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DIELECTRIC PROPERTIES OF POLYANILINE-FUNCTIONALIZED CARBON NANOTUBE/PDMS NANOCOMPOSITES

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Abstract: In recent years, carbon nanotubes (CNTs) have emerged as materials that are often used in the preparation of polymer nanocomposites with conductive or advanced dielectric properties due to their unique properties including high temperature and electrical conductivity, which allows the production of very light and robust materials with a very high length-to-diameter ratio. However, during the preparation of polymeric nanocomposites with these materials, some problems are encountered. One of the major problems is that after preparing these conductive materials or adding them into the polymer, they tend to aggregate, forming agglomerate, due to their conductive structures. Therefore, in this study, firstly, multi-walled carbon nanotubes (MWCNTs) were functionalized with conductive form of polyaniline (PANI) and subsequently, the poly (dimethyl siloxane) (PDMS) polymer nanocomposite films with different concentrations of functionalized multi-walled carbon nanotubes were prepared. Then, the structural, morphological, electrical and dielectric properties of the films were characterized. As a result, with the addition of only 1.5% PANI-CNT, the dielectric constant of PDMS was increased by 47-fold at 1 Hz. The dielectric films like presented here can be used in capacitors, flexible electronics, dielectric elastomers and artificial muscle applications.

Keywords: Carbon Nanotubes (CNTs), Conductive Polymer, Dielectric, Polyaniline (PANI), Polymer Nanocomposite, poly (dimethyl siloxane) (PDMS)

Polianilin İle Fonksiyonelleştirilmiş Karbon Nanotüp/PDMS Nanokompozitlerin Dielektrik Özellikleri

Öz: Son yıllarda, yüksek uzunluk/çap oranı ile hafif ve sağlam kompozitler hazırlanmasını mümkün kılan karbon nanotüpler, yüksek ısıl ve elektriksel iletkenlikleri gibi benzersiz özelliklerinden dolayı iletkenlik veya dielektrik özellikleri yüksek polimer nanokompozitlerin üretiminde kullanılan bir malzeme olarak ortaya çıkmıştır. Bununla birlikte, bu malzemelerle polimerik nanokompozitlerin hazırlanması sırasında bazı problemlerle karşılaşılmaktadır. En büyük sorunlardan biri, bu iletken malzemeleri hazırladıktan veya polimere ekledikten sonra, iletken yapıları nedeniyle topaklanma, topak oluşturma eğilimi göstermeleridir. Bu nedenle, bu çalışmada ilk olarak, çok duvarlı karbon nanotüpler (MWCNT'ler) polianilinin iletken formu (PANI) ile fonksiyonelleştirilmiştir. Ardından, farklı konsantrasyonlarda fonksiyonelleştirilmiş çok duvarlı karbon nanotüplere sahip nanokompozit poli(dimetil siloksan) (PDMS) polimer filmler hazırlanmıştır. Daha sonra ise, filmlerin yapısal, morfolojik, elektriksel ve dielektrik özellikleri karakterize edilmiştir. Sonuç olarak, sadece % 1,5 PANI-CNT ilavesiyle, PDMS'nin dielektrik sabiti 1

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Hz'de 47 kat arttırılmıştır. Burada ortaya konulduğu gibi dielektrik filmler kapasitörler, esnek elektronik, dielektrik elastomer ve yapay kas uygulamalarında kullanılabilir.

Anahtar Kelimeler: Karbon Nanotüp (KNT), İletken Polimer, Dielektrik, Polianilin (PANI), Polimer Nanokompozit, Poli (dimetil siloksan) (PDMS)

1. INTRODUCTION

Polymeric composite materials with high dielectric and electrical properties find wide applications in artificial muscles, actuators, flexible electronic applications where high-K gate dielectrics are required, memory devices, supercapacitors and sensors because they are lightweight, cheap, and easy to process (Dang, Wang et al. 2007, Li, Xiong et al. 2008, Kohlmeyer, Javadi et al. 2009, Brochu and Pei 2010, Wu, Huang et al. 2013). Polymeric materials, on their own, are materials with a low dielectric constant (less than ~ 10), but this value can be improved by the addition of various conductive fillers (Sain, Goyal et al. 2015). Ceramics (such as titanium dioxide (TiO_2)) (Carpi and Rossi 2005), metals (such as silver) (Rao and Wong 2002), high dielectric organic fillers (such as copper phthalocyanine oligomer (o-CuPc)) (Zhang, Li et al. 2002, Huang, Zhang et al. 2005) and conductive polymers (Huang, Zhang et al. 2005) have been used in the past to improve the dielectric and electrical properties of polymeric materials. However, these fillers should be used at a high rate to make the necessary improvements, resulting in some negative changes in the mechanical properties of the structure, such as weight gain and fragility (Bai, Cheng et al. 2000, Dang, Lin et al. 2003, Huang, Zhang et al. 2003, Li 2003, Dang, Yuan et al. 2012). In order to significantly reduce the electrical percolation threshold without changing the properties of the polymer matrix negatively, nanofillers with high aspect and surface-to-volume ratios are desirable. Therefore, the use of carbon-based nanofillers, such as carbon nanotubes and graphene, which have recently been able to make significant improvements in dielectric and electrical properties, even at low addition rates, has gained popularity (Xie, Mai et al. 2005, Kohlmeyer, Javadi et al. 2009, Yang, Lin et al. 2009, Zhu, Murali et al. 2010). The nanofillers which are added to the polymeric matrix provide an increase in the dielectric constant up to the percolation threshold while the material still remains in the insulating form. In the addition of nanofiller material over the percolation threshold, the conductive filler materials in the polymeric matrix form ways in which the electricity can be transmitted to each other, which passes the material into the conductive form, and a significant increase in conductivity is observed even in the addition of low filler material (Sain, Goyal et al. 2015). Besides conductive polymers and carbon-based nano materials can be used together in order to improve the dielectrical properties of polymer nanocomposites. For example, the synergistic effect of polyaniline functionalized graphene sheets in order to dielectric improvement (Li, Huang et al. 2012) was discussed in the literature. The main reason for using CNTs is that nanocomposites further improve the mechanical properties of nanocomposites compared to other carbon-based materials such as graphene. So, while carbon nanotubes improve dielectric properties, they also lead to higher mechanical properties (Zakaria, Abdul Kudus et al. 2017). Furthermore, PANI, which is polymerized from the inexpensive aniline and has shown a synergistic effect with carbon-based materials (as graphene) on dielectric improvement, was used as the functionalization material to enhance the relatively low dielectric properties of CNTs/polymer nanocomposites (Li, Huang et al. 2012).

On the other hand, in the production of polymeric nanocomposites, the uniform distribution of the nanofiller material in the polymeric matrix is important for the high efficiency by the addition of less filler material. Therefore, there are several studies on the functionalization of filler material by various chemical or physical methods (Chen, Wu et al. 2001, She, Chen et al. 2007, Zhao, Xiao et al. 2007, Kohlmeyer, Javadi et al. 2009, Sain, Goyal et al. 2015). Chemical functionalization of the nanofiller surface causes a change in the electrical properties of the filler, which in turn affects the properties of the composite negatively (Stankovich, Piner et al. 2006, Worsley, Ramesh et al. 2007). Although physical functionalization does not adversely affect the electrical properties of the nanofiller material, it can provide advanced properties even at low nanofiller addition ratios as it provides a more uniform distribution of the filler material (Molberg, Crespy et al. 2010, Javadi, Xiao et al. 2012, Li, Huang et al. 2012, Wang, Bao et al. 2012, Wang, Liu et al. 2015, Zhang, Yan et al. 2016, Fan, Wang et al. 2017, Maity, Mandal et al. 2017, Manna and Srivastava 2017). Bonding character of in-situ polymerization functionalization of aniline in presence of carbon-based nanomaterials is physical functionalization. In this mechanism, there are no driving force to bond the carbon-based material to aniline monomer covalently. Aniline monomers are absorbed by carbon surface by electrostatic effect (Li, Huang et al. 2012, Wang, Yuan et al. 2015). Therefore, in this study, first, polyaniline-functionalized carbon nanotubes were prepared via in situ polymerization aniline monomer on CNTs and then, polyaniline-functionalized CNT/PDMS nanocomposites were fabricated by solution casting. The effect of the various concentrations of PANI-functionalized CNTs as filler on the dielectric and electrical properties of the nanocomposites was investigated and it was seen that the dielectric properties of the polymeric nanocomposites were significantly improved with the addition of 1.5% PANI-functionalized CNTs.

2. MATERIALS AND METHODS

Sylgard 184 PDMS base and curing agent were supplied from Dow Corning Corporation. Multi-walled carbon nanotubes (Aldrich, USA), aniline monomer (Sigma-Aldrich, Portugal), ammonium persulfate (AMPS) (Sigma, Japan), tetrahydrofuran (THF) (ACS grade, Emplura®Merck, Germany), dimethyl sulfoxide (DMSO) ($\geq$ 99.9 wt%) and other required solvents were obtained from Sigma-Aldrich and used without further purification.

2.1. Preparation of PANI Functionalized CNTs

In this work, the purification of carbon nanotubes by the liquid oxidation method was followed (Zhu, Murali et al. 2010). The cleaning of multi-walled carbon nanotubes was carried out by chemical oxidation. The modified procedures are as follows (Taş, İşlek Cin et al. 2018): 0.4 g of MWCNTs in 40 ml of 2.6 M nitric acid solution were prepared using 65 wt% nitric acid and refluxed at 102 °C for 24 hours. The resulting solution was washed several times with deionized water until reaching pH 7 by centrifugation. The obtained purified carbon nanotubes were then taken up in 300 ml of DMSO. The mixture was sonicated in the ultrasonic bath for two hours to obtain a homogeneous mixture. In order to group the obtained carbon nanotubes by wall numbers, centrifugation was carried out again. This process is performed at speeds of 3000, 5000, 7000 and 9000 rpm, respectively, and centrifugal speed is carried out by grouping the carbon nanotubes having the greatest number of walls into at least the walls. CNTs which has lower wall number were used for further experiments. The required quantity of aniline monomer was added in CNTs dispersion in 1 M HCl, and then AMPS was added in solution and was stirred in an ice bath for 24 h (Figure 1). The obtained solid was washed 3 times with DI water. Then it was stored in THF to prevent agglomeration.

2.2. Fabrication of PANI Functionalized CNTs/PDMS Nanocomposites

Dow Corning® Sylgard® 184 Silicone Elastomer Kit, a two-part silicone, was used as the polymer matrix in this study. CNTs suspension in THF was sonicated with probe sonicator then PDMS base and curing agent were added and stirred. PANI functionalized CNTs/PDMS nanocomposite films were prepared using the solution casting method (Figure 1). The nanofiller concentrations of 0.25%, 0.50%, 0.75%, 1.00%, 1.50%, 2.00% were used in the preparation of PANI functionalized CNTs/PDMS nanocomposites.

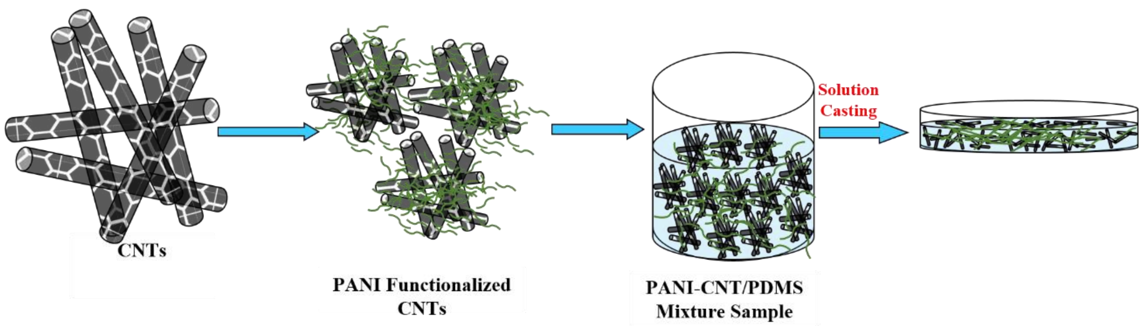

Figure 1:
Schematic drawing showing the preparation of PANI functionalized CNTs/ PDMS nanocomposite film.

2.3. Dielectric, Electrical and FT-IR Characterization of CNTs/PDMS Nanocomposites

The dielectric properties of polymer nanocomposites can be determined with several important factors including the characteristic of the nanoparticle (aspect ratio, surface/volume ratio, electrical conductivity), polymer matrix, manufacturing method and the degree of distribution of nanoparticles in the polymer matrix (Tsangaris, Psarras et al. 1996, Tsangaris, Psarras et al. 1998, Yu, Wu et al. 2000, Brosseau, Quéffélec et al. 2001, Xiao, Xiao et al. 2001, Javadi, Xiao et al. 2012). Dielectric constant can be estimated using the effective dielectric constant (1), assuming that the conductive filler concentration is f:

$$\mathcal{E} = \mathcal{E}_m \left\{\frac{f_c - f}{f_c}\right\}^{-q} \tag{1}$$

where $\mathcal{E}_m$ is the dielectric constant of the insulation polymer matrix; q is a critical exponent (~1 for a three-dimensional compound) and f_c is the electrical percolation threshold (Rao and Wong 2002, Huang and Zhang 2004, Carpi and Rossi 2005). Dielectric characterization of CNT/PDMS and PANI-CNT/PDMS nanocomposite films were performed with an impedance analyzer (Novocontrol Technologies, Alpha-AN) at room conditions. FT-IR analyses were performed on NİCOLET - İS50 infrared spectrophotometer. SEM images were taken with Carl Zeiss / Gemini 300 scanning electron microscope.

3. RESULTS AND DISCUSSION

3.1. FT-IR Analysis of Nanofiller and Nanocomposite

FT-IR characterization of PANI-CNT nanofiller and 0.75% PANI-CNT filled PDMS nanocomposite were shown in Figures 2-a and 2-b. In Figure 2-a, FT-IR spectra of PANI-CNT has no intense transmittance peaks except four points: Peaks at 1236 cm^{-1}, 1287 cm^{-1}, 1366 cm^{-1} and 1744 cm^{-1} come from C-H asymmetric stretching, 1287 N-H bending, N-C stretching and C=O stretching, respectively (Misra, Tyagi et al. 2006, Stobinski, Lesiak et al. 2010). FT-IR spectra of neat PDMS and PANI-CNT/PDMS have shown strong transmittance peaks of PDMS. In Figure 2-b, peaks at 2961 cm^{-1}, 1406 cm^{-1}, 1008 cm^{-1} and 786 cm^{-1} represent for C-H bonds, CH_3 asymmetric deformation, Si-O-Si asymmetric deform and CH_3-Si-CH_3 bonds, respectively (Bodas and Khan-Malek 2006).

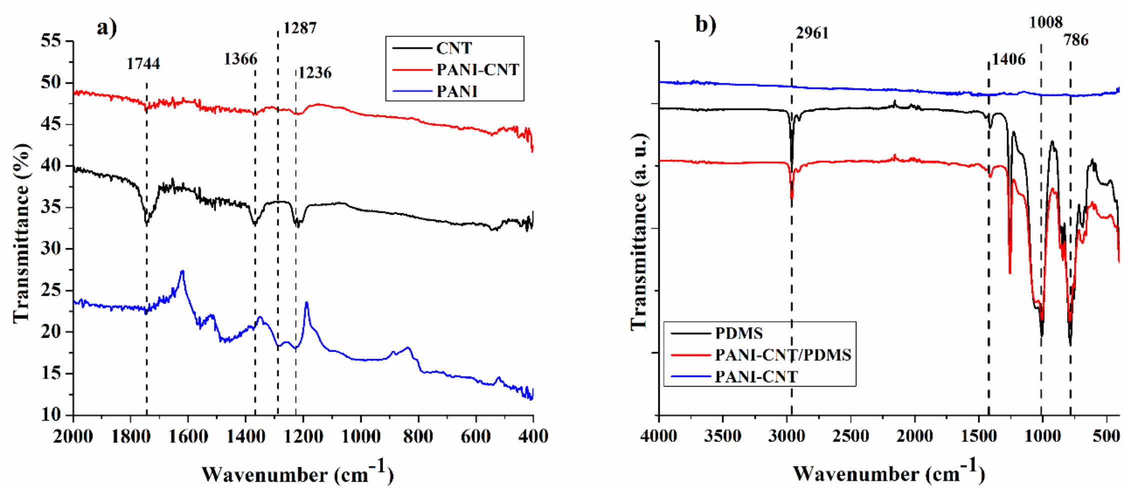

Figure 2:

FT-IR Spectra of a) neat PANI, neat CNTs and PANI-CNT and b) PANI-CNT, neat PDMS and PANI-CNT/PDMS

3.2. SEM Analysis of Nanofiller and Nanocomposite

SEM images of non-functionalized MWCNTs, PANI-CNT and PANI-CNT/PDMS nanocomposites were given in Figure 3. Figure 3-a shows the neat MWCNTs. The surface of neat MWCNTs quite smooth and the average nanotube diameter was 17 nm according to SEM images. SEM images also showed the PANI functionalization of MWCNTs with increasing mean diameter (41 nm) and rough nanotube surface compared to neat MWCNTs (Figure 3-b). Lastly, the dispersion morphology of PANI-CNT particles in the PDMS matrix has been shown in Figure 3-c. According to the SEM images of PANI-CNT/PDMS composites, PANI functionalized MWCNTs were agglomerated in some places of the matrix and PDMS resin highly diffused into agglomerated porous nanoparticles.

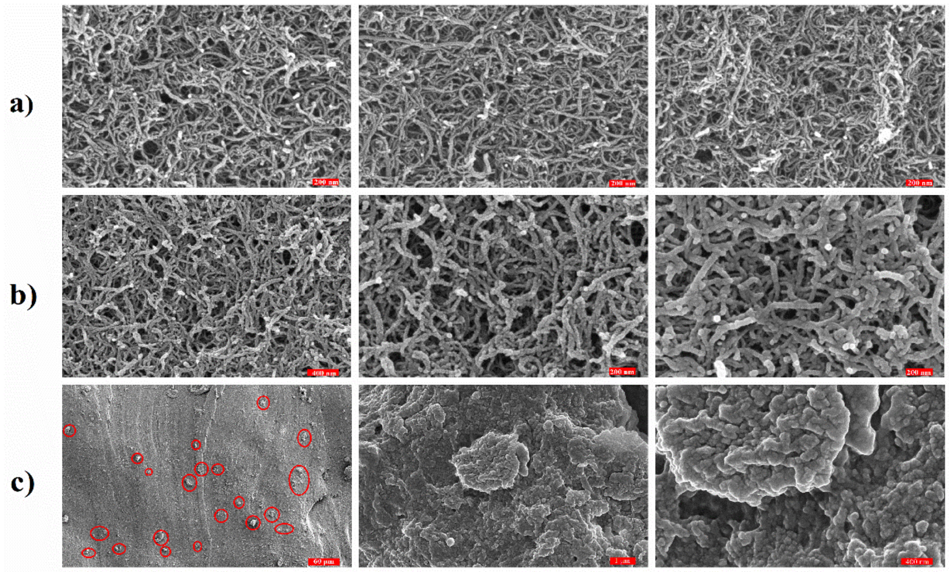

Figure 3:

SEM images of a) non-functionalized MWCNTs, b) PANI-CNT and c) PANI-CNT/PDMS nanocomposite

3.3. Dielectric and Electrical Conductivity Properties of PANI-CNT/PDMS Nanocomposites

The variation of the dielectric constant of PANI-CNT/PDMS nanocomposites according to the frequency was shown in Figure 4. PANI was utilized as the functionalization agent to homogenously and efficiently disperse CNTs throughout the PDMS matrix. This functionalization facilitated the dispersion of CNTs in the polymer matrix by isolating the CNT layers to prevent their aggregation and to form conductive pathways through the polymeric matrix. As shown in Figure 5, the highest dielectric constant value was reached with the addition of 1% PANI-CNT and a decrease in the dielectric constant was observed with the subsequent concentrations. It is thought that this decrease may be caused by the tendency of agglomerated nanofillers above certain concentrations. In a similar work (Wang, Yuan et al. 2015), the maximum dielectric constant value was about 20 with approximately 1.50% nanofiller concentration formed by the hybridization process of PANI, CNTs and reduced graphene oxide. On the other hand, while fillers such as PANI as high dielectric constant filler increases the dielectric constant of polymer-based dielectrics, they cause a large reduction of the electric breakdown strength due to high local electric fields in the polymer nanocomposites (Thakur, Zhang et al. 2017).

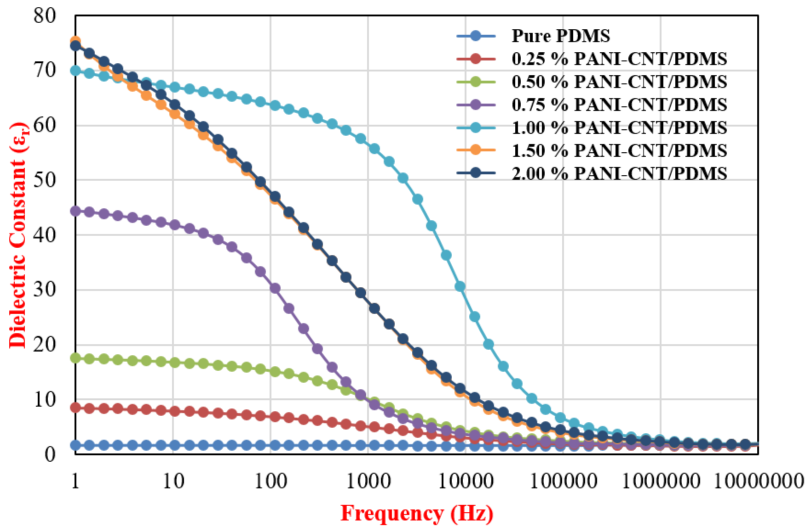

Figure 4:

Variation of the dielectric constant of CNT/PDMS nanocomposites functionalized by PANI.

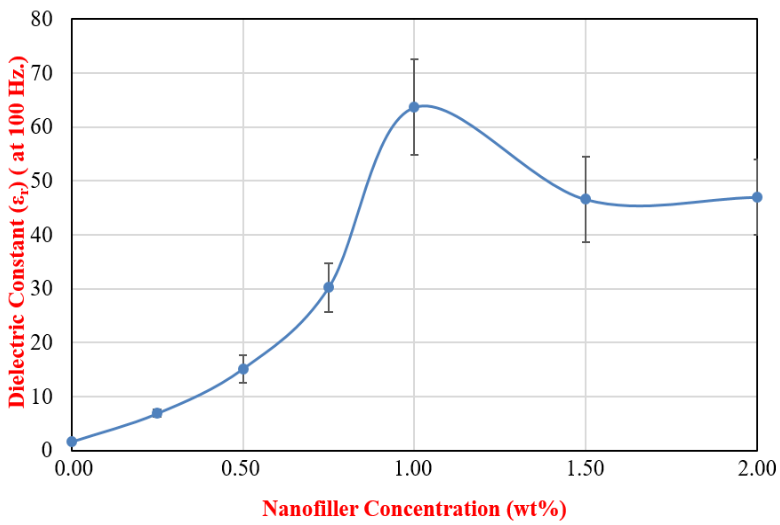

Figure 5:

The variation of the dielectric constant of the CNT/PDMS nanocomposites functionalized by PANI depending on the nanofiller concentration

The variation of the dielectric loss (Tan δ) of PANI-CNT/PDMS nanocomposites depending on the frequency and filler concentration was presented in Figure 6 and Figure 7, respectively. Although dielectric loss increases with increasing concentration in general, no complete correlation has been detected. In Wang's work (Wang, Yuan et al. 2015) dielectric loss values were quite high besides the high dielectric constants. Additionally, in another work (Xu, Ding et al. 2017), the dielectric loss was 1.7 with a 5.0% nanofiller concentration. As reported before, dielectric loss values in similar dielectric nanocomposite works were above 2.0 (Xu, Ding et al. 2017), in our study, the maximum dielectric loss was 1.33 with 1.00% PANI-CNT concentration.

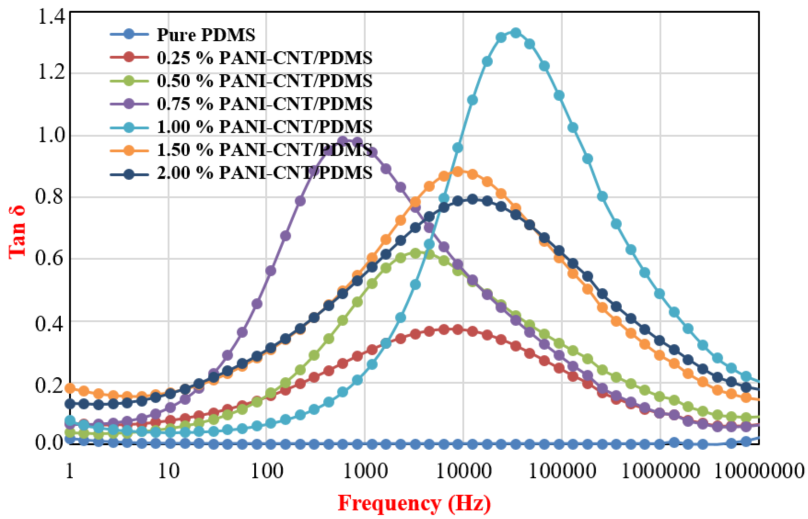

Figure 6:
Variation of the dielectric loss (Tan δ) of CNT/PDMS nanocomposites functionalized by PANI

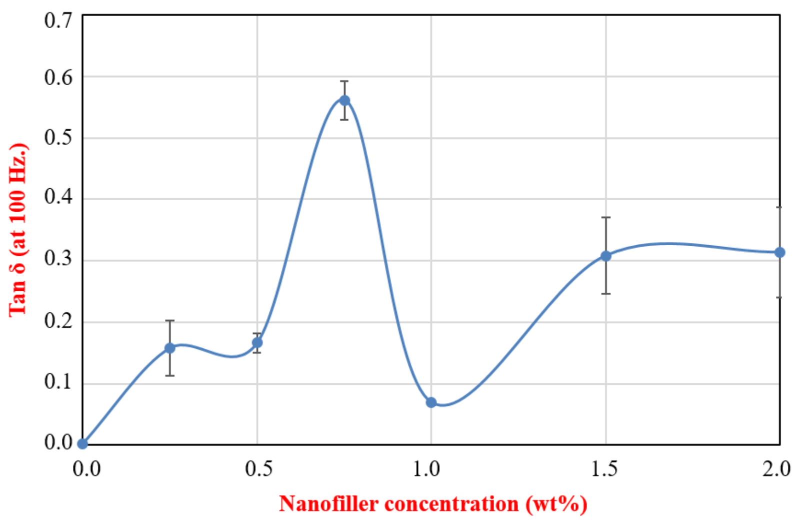

Figure 7:
Variation of the dielectric loss (Tan δ) of the functionalized CNT/PDMS nanocomposites with PANI depending on the nanofiller concentration.

Figure 8 shows the effect of PANI-CNT addition on the electrical conductivity of nanocomposites, that is, the change in electrical conductivity with concentration. Electrical conductivity increased slightly up to 1% concentration and increased sharply with the addition of 1% PANI-CNT. While the PDMS film at 100 Hz had an electrical conductivity of $23.83*10^{-13}$ S/cm, its electrical conductivity was increased to approximately $8182*10^{-13}$ S/cm by the addition of 1.5% PANI-CNT and became stable after (Figure 9) that. Conductivity measurements were coherent with two works mentioned before (Wang, Yuan et al. 2015, Xu, Ding et al. 2017) in a range between 10^{-12} S/cm – 10^{-5} S/cm.

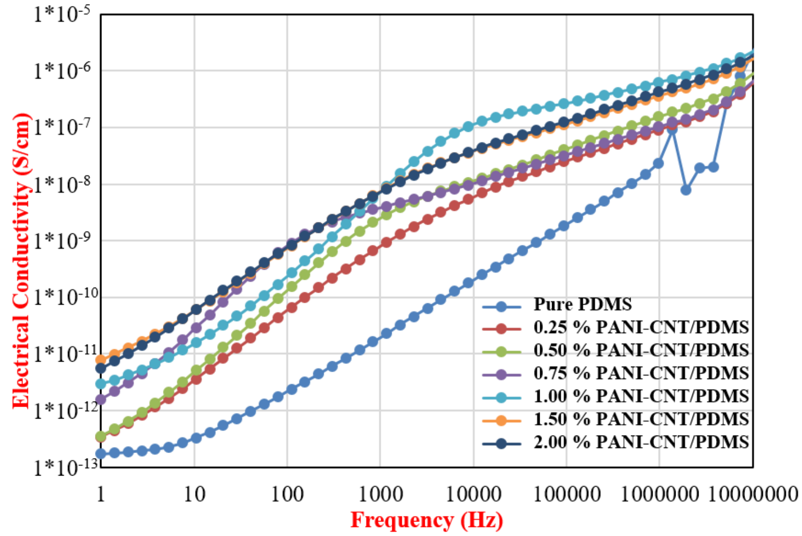

Figure 8:

The electrical conductivity of CNT/PDMS nanocomposites functionalized by PANI depending on the frequency.

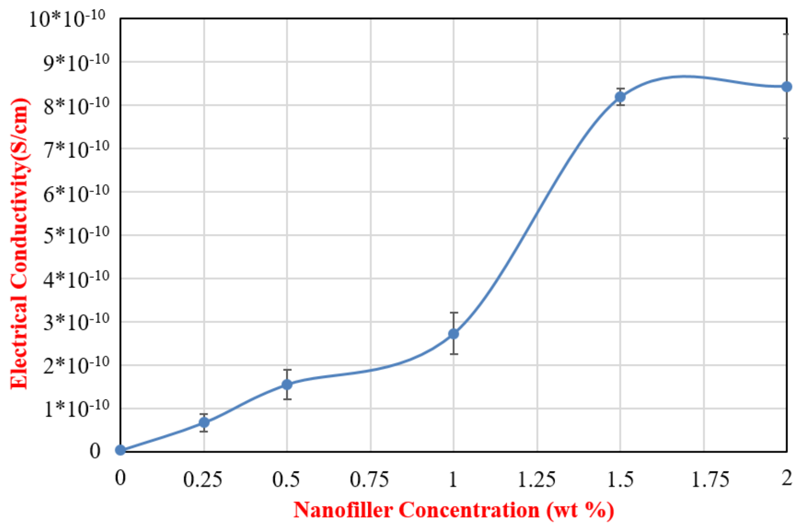

Figure 9:

The electrical conductivity of CNT/PDMS nanocomposites functionalized by PANI depending on the nanofiller concentration.

4. CONCLUSION

The PANI functionalized CNTs were successfully synthesized by in situ polymerization method and PANI-CNT/PDMS nanocomposites produced via solvent casting technique. When the dielectric and electrical properties of nanocomposites were investigated, it was seen that, by the addition of nanofiller into the polymer, there became a significant increase in the dielectric constant, while at the same time causing a significant increase in the dielectric loss. The addition of conductive filler also resulted in a significant increase in the electrical conductivity of nanocomposite materials. Moreover, with the addition of only

1.5% PANI-CNT, the dielectric constant of PDMS was increased by 47 fold at 1 Hz. On the other hand, the electrical conductivity increased by 343 times with the addition of PANI-CNT. The resulting dielectric and electrical properties of these nanocomposite materials can be an important candidate for the flexible capacitors, electronics, dielectric elastomer and artificial muscle applications.

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