator to improve the mechanical properties of the composite.¹⁶ Various conductive nanoparticles were aligned by applying an acoustic field during the additive manufacturing of polymer matrix nanocomposites.¹⁷ In addition, acoustic waves were used to align nanoparticles that were then coupled with a fused deposition modeling extruder to fabricate 3D printed structures.¹⁸ Although these previous efforts have demonstrated the ability to align the filler in 3D printed nanocomposites to further tune their properties, these previous works have not only added significant complexity to the fabrication process, but also increased the time required to fabricate these materials. Recently, a newly reported technique to alleviate the agglomeration of MWCNT-polymer composites was the application of an electric field to MWCNT-polymer during fabrication.^{19,20} MWCNT alignment in different media occurs due to the dielectrophoresis-induced torque when an alternating current (ac) external electric field is applied.¹⁹ The alignment torque, T_{align} , applied due to the dielectrophoretic effect is given by

$$T_{\text{align}} = \frac{1}{4} \Omega \epsilon_m \text{Re}[\alpha^*] E^2 \sin 2\theta \quad (1)$$

$$\alpha^* = \frac{(\epsilon_p^* - \epsilon_m^*)^2}{[\epsilon_m^* + (\epsilon_p^* - \epsilon_m^*) L_x][\epsilon_p^* + \epsilon_m^*]} \quad (2)$$

where Ω is the volume of the particle, ϵ_m is the permittivity of the surrounding media, E is the electric field applied, ϵ_p^* and ϵ_m^* are the complex numbers based on the electrical permittivity and conductivity of the particle and media, respectively, Re stands for the real part of the complex expression of α^* , and L_x is the depolarization factor. Compared with other chemical-based surfactant treatments, electrical field dispersion does not hinder mechanical, electrical, or dielectric properties of the final composite material. With this technique, dispersion of MWCNTs can be controlled by varying the intensity and frequency of the electric field applied, further improving the tuning ability over the final characteristics of the nanocomposite.²¹ Alignment of MWCNTs in nanocomposites has been used in the past to tune thermal, electrical, and mechanical properties.^{22,23} Therefore, the implementation of an electrical field during 3D printing presents with the potential capability of tuning properties of additive manufactured nanocomposites.

In this research, the use of *in situ* dispersion of MWCNT through the application of an electric field during the additive manufacture of MWCNT-photopolymer nanocomposites to tune their electrical and mechanical properties is studied. A concentration of 1 wt % of MWCNT was used due to its good compromise between the improved properties of the material and the printability of the nanocomposites. Samples were fabricated using a commercially available SLA 3D printer while several electric fields were applied using a set of custom fixtures. Electrical conductivity and stress-strain measurements of the sample were carried out to study the impact of the dispersing electric field in the final properties of the nanocomposites. Improvement in mechanical and electrical properties is observed for samples fabricated under electrical fields.

EXPERIMENTAL

Resin Preparation

Genesis development photopolymer resin (Tethon3D, Omaha, NE, USA) was used as the matrix for all experiments. MWCNTs with a diameter of 5–10 nm and a length of 10–20 μm (Cheap Tubes Inc., Cambridgeport, VT, USA) were used as the reinforcement of the nanocomposite. Chemical functionalization was performed on the MWCNTs through acid treatment. MWCNTs were treated in a 12 M nitric acid solution at 70 °C for 4 h. Functionalized MWCNTs were then neutralized using deionized water and later dried overnight in air at 120 °C. Dried functionalized MWCNTs are then crushed and ground into a fine powder using a mortar and pestle. Finally, functionalized MWCNTs powder is mixed in a 1:99 weight ratio with the Genesis resin to form the printable nanocomposites.

Fabrication

An SLA 3D printer (Form1+; Formlabs Inc., Somerville, MA, USA) was used to print the samples in compliance with ASTM standards D638 Type V tensile bars for tensile test. Two electrodes were installed in opposite sides of the resin tank as shown in Figure 1. The electrodes were connected to an ac power source to apply a variety of ac electric fields. The ac electric field was

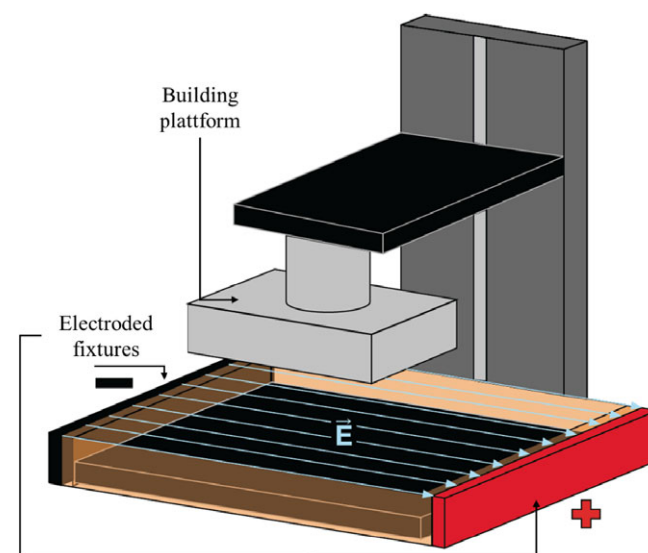


Figure 1. Fabrication setup showing the electric field applied through the custom fixtures. [Color figure can be viewed at wileyonlinelibrary.com]

Table I. Parameters of Electric Fields Applied

Sample	Frequency (kHz)	Electric field (V cm ⁻¹)
Random	0	0
Parallel	10	300
Low frequency	1	300
High voltage	10	1000
Perpendicular	10	300

applied using an Agilent 33210A function waveform generator signal generator, an Acopian P030HP2 high voltage regulator, as well as a set of custom electrodes.

Once the 3D printing process started, electric fields were applied concurrently to the resin. This allowed for the application of a uniform dispersing electric field throughout all the layers of the fabricated samples. The parameters of the electric field applied to the fabricated samples are described in Table I. The electrical field applied was oriented in parallel to the tensile direction in most groups while the perpendicular group was treated with a field normal to the tensile loading direction during testing. Furthermore, a set of control samples with only the base polymer was also fabricated with no electric field.

Characterization

Mechanical and electrical characterizations were performed on all sample groups. For mechanical testing, an axial displacement of 1 mm s⁻¹ was applied to all samples, while keeping track of the stress and strain generated in the sample using an Instron 5960 series tensile testing machine. Elastic moduli, strain at rupture, and ultimate tensile strength for each group were obtained from these tests. For electrical testing, electrical conductivity measurements were carried out in the samples. Silver paint electrodes were applied on the faces perpendicular to the electric field applied to the MWCNT. Resistance was measured using an LCR meter (IET Labs Inc, Roslyn Heights, NY, USA; 1920 Precision LCR meter) at a fixed frequency of 1 kHz. From these electrical resistance readings, electrical conductivity, σ , was calculated using eq. (3)

$$\sigma = \frac{l}{RA} \quad (3)$$

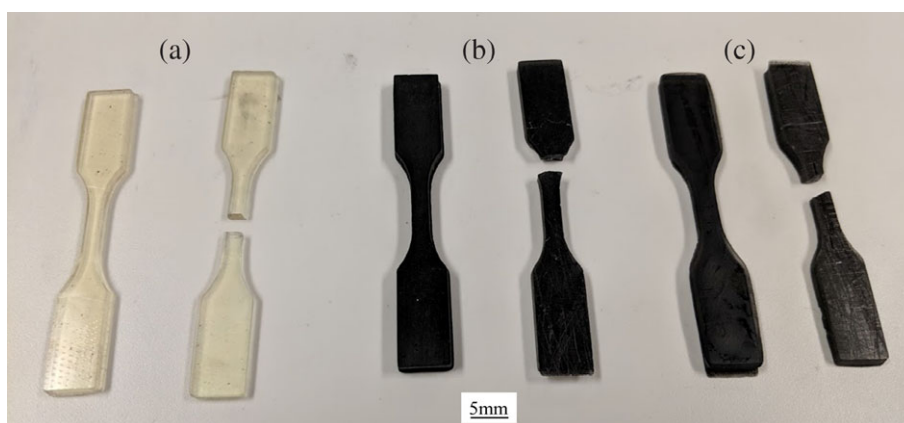


Figure 2. (a) Genesis sample, (b) random sample, and (c) electrical field-assisted sample. [Color figure can be viewed at wileyonlinelibrary.com]

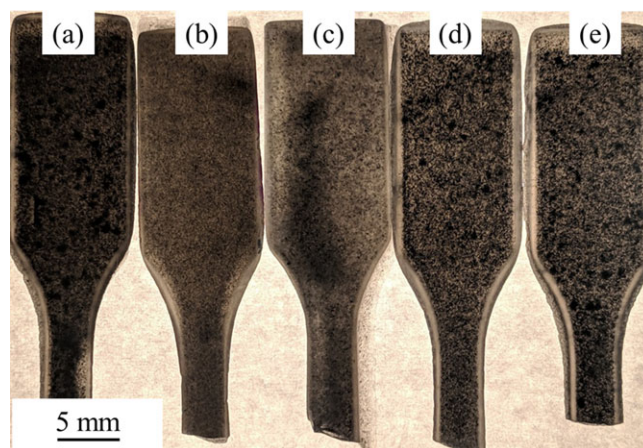


Figure 3. Transmission image of MWCNT agglomerations across (a) random, (b) parallel, (c) perpendicular, (d) low-frequency, and (e) high-voltage samples. [Color figure can be viewed at wileyonlinelibrary.com]

where R is the resistance measured of the sample, A is the cross-sectional area of the electrodes, and l is the distance between the them.

RESULTS AND DISCUSSION

In order to determine the electric field influence on the nanocomposites properties, samples fabricated under the different electric fields were mechanically tested first. Different samples before and after rupture are shown in Figure 2. From this figure, it can be observed that the Genesis sample, as well as the field-treated sample, present ruptures in the thinner section of the piece. Meanwhile, it can also be seen that the sample with random MWCNT inclusions ruptured in a thicker section, which is an indication of the presence of MWCNT agglomerations in the sample. The impact of the application of different dispersing fields on the agglomeration of MWCNT in the printed samples can be observed in Figure 3. From these optical transmission images, it can be observed that both the strength and frequency of the field had an impact on the MWCNT agglomerations. First, an evident decrease in the visible MWCNT agglomeration size was observed when the parallel and perpendicular dispersing fields were applied to the samples. This decrease in the presence

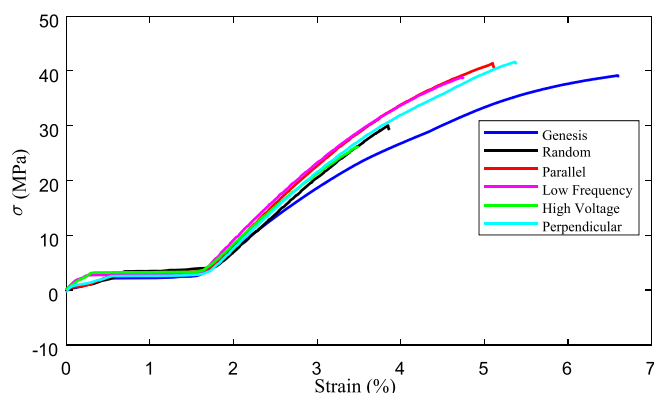


Figure 4. Representative plot of the mechanical properties of the different samples. [Color figure can be viewed at wileyonlinelibrary.com]

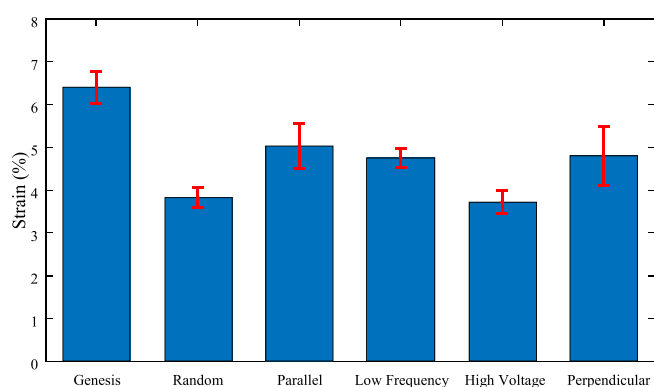


Figure 5. Elongation at break. [Color figure can be viewed at wileyonlinelibrary.com]

of visible MWCNT aggregates is consistent with other efforts reported in literature.²⁰

In order to easily visualize the mechanical properties from the samples subjected to the different electric fields, representative plots of the different group of samples were generated. A single curve representative of the typical mechanical behavior of the different sample

groups was plotted. These mechanical testing results are shown in Figure 4. The intensity and frequency of the electric field applied for the *in situ* dispersion are described in Table I. Since MWCNTs are rigid and brittle reinforcements, the pure polymer samples presented the highest elongation at break with an average of 6.4%, while MWCNT reinforced nanocomposites returned an average of only 3.82% strain at failure. However, the average elastic modulus of the Genesis sample was 695 MPa, being the lowest from all the samples. While all MWCNT nanocomposites have shown an increase of the elastic moduli, up to 1.233 GPa. This increase in the elasticity modulus and decrease in maximum elongation is consistent with other research where MWCNTs were used as mechanical reinforcements in nanocomposites.^{24,25}

Furthermore, it was observed that the application of the electric field had a clear impact on the mechanical properties of the composites, as shown in Figures 5–7. For all samples with MWCNTs, the set of samples with the highest ultimate tensile strength, as well as elongation at break were the parallel and perpendicular groups. Meanwhile, samples with a lower frequency presented similar results with slightly lower elongation at break. Finally, it was also observed that the application of the electrical field can adversely affect the mechanical properties of the composites as shown by the samples where a higher field was applied. Since PMMA is a brittle material, the Young's moduli for all the samples were calculated using the stress and strain characteristics of the sample after the strengthening of the sample was completed.²⁶ Average values for the elongation at break, Young's modulus, and ultimate tensile strength of the different sets, as well as the standard deviation of every group, are shown in Figures 5–7, respectively.

As previously described, elongation at break decreased when MWCNT inclusions were introduced to the composites. In Figure 5, it can be observed that a significant decrease of maximum strain was present. When the MWCNT inclusions were introduced without the application of an electric field, elongation at break decreased an average of 40.3%, with similar results observed when the highest electric field was applied. In contrast,

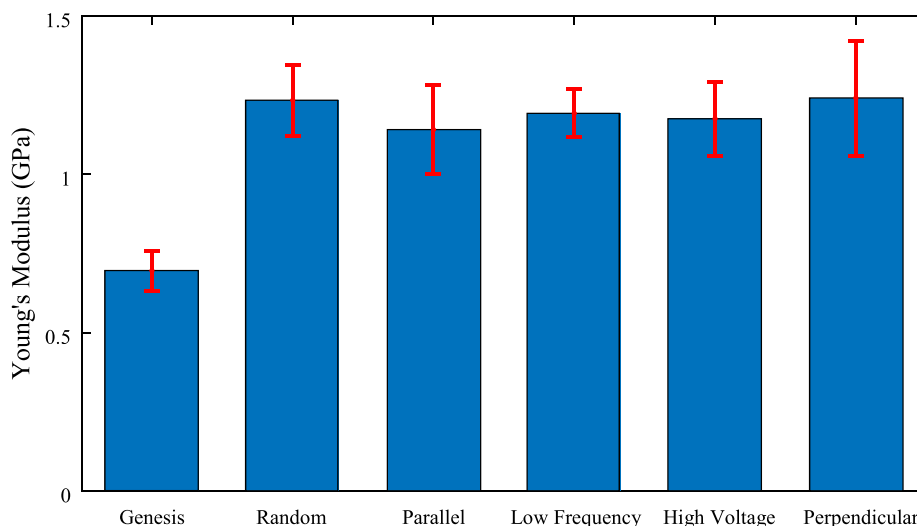


Figure 6. Elastic moduli. [Color figure can be viewed at wileyonlinelibrary.com]

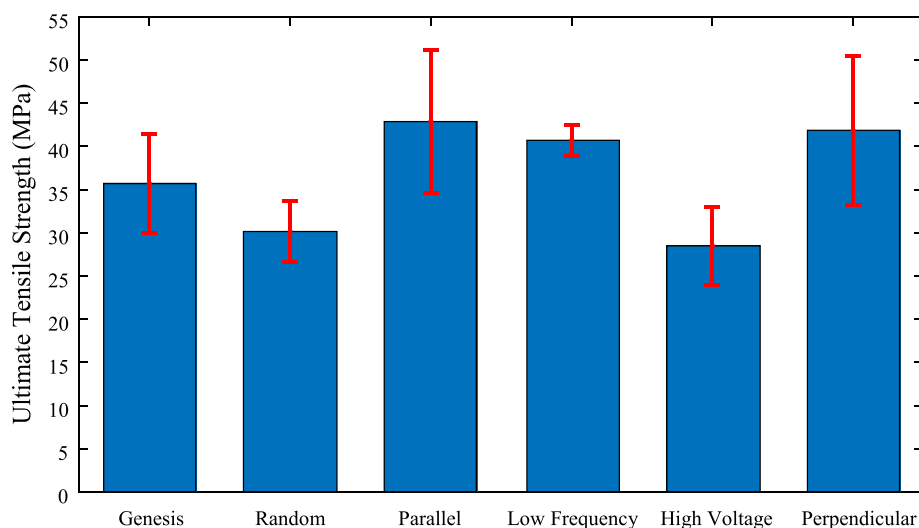


Figure 7. Ultimate tensile strength. [Color figure can be viewed at wileyonlinelibrary.com]

when parallel and perpendicular fields were applied, a decrease of only 21% was observed. This partial recovery of the maximum elongation at break can be attributed to a higher number of sites where MWCNTs and resin can interact, thus allowing for a greater toughening of the composite. This toughening and increased strain at break is due to better dispersion of reinforcements has been described by Ladani *et al.*²⁷

It was also observed as shown in Figure 6 that the introduction of MWCNT to the composites increased the elastic moduli of the different sets of samples by over 70%. The application of the electric field did not have a significant impact in the elastic moduli of the MWCNT modified composites. Next, ultimate tensile strength decreased for both random and samples with the higher electric field due to their premature failure as seen in Figure 7. The premature failure observed in the samples is expected for samples with poor MWCNT distribution, as these MWCNT agglomerated become stress concentration points. A high concentration of agglomerates is expected for the random samples, as no dispersing electric field was applied. On the other hand, high-

voltage samples presented a considerable amount of agglomerations due to the introduction of a higher electric field which can be associated with the creation of electrically percolative paths. As a result of this, a higher amount of the electrical energy introduced by the electrodes is concentrated in this section, lowering the overall capacity of the field to disperse the MWCNT.²⁰ Due to this diminished dispersing capability, a smaller impact in the reduction of agglomerates size is expected and clearly observed in Figure 3. As a result of the recovery observed in the maximum elongation that parallel, low frequency, and perpendicular sets presented, their ultimate tensile strength also increased. These sets of samples presented an average increase of 20% over the pure polymer sample and of 42% over that observed for randomly distributed MWCNT nanocomposites.

Finally, electrical conductivity measurements were performed in every set of samples. Figure 8 shows that the introduction of MWCNT to the polymer matrix increased the conductivity by 50.5%. Furthermore, the introduction of electrical fields proved the ability to tune the electrical properties of the samples. As

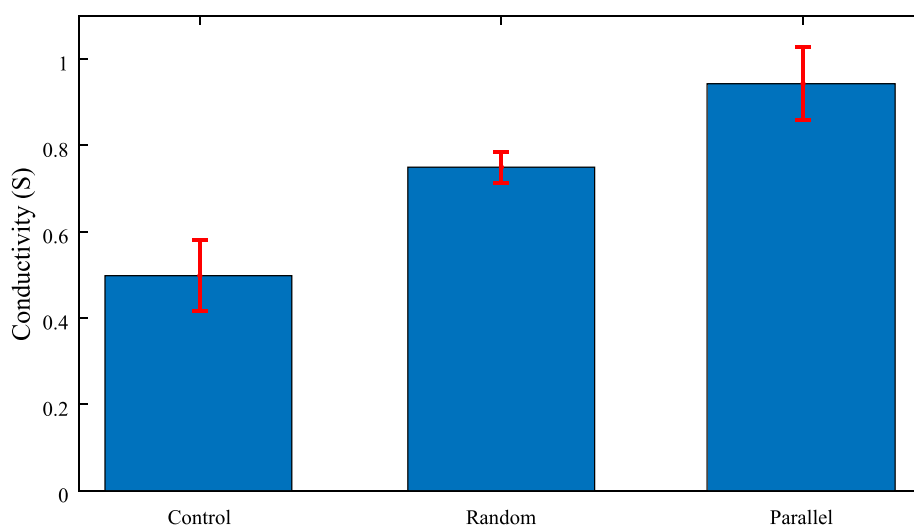


Figure 8. Conductivity of pure polymer, random MWCNT, and parallel MWCNT. [Color figure can be viewed at wileyonlinelibrary.com]

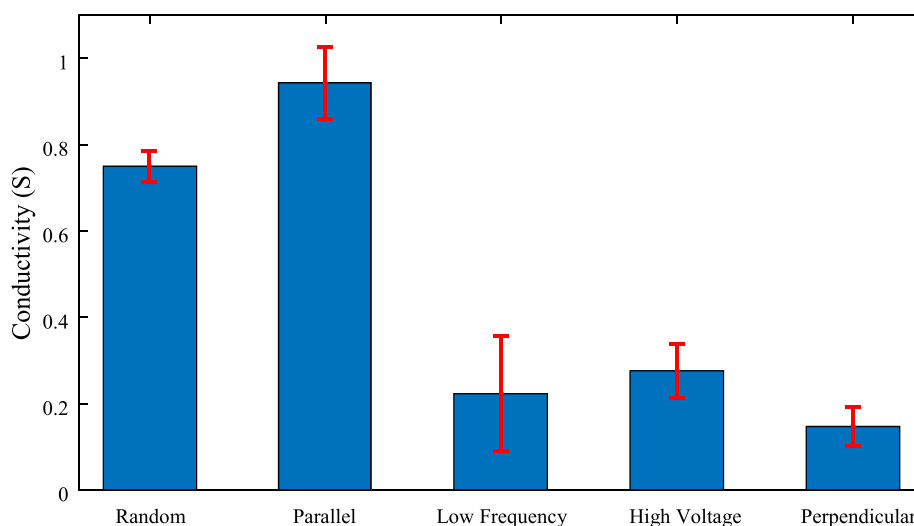


Figure 9. Conductivity under different electric field conditions. [Color figure can be viewed at wileyonlinelibrary.com]

shown in Figure 9, the electrical conductivity can be further increased to a total improvement of 89.3% on average. This further increase in the electrical conductivity for the parallel samples was attributed to the alignment of the MWCNTs from the application of the electric field, effectively forming electrically conductive pathways between the testing electrodes. This behavior has been seen in the past in similar nanocomposites with conductive fillers.²⁸ Meanwhile, conductivity was also sharply decreased by applying an electrical field perpendicular to the testing direction. The electrical conductivity observed in the perpendicular condition was found to be over six times lower than that observed when a parallel electrical field of the same strength was applied. The ability to tune the direction in which the improvements in conductivity are present has also been demonstrated for nanocomposites with carbon nanomaterials as fillers.^{19,28} From this, it was demonstrated that not only mechanical properties can be improved by the introduction of an electric field during the additive manufacturing, but also that the electrical conductivity and directionality of this property can be tuned through the use of electrical fields.

CONCLUSIONS

The *in situ* dispersion of MWCNTs in 3D printed polymer nanocomposites was demonstrated. Mechanical and electrical characterizations of these composites were performed. The introduction of MWCNTs increased the elastic modulus of the resin by 77%. Furthermore, the use of an electric field for *in situ* dispersion helped recover the average elongation at break of the samples with MWCNTs by 32%. As a result, the electric field increased the ultimate tensile strength of the MWCNT reinforced nanocomposites by 42%. An increase of over 20% in the ultimate tensile strength of *in situ* dispersed MWCNT nanocomposites over the pure polymer material was observed. Finally, it was demonstrated that the magnitude and directionality of the electrical conductivity of MWCNT nanocomposites can be tuned and controlled through the application of *in situ* electric fields during 3D printing using commercially available machines. The electrical conductivity of the samples with the electric field applied parallel

to the testing direction were found to be over six times more conductive than those with the field applied perpendicularly.

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