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Study the Effect of Hybrid Nanofillers Content on the X-ray Diffraction and Thermal Conductivity Properties of Epoxy-Based Nanocomposites

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Abstract

High-performance polymer nanocomposites utilizing different-sized nanofillers had a lot of interest recently. Due to their distinct structural, and thermal characteristics. Multi-wall carbon nanotubes (MWCNT) and nanoclay (NC) have the most interest among the numerous types of reinforcing as filler elements for a polymer. The formation of hybrid from MWCNT and NC at various loadings (0.5%, 1%, and 2wt%) on the characteristics of epoxy polymer have been assessed in this work. The specimens have been created using solution blending procedures with the addition of solvent ethanol at a ratio of 1:1 for dispersed nanofillers, and then they have been re-mixed with epoxy. Tests like X-Ray diffraction (XRD), and thermal conductivity were used to identify properties of epoxy. According to the test results, the thermal conductivity rise as the filler content rises at 1wt%, then start to decrease after 1wt%. The sample with the hybrid filler loading of 1 wt% produced the best performance. Since hybrid epoxy exhibits the best result of the thermal conductivity 135% over MWNT and NC nanocomposites of 1 wt.% reached 0.3568 W/m.K in the increased thermal conductivity property. By examining the EP nanocomposites XRD pattern. The hybrid of epoxy nanocomposites exhibits all of the NC and MWCNT characteristic peaks. Since interactions between the filler and the epoxy cause a shift in the peak location of 1wt%. Due to the homogeneity of the nanofillers entire epoxy matrix, there may be changes in the intensity or location of the peaks at 1% for 2θ= 20.13°, which corresponds to an interlayer distance of d=0.461nm.

Keywords: Nanoclay, MWCNTs, Epoxy, Hybrid, Thermal Conductivity, XRD.

تأثير المحتوى الهجيني النانوي على اداء مركبات الايبوكسي

هاجر حداد الحسيني ، مؤيد ال ابو زاهد

الخلاصة:

إعداد مركبات بوليمر نانوية عالية الأداء باستخدام مزيج من الحشوات النانوية بنسب وزنية مختلفة. من بين الأنواع المختلفة من عناصر التقوية وجد أن الأنابيب النانوية الكربونية متعددة الجدران والطين النانوي اهتمامًا أكبر بكثير كعناصر تقوية لمصفوفة البوليمر نظرًا لخصائصها والحرارية الفريدة. في هذه الدراسة، تم إنتاج مركبات نانوية هجينة وتأثير محتوى MWCNTو NC على خصائص وخليط بوليمرات الايبوكسي. تم تحضير العينات من خلال عملية مزج عن طريق إضافة مذيب الإيثانول عند نسبة ١:١ لتشتت الحشوة النانوية ومن ثم خلطه مع الايبوكسي .تم تحضير العينات المقواة باستخدام اوزان مختلفة بنسبة ٠,٥٪ و ١٪ و ٢٪ من المواد النانوية. تميزت الخصائص المحسنة للإيبوكسي باختبار حيود الأشعة السينية و الموصلية الحرارية.

أظهرت نتائج الاختبار تحسين في خاصية التوصيل الحراري، أظهر الايبوكسي الهجين أعلى موصلية حرارية بنسبة ١٣٥٪ من المركبات النانوية MWNT و NC بنسبة ١٪ ، حيث وصلت النسبة إلى ٠,٣٥٦٨واط/متر.كلفن مقارنة الى الايبوكسي النقي. كما أظهر تحليل حيود الاشعة لمركب الايبوكسي النانوي. الهجين من المركبات النانوية للإيبوكسي يظهر جميع خصائص القمم من NC و MWCNTs. حيث يوجد تحول في موضع القمة عند ١ ٪ بسبب التفاعل بين المادة النانوية والإيبوكسي. كما أن هناك تغييرات في شدة أو موضع القمم التي تنشأ عند ١ ٪

لـ 2θ = ٢٠,١٣° المقابلة لمسافة الطبقة البينية ٠,٤٦١ نانومتر ، بسبب التشتت المتجانس والخالي من التكتلات داخل الايبوكسي.

1. Introduction

Epoxy resins are among the most widely used thermoset polymers for use in the production of composites. They are frequently utilized in coating and structural applications, such as adhesives, castings , electrical laminates, and tooling components, due to their outstanding mechanical, thermal, and electrical properties [1]. The brittleness, weak strength, low-temperature stability, and low fracture toughness of the pure epoxy polymer, are drawbacks that restrict its usefulness [2].In order to get over these problems, epoxy nanocomposite is made using reinforcing nanofillers such as nanoclay ,CNTs, and hybrid nanofillers are used to enhance the properties of epoxy in order to create high-performance epoxy composites with even better properties[3].Carbon nano-tubes (CNT) are characterized by a distinct atomic structure, a high tensile modulus, and exceptional thermal and electrical conductivities [4].So that multiwall carbon nanotubes (MWCNTs) have been used by several researchers to improve properties of polymer nanocomposite materials. Nanoclays have been shown to be effective polymer reinforcing fillers due to their lamellar structure and large specific surface area (750 m^2/g) [5]. They provide a substantial alternative for the production of polymer nanocomposites because of their inexpensive cost, outstanding characteristics, and high cation exchange capacities [6]. One of the most widely utilized types of nanoclay is montmorillonite clay, which is mostly composed of silica and alumina. MMT possesses the right combination of specific surface area, elastic modulus, low material cost, density, low thermal expansion coefficient, and thermal stability [7]. In order to create composite materials, which have at least one dimension in the micro-nanometer range, different matrices, fillers, and reinforcements are combined [8,9]. The dispersion of various fillers inside polymer matrices results in large interfacial contacts between the organic-inorganic phases, producing an interfacial material with very distinct shape and superior properties compared to bulk polymer phase qualities [10,11]. Sanaa Haider. M and et al. (2021). Studied improve performance epoxy matrix by using various weight of the MWCNT. The samples were manufactured by utilizing an ultrasonic machine and a solution mixing method. Resulted enhanced the impact of MWCNTs was increase as 33 %, 46 %, 75 %, and 108 %, respectively. Furthermore, improved their hardness to be as 0.4% ,2.20% ,2.89%. Finally, the FTIR and FE-SEM were also tested to find the structure of MWCNTs and dispersion quality [12]. Tuan Anh et al.(2020), studied FE-SEM, and XRD Mechanical of Nanoclay. The mechanical properties of the nanocomposite, including tensile strength, flexural strength, compression strength, and impact resistance, enhanced with a little addition of nano clay (2%). Izod. 63.05 MPa of tensile strength grew by 13.59%, 116.80 MPa of bending strength increased by 34.63 %, 179.67 MPa of compressive strength increased by 15.11 %, and 12.81 kJ/m2 of Izod impact resistance increased by 80.16%, or 63.5 MPa. [13]. Sunil Kumar and et.al (2021), investigated the mechanical properties of epoxy matrix with three different types of nanocomposites (NC, MWCNT, and hybrid). Nanoparticles were completely dispersed into epoxy resin utilizing homogenizer and ultrasonic processing methods. The results were shown for the mechanical (tensile strength and hardness) qualities. Tensile strength was raised from 50.5 MPa to 55.5 MPa (9.4% increases) compared to pure epoxy where it is found at 0.3 wt% MWCNT and 4% NC content hybrid composite. Also, at 0.3 % MWCNT-4%NC, the elastic modulus was measured at a higher value. Nanoclay has a 68% higher pure epoxy content. The MWCNT/epoxy resin at 0.5 % has the highest Rockwell hardness (HRB), 12.5 % higher than neat epoxy [14].

In this research, MWCNT and nanoclay will be employed to improve the thermal conductivity, and morphological properties. And combining 50% MWCNT and nanoclay by weight ratios to achieve high performance epoxy polymer nanocomposites.

2. Experimental Work:

2.1. Materials

Three materials were employed in this study at 2:1 weight ratio of epoxy resin and the hardener Sikodor-52 (Sika Turkey) was utilized. The use of industrial-grade multi-walled carbon nanotubes (MWCNTs) from Nanjing XFNANO Materials Tech Co. Ltd. with dimensions of outer diameter (8-15 nm), purity (>90 weight percent), inner diameter (3-6 nm), tube length (30-50 m), apparent density (0.1 g/cm3), tap density (2.1 g/cm3), and conductivity (>100 s/cm) is the second materials. Third Nanoclay (NC) Sigma Aldrich was used, which has the following characteristics: density (2.53 kg/m3), diameter (30-70 nm), length (1-3 m), and surface area (64 m2/g). The use of ethanol (99.9% purity) as the solvent aided in the surface modification and dispersion of the nanofillers.by combining solutions, epoxy nanocomposite is produced.

2.2. Preparation of Neat Epoxy

To investigate the effect of nanoclay and MWCNTs, pure epoxy samples were also fabricated. In silicone molds, the samples were molded. The preparation of the impact test samples and the tensile moulds is shown in Figure 1. First, a 2:1 mixture of the resin and hardener was prepared, and then 10 minutes of hand stirring. In order to remove any bubbles that may have formed in the mixture after it had been uniformly mixed, it was degassed in a specified way (at 35° C and a pressure of -80 Kpa) for 30 minutes. The mixture was then poured into silicone molds using a syringe for tensile and impact tests. The samples were then kept for 24 hours at room temperature. Table1 displayed the specifics of the EP matrix formulation.

Table (1): Epoxy and Epoxy Nanocomposites Samples.

No.	samples	No.	samples
1	Pure epoxy	16	NC 1% / Epoxy
2	Pure epoxy	17	NC 1% / Epoxy
3	Pure epoxy	18	NC 1% / Epoxy
4	MWCNTs0.5% / Epoxy	19	NC 2% / Epoxy
5	MWCNTs0.5% / Epoxy	20	NC 2% / Epoxy
6	MWCNTs0.5% / Epoxy	21	NC 2% / Epoxy
7	MWCNTs0.1% / Epoxy	22	MWCNTs0.5%–NC 0.5% / Epoxy
8	MWCNTs0.1% / Epoxy	23	MWCNTs0.5%–NC 0.5% / Epoxy
9	MWCNTs0.1% / Epoxy	24	MWCNTs0.5%–NC 0.5 % / Epoxy
10	MWCNTs 2% / Epoxy	25	MWCNTs1%–NC1% / Epoxy
11	MWCNTs 2% / Epoxy	26	MWCNTs1%–NC1% /Epoxy
12	MWCNTs 2% / Epoxy	27	MWCNTs1%–NC1% /Epoxy
13	NC0.5%/Epoxy	28	MWCNTs2%–NC2% /Epoxy
14	NC0.5%/Epoxy	29	MWCNTs2%–NC2% /Epoxy
15	NC0.5%/Epoxy	30	MWCNTs2%–NC2% /Epoxy

2.3. Dispersion of MWCNT/Nanoclay Nanofillers in Epoxy:

Three different types of samples were used in the fabrication process: MWCNT/epoxy, NC/epoxy, and hybrid (MWCNT-nanoclay) epoxy. These samples were all made in accordance with the following steps. To decongest the nanoparticle agglomeration and ensure adequate dispersion of nanoparticles in the resin, various dispersion techniques were used. In our investigation, MWCNTs and NC were added to the mixture in proportions of 0.5%, 1%, and 2% of the total weight. MWCNT were initially dissolved in ethanol at a 1:1 ratio. According to a prior work [15], the solvent was used as the dispersing medium to achieve a superior dispersion. The nanofillers were distributed by hand-stirring ethanol and CNTs. For 15 minutes, the CNT combination in ethanol was performed under strictly regulated circumstances. Then 15 minutes at room temperature magnetic stirring. Epoxy resin in the needed quantity was simultaneously taken and heated for 30 minutes at 60°C to reduce viscosity. In order to obtain a perfectly homogenous preheated epoxy resin, MWCNT/ethanol mixture was continuously added to epoxy after it had been heated for 1 hour at 40°C using an ultrasonicator. The beaker was then surrounded by bits of ice for an hour to stop the acetone from evaporating and maintain the proper temperature. Finally, the sample was heated at 60 °C for 2 hours to guarantee that all of the ethanol had been eliminated. Both nanoparticles were then evenly and consistently dispersed throughout the epoxy by continuous high-speed stirring. The liquid was then let to cool till room temperature so that the hardener "part B" could be added.

2.4 Fabrication of Nanocomposites

After dispersion of MWCNT in epoxy part A. The hardener was then added to the mixture in a 2:1 ratio. To create a homogenous mixture, high-speed mechanical mixing was done for 10 min at RT. To get rid of the bubbles that had formed in the resin as a result of the mechanical mixing in both situations, the resin mixture was degasified by putting it in a vacuum oven for around 30 minutes. The mixture was then poured into the mold as seen in Figures 1 and 2. the remaining steps for hybrid epoxy with MWCNT/Nanoclay and EP/NC. Were the processes used to create nanocomposites for Ep/MWCNT as shown in Figure (1).

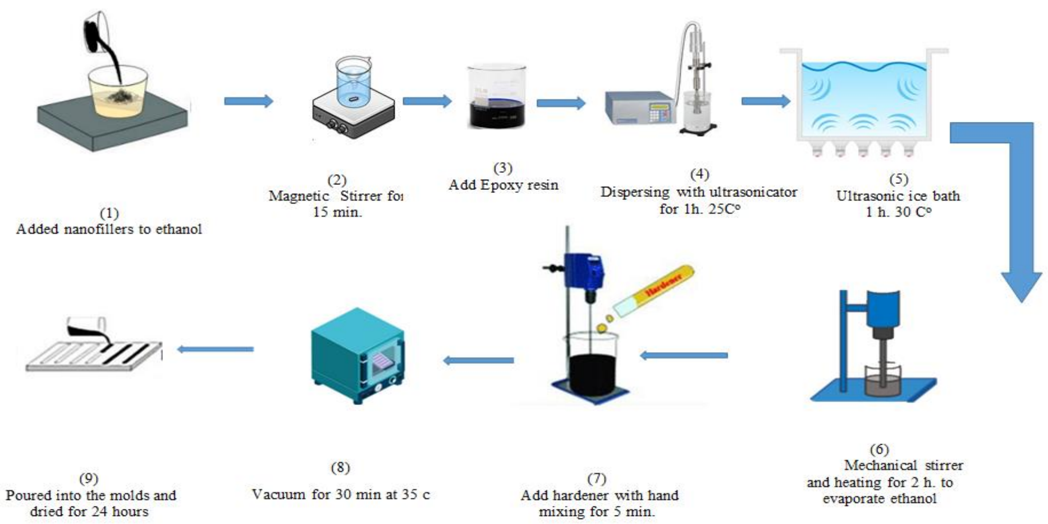


Figure (1): The schematic of manufacturing process for fabricating nanocomposites

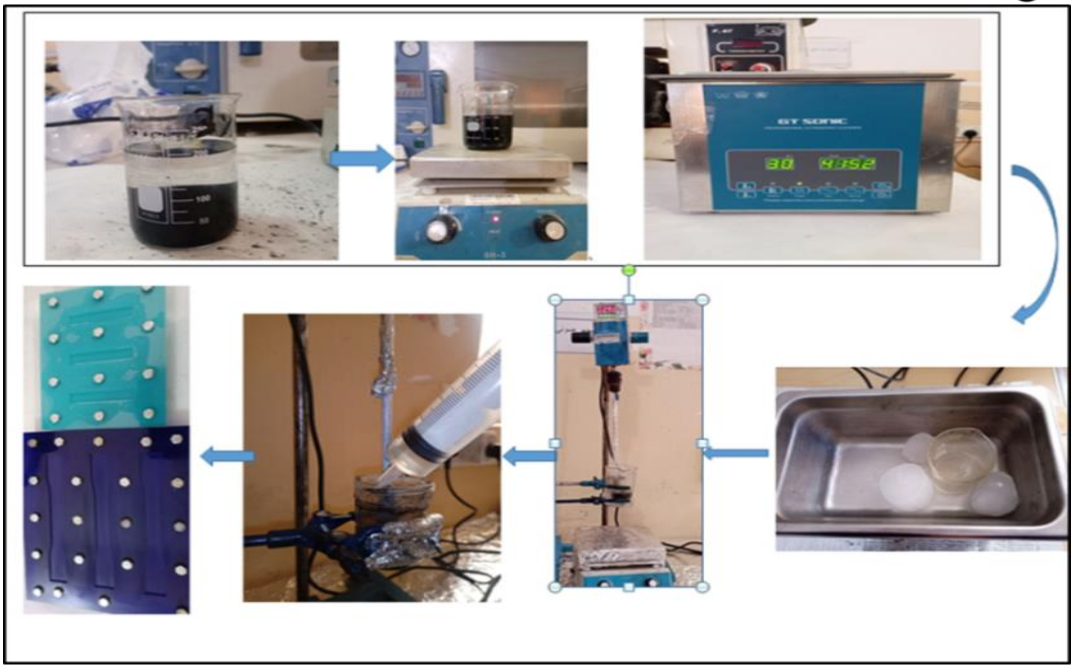


Figure (2): The processing steps of nanocomposites fabricating.

3.Charactrictization Technique

3.1. Thermal Conductivity Machine

KD2 PRO made in Decagon Devices, Inc, in College of Engineering materials / University of Kufa was used to measure the thermal conductivity. The gadget has a sensor that is submerged in the fluid during testing to acquire trustworthy findings. At least three readings should be collected for each test to assure accuracy. a smidgeon of liquid.

3.2. X-Ray Diffraction (XRD)

For analyzing ordered groupings of atoms or molecules through the interaction of electromagnetic radiation, the X-ray diffraction technique produces interference effects with structures close in size to the radiation wavelength [16]. The crystallinity of the blend's particles was evaluated using XRD on the advanced X-ray diffractometer SHIMADZU-XRD 6000.The crystalline extent was calculated using diameters (D) obtained from XRD peaks using Debye-Scherer's equation [17].

$$D=K\,\lambda/(\beta \cos\theta) \qquad (1)$$

Whereas: K is 0.89 as a constant, λ is the incident X-ray beam wavelength (Cu Kα=1.5406 A°), θ is the angle of diffraction of Bragg, and β is the full X-ray pattern line width at half peak radius height. The samples were prepared by placing small piece of each sample in a 200 mesh sieve. The sample was taken out from the sieve and placed in the sample holder, which consists of a circle of 20mm diameter and depth of 2 mm, then press well so that the powder is at the surface level of the sample holder.

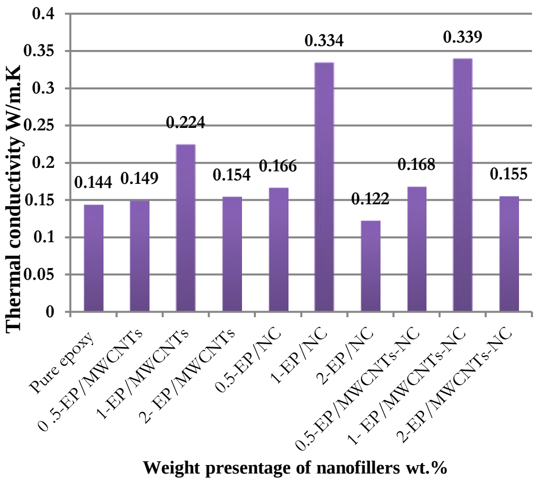
4. Results and Discussion

4.1 Results of Thermal Conductivity

Figure 3 and Table 2 show the variation of thermal conductivity as a function of wt.% contents for all the nanocomposites. The weight fraction of the fillers 0.5 and 1%increases linearly with the thermal conductivity. The thermal conductivities of epoxy nanocomposites containing 1wt.%MWCNT and NC were, respectively, 55% and 56% higher than those of clean epoxy. Hybrid epoxy has a thermal conductivity of 0.3568 W/m.K, which is 1wt.% higher than that of MWNT, NC nanocomposites. The large improvement in thermal conductivity of hybrid/epoxy composites with higher filler concentrations can be attributed to the high inherent thermal conductivity of MWNT and NC as well as the good contact between the filler and matrix. When hybrid (EP/MWNT-NC) concentration increased from 0.5 wt% to 2.0 wt%, epoxy nanocomposites' thermal conductivity dropped from 89% to 39%. As a result, it was discovered that adding CNT and NC to the epoxy matrix had a considerable impact on the heat conductivity of epoxy composites. However, the thermal conductivity coefficient rises when the weight ratio of EP/MWNT-NC is (1wt%). The largest percentage increase in thermal conductivity of epoxy nanocomposites due to the superior thermal conductivity of the nanofillers is 135%.

4.2. X-ray Diffraction Analysis (XRD)

An analytical approach for determining the crystal structure, particle size, and distance between crystal planes of produced nanoscale materials.X-ray diffraction for epoxy and its nanocomposites is shown in Figures 4 and table3. Due to scattering from the crosslinked network of epoxy, pure epoxy produces large peaks at 2θ=17.5°,indicating the amorphous nature of epoxy [18]. In the case of EP/MWCNTs at 1%, a peak can be detected at 2θ= 19.3°, which corresponds to an interlayer distance of 0.481nm according to the Bragg equation, with a little shift in the peak's position and a decrease in its intensity.This demonstrates the interfacial interactions between MWCNT and epoxy resin, which result in MWCNT dispersion in an epoxy matrix.The NC weight ratio relates to the clay's capacity to bond with the epoxy resin via van der Waals forces. Due to the homogeneous and cluster-free dispersion nanofillers in the whole epoxy matrix, hybrid-epoxy nanocomposites exhibit all distinctive peaks of NC and MWCNTs that may form at 1 wt.% for 2θ= 20.13° for d = 1.578. There is no major movement in the peak position here. There were no voids in neat epoxy or the NCs comprising 0.5-1wt.%generated by solution mixing. The X-ray diffraction spectrum of the nanocomposite hybrid 1wt.% showed a broad peak at (2θ = 17.97). While the diffraction spectrum of the EP/MWCNT-NC nanocomposite 2wt%) showed a slight displacement at the apex up to (2θ = 20.13°), due to the increase in the nanoscale scattering rate for both materials over epoxy matrix surface,which confirms the non-crystalline nature and the success of the bonding of the MWCNT ,and NC on the surface of epoxy resin, that transform from amorphous (solid phase) to rubbery phase during curing process at high temperature.



Figure(3): The thermal conductivity as function of wt.% of the pure epoxy and nanocomposites.

Table (3): XRD data of nanocomposites epoxy

Type of Sample	2θ	FWHM	Intensity (I%)	Height	d-spacing (nm)	Sample
Pure EP	17.5	0.756	99	276	0.506	10
0.5% CNT/EP	19.15	0.991	94.6	201	0.462	8
1%CNT/EP	19.3	1.379	91	229	0.481	5
2% CNT/EP	18.3	1.632	100	193	0.457	4
0.5% NC/EP	18.2	1.610	100	201	0.487	5
1% NC/EP	18.59	1.831	100	228	0.476	8
2% NC/EP	17.09	0.955	96.9	221	0.518	4
0.5%NC/EP	17.32	1.029	91.3	210	0.511	7
1% NC/EP	20.13	1.578	100	230	0.493	9
2% NC/EP	17.97	0.859	100	184	0.440	5

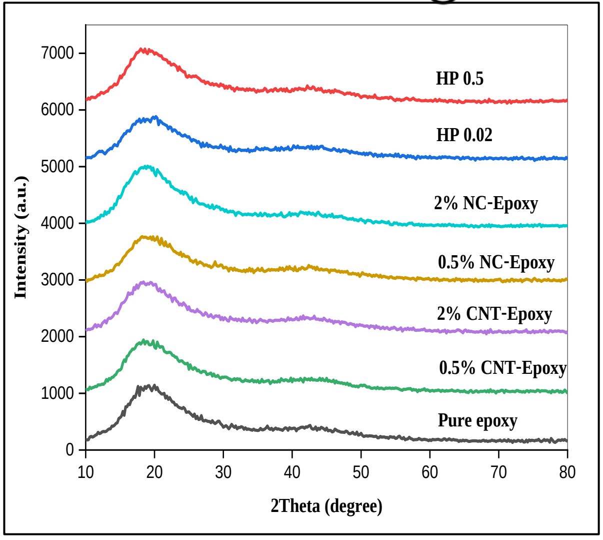


Figure (4): The X-ray diffraction spectrum of pure epoxy and its nanocomposites.

5.Conclusions

This study investigates the effects of MWCNT, NC and hybrid loading on the properties of EP nanocomposite. The following conclusions were XRD pattern of the epoxy nanocomposite. The hybrid-epoxy nanocomposites show all characteristics peaks of NC and MWCNTs. Since There are changes in the intensity or position of the relevant peaks. that may arise at 1wt.% due to the homogenous and cluster free dispersion nano filler in the entire epoxy matrix. An increase in thermal conductivity was obtained after the incorporation 1wt.% hybrid epoxy, while the other contents, noticeably for the 2wt.% concentration reduce conductivity. This indicates of agglomeration and the formation of filler clusters in the epoxy matrix with ratio 2wt% of MWCNTs and NC content

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7. References:

1. Muskopf JW. Mccollister SB. Ullman's encyclopedia of industrial chemistry. New York: Wiley; 2002.
2. Z. Wang, F. Liu, W. Liang, and L. Zhou, Adv. Mater. Sci. Eng. 2013, 1 (2013).
3. J. Wu, K. Yu, K. Qian, and Y. Jia, Fibers Polym. 16, 1540 (2015).
4. Mahesh, Hosur, Tanjheel, H. Mahdi, Mohammad E. Islam, Jeelani, S. Mechanical and viscoelastic properties of epoxy nanocomposites reinforced with carbon nanotubes, nanoclay, and binary nanoparticles (2017). https://doi.org/10.1177/0731684417691365.
5. Gojny, F.H., Wichmann, M.H.G., Fiedler, B., Karl, S. Influence of different carbon nanotubes on the mechanical properties of epoxy matrix composites. (2005). https://doi.org/10.1016/j.compscitech.2005.04.021
6. A. Jumahat, C. Soutis, N. Ahmad, and W. M. Wan Mohamed, "Fracture toughness of nanomodified-

epoxy systems," Applied Mechanics and Materials 393,206211.(2013).https://doi.org/10.4028/www.scientific.net/AMM.393.206.
7. M.A.M.a. Albozahid, Design of Novel High Modulus TPUs for NanoComposite Applications, School of Materials, University of Manchester, The UK, 2018, p. 277.
8. M. Albozahid, H.Z. Naji, Z.K. Alobad, A .Saiani, Effect of OMMT reinforcement on morphology and rheology properties of polyurethane copolymer nanocomposites, Journal of Elastomers Plastics(2021) https://doi.org/00952443211006 .
9. M. Albozahid, H.Z. Naji, Z.K. Alobad, A. Saiani, Enhanced mechanical, crystallisation and thermal properties of graphene flake-filled polyurethane nanocomposites: the impact of thermal treatment on the resulting microphase-separated structure, Journal of Polymer Research 28(8) (2021).
10. S.A.H. Zoalfokkar Kareem Alobad, Muayad Abdulhasan Albozahid, The Effecting of Physical Properties of Inorganic Fillers on Swelling Rate of Rubber Compound: A review Study, Journal of University of Babylon for Engineering Sciences 27(1) (2019).
11.Gorga, R.E. and Cohen, R.E. Toughness Enhancements in Poly(methyl methacrylate) by Addition of Oriented Multiwall Carbon Nanotube, J. Polym. Sci., Part B: Polym. Phys., 42(14): 2690–2702(2004).
12.Sanaa Haider Mateab , Muayad Albozahidb .Study the Effect of Adding MWCNTs on the Hardness, Impact Strength, and Structural Properties of Composite Materials based on Epoxy Polymer.2021.
13. Tuan Anh Nguyen, Thi Mai Huong Pham, Thi Huong Dang, Thi Hanh Do, and Quang Tung Nguyen. Study on Mechanical Properties and Fire Resistance of Epoxy Nanocomposite Reinforced with Environmentally, Friendly Additive: Nanoclay I.30E. (2020). doi:10.1155/2020/3460645.
14.Sunil Kumar, and Arun Gupta. perpetration, and mechanical properties of MWCNTs, NC/epoxy .2021. https://doi.org/10.4995/jarte.2021.14239.
15. Junjie Chen, Xuhui Gao,and Wenya Song. 16.Effect of various carbon nanofillers and different filler aspect ratios on the thermal conductivity of epoxy matrix nanocomposites.2019.
17.ASTM 792D, (2006), Standard Test Method for Density and Specific Gravity, Annual Book of ASTM Standard, Vol. 09.01.
18. J. Tian, C. Yang, J. Yang, S. Hao, The correlated effects of filler loading on the curing reaction and mechanical properties of graphene oxide reinforced epoxy nanocomposites, Journal of Materials Science 56(5) (2021) 3723-3737.
19.M Hossein Pol, GH Liaghat and F Hajiaraz, Effect of nanoclay on ballistic behavior of woven fabric composites: Experimental investigation,2012.