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Mechanical and Thermal Properties of Epoxy Composites Containing Zirconium Oxide Impregnated Halloysite Nanotubes

Moon il Kim, Suhyun Kim, Taehee Kim, Dong Koo Lee, Bongkuk Seo * and Choong-Sun Lim *

Center for Chemical Industry Development, Korea Research Institute of Chemical Technology, Ulsan 44412, Korea; mikim@krict.re.kr (M.i.K.); tngus266@krict.re.kr (S.K.); kimth@krict.re.kr (T.K.); dklee@krict.re.kr (D.K.L.)

* Correspondence: bksea@krict.re.kr (B.S.); chsunlim@krict.re.kr (C.-S.L.); Tel.: +82-52-241-6060 (B.S.); +82-52-241-6021 (C.-S.L.)

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Abstract: Liquid epoxy resins have received much attention from both academia and the chemical industry as eco-friendly volatile organic compound (VOC)-free alternatives for applications in coatings and adhesives, especially in those used in households. Epoxy resins show high chemical resistance and high creep resistance. However, due to their brittleness and lack of thermal stability, additional fillers are needed for improving the mechanical and thermal properties. Halloysite nanotubes (HNTs) are naturally abundant, inexpensive, and eco-friendly clay minerals that are known to improve the mechanical and thermal properties of epoxy composites after suitable surface modification. Zirconium is well known for its high resistance to heat and wear. In this work, zirconium oxide-impregnated HNTs (Zr/HNTs) were added to epoxy resins to obtain epoxy composites with improved mechanical and thermal properties. Zr/HNTs were characterized by field-emission transmission electron microscopy, transmission electron microscopy with energy-dispersive X-ray spectroscopy, X-ray diffraction, and X-ray photoelectron spectroscopy. Changes in the thermal properties of the epoxy composites were characterized by thermo mechanical analysis and differential scanning calorimetry. Furthermore, flexural properties of the composites were analyzed using a universal testing machine.

Keywords: epoxy composite; halloysite nanotube; zirconium oxide; flexural strength; flexural modulus; coefficient of thermal expansion

1. Introduction

Liquid epoxy resins are widely used as structural adhesives and coating materials due to their low cost, good workability, volatile organic compound (VOC)-free eco-friendliness, good adhesion, heat resistance, electrical insulation, chemical resistance, and excellent weather resistance. However, most epoxy resins need additional fillers to realize improved mechanical and thermal properties, because of their inherent brittleness and industrial requirements. Various inorganic materials have been used as fillers to improve the mechanical and thermal strengths of epoxy composites [1–9].

One of the clay materials that can be applied as a filler material is halloysite nanotubes (HNTs). HNTs are naturally abundant, inexpensive, and eco-friendly. They are known to improve the mechanical properties of epoxy composites after proper surface modification, and lack of surface modification can lead to poor nanotube dispersion and inefficient stress transfer [2]. Moreover, poor load transfer between the HNTs and the surrounding polymer chains can cause interfacial slippage, leading to deteriorated mechanical properties of the composites [10]. Therefore, optimizing the HNT surface is essential to enhance the properties of the nanocomposites.

Zirconium oxide is well known for its resistance to abrasion, corrosion, and heat. In addition, it is the first ceramic material reported to show low brittleness. Zirconia nanoparticles have been used as fillers in polymer nanocomposites to improve their strength and stiffness [11]. However, due to the high aggregation tendency of the nanoparticles, structural defects occur in the nanocomposites, resulting in a decreased possibility of mechanical property improvement [12]. Organic modifiers have been used to improve the interfacial bonding strength between the fillers and the resin, and thus reduce the aggregation of zirconia [12,13].

In this study, zirconia-impregnated HNTs (Zr/HNT) were used to improve the mechanical and thermal properties of epoxy composites. The effect of Zr/HNT doping on the mechanical and thermal properties of the epoxy composites was studied using a variety of techniques. In particular, the epoxy composites with Zr/HNT were tested for their flexural strength, flexural modulus, and coefficient of thermal expansion (CTE).

2. Materials and Methods

2.1. Materials

HNT used in this study, Dragonite-HP (Si/Al = 1), was purchased from Applied Minerals (New York, NY, USA). Zirconyl chloride octahydrate (reagent grade, 98%) purchased from Sigma-Aldrich (Darmstadt, Germany) was used as the precursor for impregnation.

The epoxy composite consisted of an epoxy resin, a hardener, an accelerating agent, and fillers (HNT, Zr/HNT). Bisphenol A diglycidylether (DGEBA, EPIKOTE 828) from Momentive (Waterford, NY, USA) was used as the epoxy resin. It has an epoxy equivalent weight of 187 g/eq. The hardener, dicyandiamide (DICYANEX 1400F) from Air Products (Allentown, PA, USA), maintains its solid state and does not react with the epoxy resin at room temperature. To accelerate the curing process, 1,1-dimethyl-3-phenylurea (AMICURE UR 7/10) from Air Products (Allentown, PA, USA) was used.

2.2. Prereration of Zr/HNT and Epoxy Composites

The preparation method for Zr/HNT is illustrated in Figure 1. 2 wt % Zr/HNT was prepared through the wet impregnation method using a solution of $ZrOCl_2 \cdot 8H_2O$ in double-distilled water. Finally, the sample was dried at 90 °C overnight and calcined at 500 °C for 6 h.

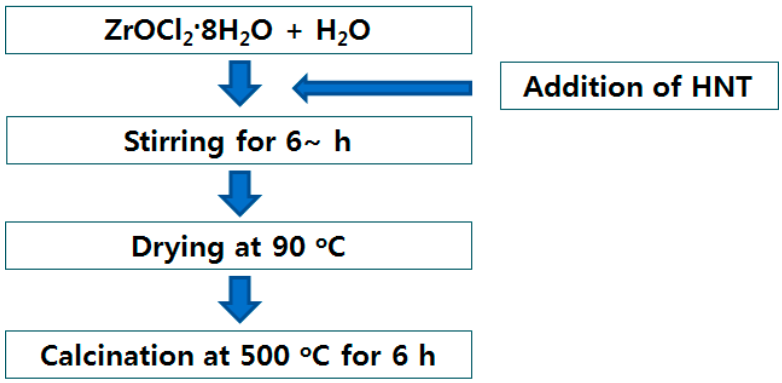


Figure 1. Schematic of the synthesis of Zr/HNT by wet impregnation.

Epoxy composites containing different weight fractions (2.5, 5, 7.5, and 10 wt %) of Zr/HNT and untreated HNT were prepared. The epoxy resins were mixed with designated amounts of the filler at 80 °C for 30 min. Then, the hardener and the accelerating agent were sequentially added to the mixture at weight ratios of 100/11.24 and 100/0.21 with respect to epoxy resins, respectively, with stirring. The heating and stirring were continued for an additional 30 min. Finally, the mixture was transferred to a mold for solidification and cured in two stages: 170 °C for 1 h and 190 °C for 2 h.

2.3. Characterizations

2.3.1. Characterizations of Zr/HNT filler

Electron micrographs of the synthesized Zr/HNT fillers were obtained using a field-emission scanning electron microscope (FE-SEM, Tescan Mira3, Brno, Czech Republic). A field-emission transmission electron microscope (FE-TEM, JEM-2100F, JEOL, Tokyo, Japan) was also used to image the HNT and Zr/HNT samples, and elemental analysis of each filler was performed using an energy dispersive X-ray spectroscope (EDS, X-MAX, Oxford, UK) attached to the microscope. To verify the dispersion pattern of the zirconium oxide on HNT, X-ray diffraction (XRD, Rigaku Ultima IV, Rigaku, Tokyo, Japan) was carried out. The oxidation state of the zirconium in Zr/HNT was determined by X-ray photoelectron spectroscopy (XPS, AXIS NOVA, Kratos, Manchester, UK).

2.3.2. Thermal and Mechanical Tests on Zr/HNT-Epoxy Composites

The curing conditions for the epoxy composites with Zr/HNT were studied by differential scanning calorimetry (DSC, Q1000, TA Instruments, New Castle, DE, USA). The composites were heated to 300 °C at the rate of 10 °C/min under a N_2 atmosphere, during the DSC analysis. The coefficient of thermal expansion (CTE) was obtained from the slope of thermal strain versus temperature curve below the glass transition temperature (T_g) [14] obtained by a thermomechanical analyzer (TMA, Q2940, TA Instruments, New Castle, DE, USA). During the TMA analysis, the specimens ($5 \times 5 \times 3$ mm^3) were heated from room temperature to 200 °C at the rate of 5 °C/min.

Flexural tests were carried out at room temperature using a universal test machine (UTM 5982, INSTRON, Leicester, UK) at the strain rate of 1.2 mm/min. The specimens for the flexural strength test had dimensions of 60 mm × 25 mm × 3 mm (length × width × thickness) in accordance with the ASTM D790M standard [15].

3. Results and Discussion+

3.1. Characterization of Zr/HNT Filler

Figures 2 and 3 show electron micrographs of native or unmodified HNTs and Zr/HNTs obtained using the FE-SEM and TEM, respectively. There was no significant morphological difference between HNT and Zr/HNT, even though zirconium oxides were impregnated in the latter, as confirmed subsequently by EDS and XPS. The similarity in the morphologies suggests that zirconium oxides are well dispersed on the surface of the HNTs, without the formation of any bulk zirconium oxides. EDS analysis confirmed the presence of zirconium in the Zr/HNT filler, as shown in Figure 3.

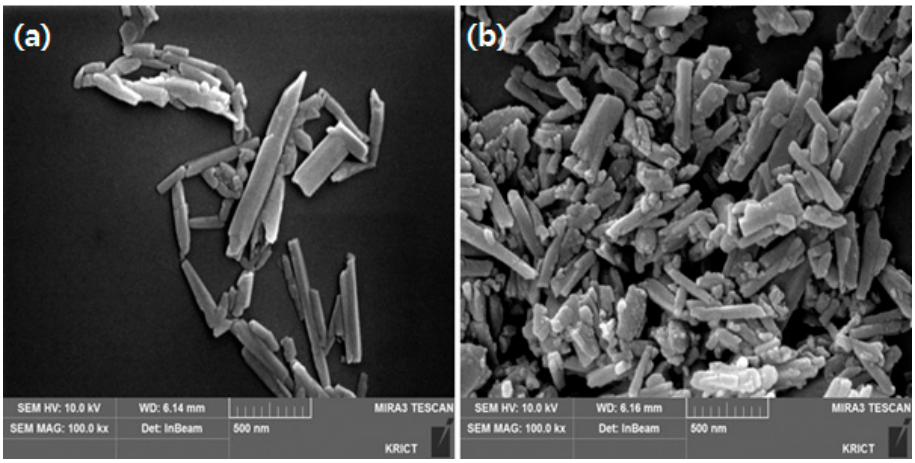
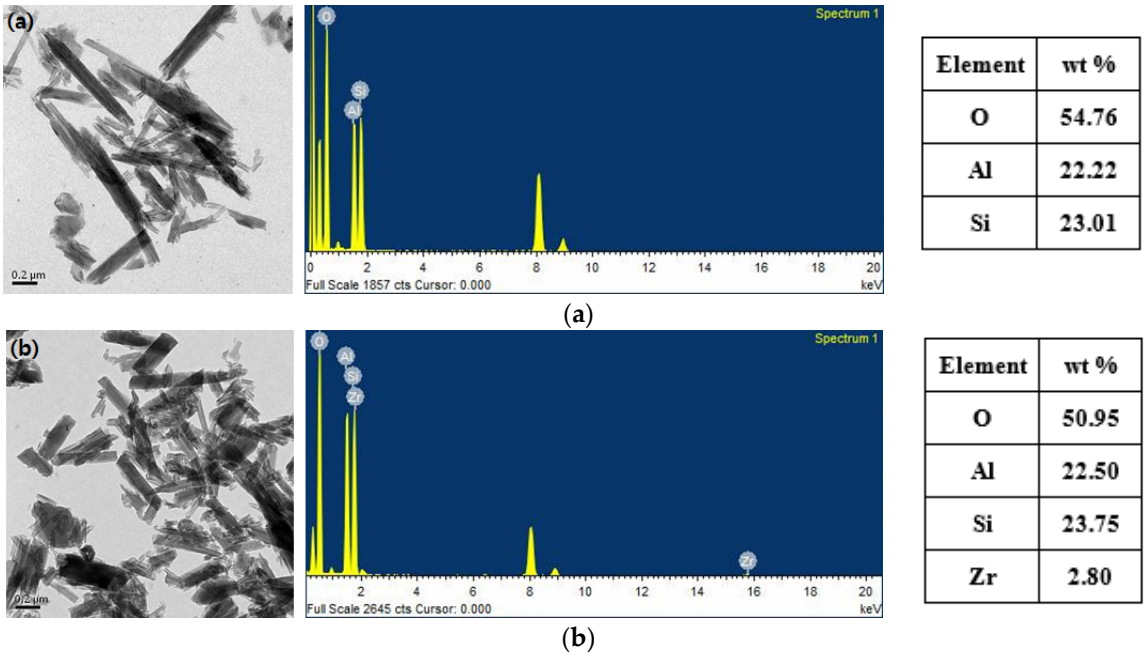


Figure 2. SEM images of (**a**) HNT and (**b**) Zr/HNT.



Element	wt %
O	54.76
Al	22.22
Si	23.01

Element	wt %
O	50.95
Al	22.50
Si	23.75
Zr	2.80

Figure 3. TEM images of (**a**) HNT and (**b**) Zr/HNT with the corresponding EDS elemental analysis shown in the middle and the element composition on the right.

Figure 4 shows the high-angle XRD patterns of HNT and Zr/HNT. The XRD patterns of HNT after impregnation with zirconium oxides were similar to those of HNT, with no peaks associated with crystalline zirconium oxide. This implies that zirconium oxide is neither in the bulk state nor in the crystalline phase. This confirms that the impregnated zirconium oxide is well distributed on the surface of the support [16]. The XRD results agree well with the FE-SEM and TEM observations.

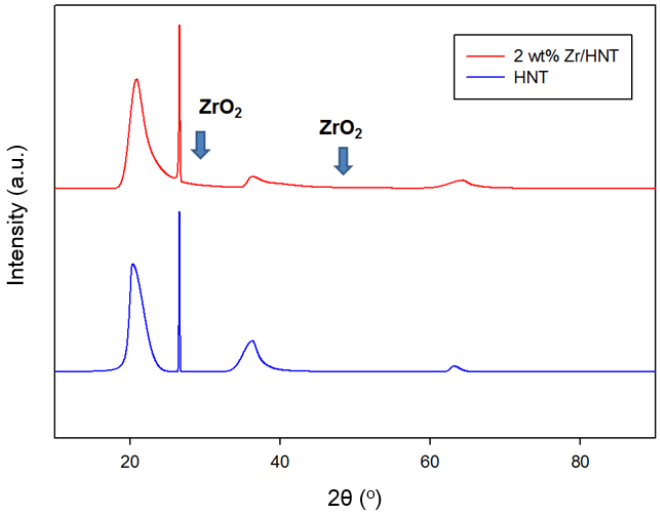


Figure 4. X-ray diffraction patterns of HNT and Zr/HNT.

The XPS analysis of Zr/HNT is shown in Figure 5. Two peaks were observed, whose identity was confirmed by using the Joint Committee on Powder Diffraction Standards (JCPDS) database. The peak with the binding energy of 182.4 eV represents Zr3$d_{5/2}$, and the other with the binding energy of 180.0 eV represents Zr3$d_{5/2}$ of Zr sub-oxides. The spectral data indicate that zirconium occurs as both +4 and +3 oxidation state on the HNT support, meaning that ZrO_2 and ZrO both coexist on the HNT surface.

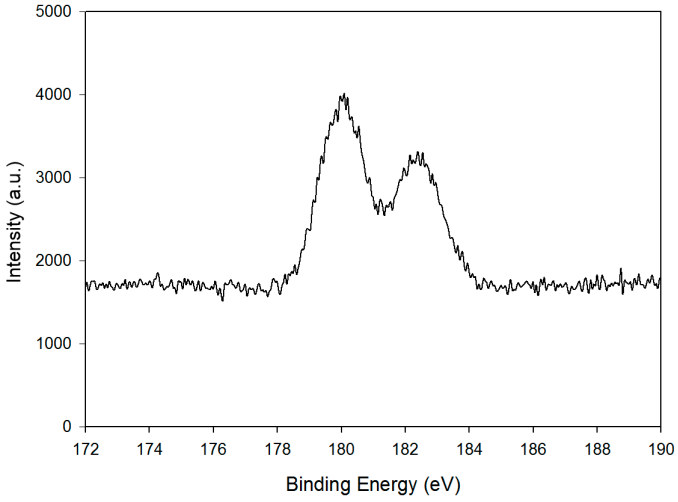


Figure 5. X-ray photoelectron spectrum of Zr/HNT.

3.2. Thermal Properties of Zr/HNT-Epoxy Composites

Figure 6 shows the DSC curves for the pristine epoxy resin, epoxy-HNT composite, and epoxy-Zr/HNT composite. A single peak from the DSC curve represents the exothermic nature of epoxy curing. Each DSC curve shows similar characteristics for the onset temperature (T_{onset}) and the maximum temperature (T_{peak}). The curing temperature (T_{cure}) of each composite was determined as the mid-point between T_{onset} and T_{peak}. The temperature profile data of these samples are shown in Table 1. Based on this, T_{cure} was determined to be 170 °C for all the composite samples.

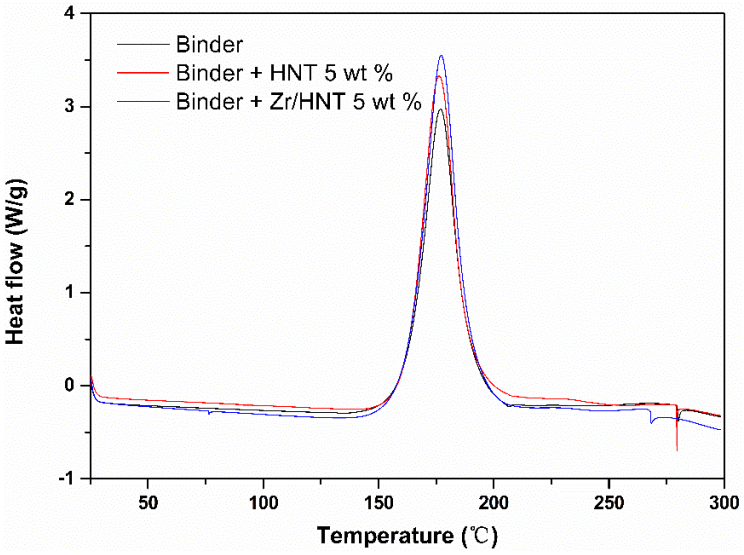


Figure 6. DSC profile of the epoxy resin and the epoxy composites.

Table 1. Curing temperature (T_{cure}) of the composites calculated from T_{peak} and T_{onset}.

Composite	T_{peak} (°C)	T_{onset} (°C)	T_{cure} (°C)
Pristine epoxy resin	181.22	160.21	170.72
Epoxy resin + HNT (5 wt %)	178.56	160.55	169.56
Epoxy resin + Zr/HNT (5 wt %)	176.32	161.17	168.75

A low CTE is desired to achieve dimensional stability [17]. The dimensional change curves for the epoxy composites with various amounts of the HNT and Zr/HNT fillers are shown in Figure 7. Dimensional changes for the composites were mostly smaller than those in the pristine epoxy resin, except for the composite with 2.5 wt % Zr/HNT at 200 °C. Since the amount of filler is too small, and the amount of Zr on the HNT filler is only 2 wt %, the performance of Zr was not significant. It might lead to weak filler matrix interactions in the composites, resulting in a similar pattern with neat epoxy [18]. The thermal properties of these epoxy composites from TMA analysis were summarized in Table 2. T_g was obtained by measuring the mid-point of the linear section between the initial and final linear section. CTE values were calculated for the linear sections of the TMA curves in the range of 60–120 °C, which are below T_g. The nanocomposites with HNT showed decreasing T_g with increasing filler content. This might be due to less interaction between the polymer and filler particle, resulting in a free surface [19]. HNT without any modification had a weak interaction with the polymer, compared to the modified one. Also, as the filler content increases, agglomeration of the particle can occur, which will increase the free volume, resulting in a lower T_g. The nanocomposites with Zr/HNT showed lower T_g than the pristine epoxy resin at the low content. However, it was increased as the filler content increased, and finally, the T_g value became larger when the Zr/HNT content reached 10 wt %. With the filler content below 10 wt %, Zr/HNT showed a lower T_g than the HNT, due to the low content of zirconium oxide to form an interaction with the polymer and removing –OH functional group by calcination, which the unmodified HNT had. However, when the Zr/HNT reached 10 wt %, the interaction between the filler and epoxy resin finally became strong enough, leading to better dispersion [18]. This can be proved by TEM analysis of composites with HNT filler and Zr/HNT filler, for which the images are shown in Figure 8. The composite with unmodified HNT showed some aggregation tendency compared to the Zr/HNT-epoxy composite. After zirconium oxide impregnation, the dispersion state of the filler improved, which supports the discussion.

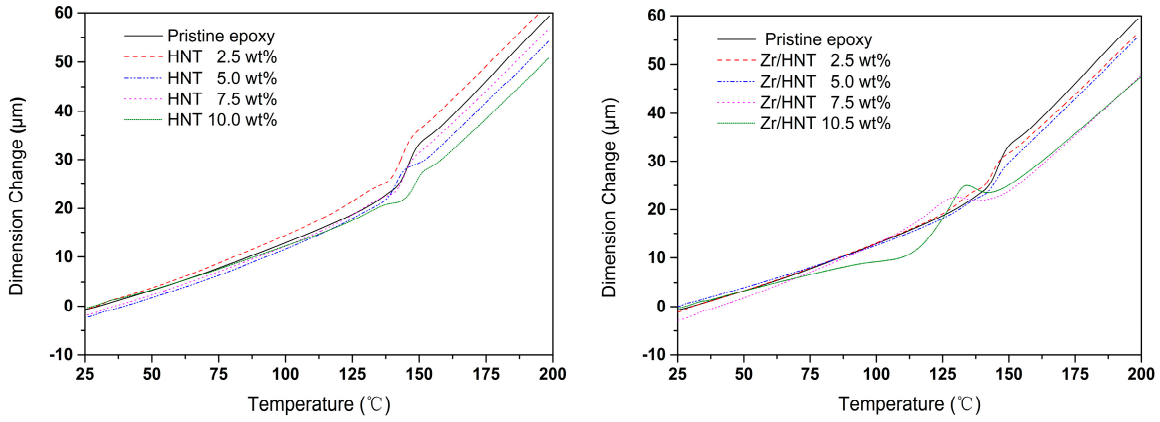


Figure 7. Dimensional change curves for epoxy composites with (**a**) HNT and (**b**) Zr/HNT fillers at different filler contents.

Table 2. Thermal properties of the epoxy composites with different fillers and filler contents from TMA analysis (a_1: CTE below T_g).

Filler Content (wt %)	T_g (°C)		a_1 (μm/(m·°C))	
	HNT	Zr/HNT	HNT	Zr/HNT
0	146.14		82.32	
2.5	145.33	143.57	74.70	79.29
5	142.30	141.15	73.00	73.72
7.5	141.29	144.89	72.18	68.86
10	134.86	148.42	68.68	60.94

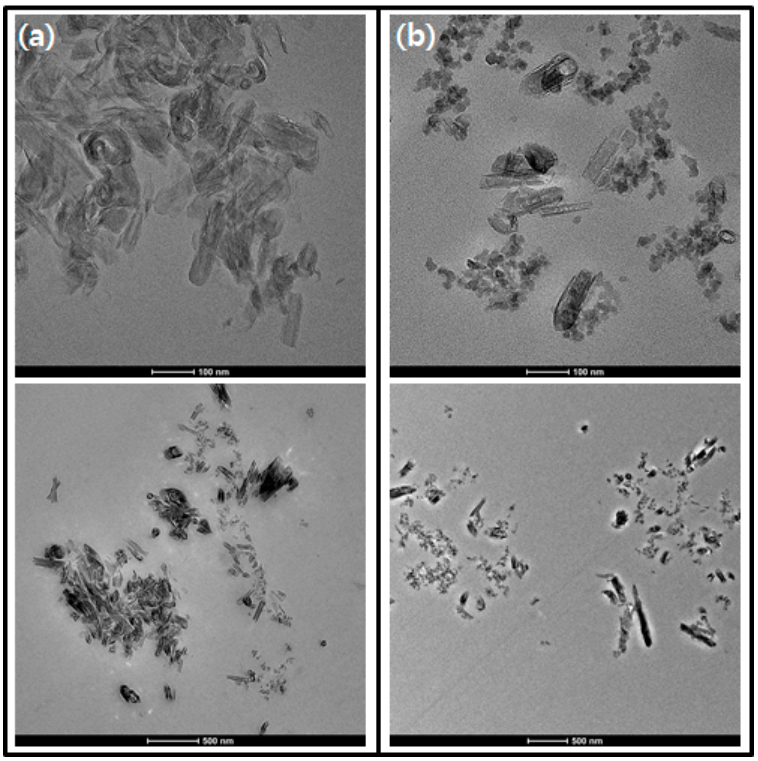


Figure 8. TEM images of epoxy composites with (**a**) HNT and (**b**) Zr/HNT at 10 wt % filler content.

The CTE values (a_1) of epoxy composites with different fillers and filler contents are shown in Figure 9. The composite with 2.5 wt % Zr/HNT had a higher CTE compared to the epoxy-HNT composite at the same loading. However, CTE values became similar when the filler content was 5 wt %. At higher loadings, the epoxy-Zr/HNT composites showed better CTE values. It has been reported that the thermal stability of the nanocomposite can be increased with the addition of HNT as a filler material [2]. Moreover, Zr has been reported to effectively catalyze the epoxy polymerization/crosslinking reaction. Additionally, the thermal stability of the epoxy composite can be improved in the presence of Zr [11]. Therefore, the improvement in the thermal properties of the epoxy composite with Zr/HNT may be attributed to the combined effects of the high thermal stability of HNT, heat resistance of zirconia, and potentially better interfacial bonding between the fillers and the polymer.

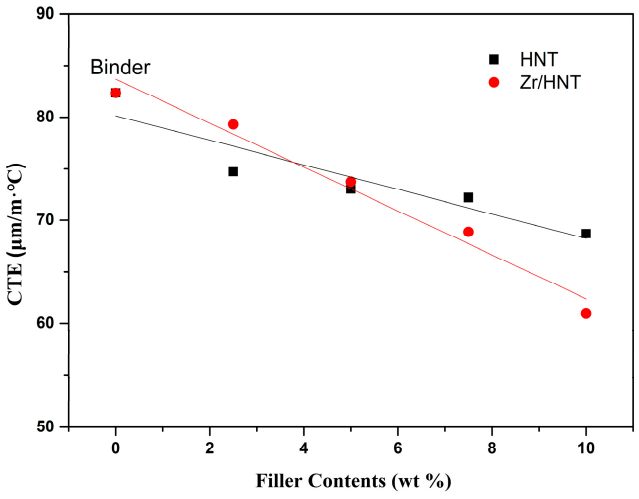


Figure 9. CTE of epoxy composites with different fillers and filler contents.

3.3. Mechanical Properties of Zr/HNT-Epoxy Composites

The flexural strength and flexural modulus of the prepared epoxy composites were measured using a UTM. The results are shown in Table 3. The flexural strengths and flexural moduli of the composites increased with the addition of HNT and Zr/HNT fillers. The Zr/HNT-epoxy composites had lower flexural strengths than the HNT-epoxy composites with the same loading when the filler content was lower than 10 wt %. Some studies have reported that the presence of zirconium oxides within the nanocomposite network leads to improved mechanical properties [11,12]. The lower flexural strength of the composite with Zr/HNT as compared to that of the composite with HNT is due to the extremely small amount of zirconia in the epoxy network. However, when the filler content was increased to 10 wt %, the flexural strength was improved with the impregnation of zirconium oxide into the HNTs. The flexural moduli of the Zr/HNT-epoxy composites were higher than those of the HNT-epoxy composites with the same loading. The modulus gradually increased with the filler content. It has been reported that overloading of zirconium oxide leads to a decreased flexural strength and minimal improvements in flexural modulus, owing to aggregation [12]. However, with the impregnation of zirconia, it can be well-distributed on the HNT surface without any crystalline domains, which was proven by XRD analysis. This leads to a decrease in the aggregation tendency of zirconia, resulting in an increased flexural strength and flexural modulus at a higher filler content.

Table 3. Flexural strength and flexural modulus of the nanocomposites with HNT and Zr/HNT fillers.

Filler Content (wt %)	Flexural Strength (MPa)		Flexural Modulus (MPa)	
	HNT	Zr/HNT	HNT	Zr/HNT
0	124.23 ± 0.3		3740 ± 9	
2.5	125.18 ± 1.97	124.11 ± 0.86	3747 ± 30	3746 ± 13
5	132.08 ± 0.67	130.15 ± 1.10	3899 ± 42	3981 ± 9
7.5	132.40 ± 0.46	132.21 ± 1.36	4013 ± 82	4060 ± 72
10	132.16 ± 1.11	134.16 ± 0.73	4229 ± 57	4249 ± 20

4. Conclusions

Zirconium oxides were impregnated on HNT by a wet impregnation method, with the objective of improving the performance of HNTs as a filler material in epoxy composites. FE-SEM and TEM observations, as well as XRD analysis, indicated that zirconium oxide was well dispersed on the HNT surface without any crystalline oxide phase. Zirconium on Zr/HNT had oxidation states of both +4 and +3. The CTE values of the epoxy composites decreased with increased filler (HNT, Zr/HNT) content. This improvement is attributed to the effects of the high thermal stability of both HNT and zirconia, and the potentially better bonding between the fillers and the epoxy resin. Upon the addition of zirconium oxide to HNTs, the flexural strengths and flexural moduli of the epoxy composites were improved with the increase in the filler content, owing to the enhanced dispersion of zirconia.

5. Patents

For the results from this work, a patent was submitted with the title "Halloysite nanotube coated with zirconia, synthesis method and polymer composite containing it" (Application No.: 2016-0159886).

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Author Contributions: Moon il Kim, Bongkuk Seo, and Choong-Sun Lim conceived and designed the experiments; Moon il Kim, Suhyun Kim, and Taehee Kim performed the experiments; Moon il Kim and Suhyun Kim analyzed the data; Dong Koo Lee contributed reagents/materials/analysis tools; Moon il Kim wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Yasmin, A.; Luo, J.J.; Abot, J.L.; Danie, I.M. Mechanical and thermal behavior of clay/epoxy nanocomposites. *Compos. Sci. Technol.* **2006**, *66*, 2415–2422. [CrossRef]
2. Liu, M.; Guo, B.; Du, M.; Lei, Y.; Jia, D. Natural inorganic nanotubes reinforced epoxy resin nanocomposites. *J. Polym. Res.* **2008**, *15*, 205–212. [CrossRef]
3. Shiu, S.C.; Tsai, J.L. Characterizing thermal and mechanical properties of graphene/epoxy nanocomposites. *Compos. Part B* **2014**, *56*, 691–697. [CrossRef]
4. Zhu, J.; Wei, S.; Yadav, A.; Guo, Z. Rheological behaviors and electrical conductivity of epoxy resin nanocomposites suspended with in-situ stabilized carbon nanofibers. *Polymer* **2010**, *51*, 2643–2651. [CrossRef]
5. Sun, D.; Chu, C.-C.; Sue, H.-J. Simple approach for preparation of epoxy hybrid nanocomposites based on carbon nanotubes and a model clay. *Chem. Mater.* **2010**, *22*, 3773–3778. [CrossRef]
6. Kim, H.J.; Jung, D.H.; Cifuentes, J.I.; Rhee, K.Y.; Hui, D. Enhancement of mechanical properties of aluminium/epoxy composites with silane functionalization of aluminium powder. *Compos. Part B* **2012**, *43*, 1743–1748. [CrossRef]
7. Yu, W.; Fu, J.; Dong, X.; Chen, L.; Jia, H.; Shi, L. Highly populated and nearly monodispersed nanosilica particles in an organic medium and their epoxy nanocomposites. *ACS Appl. Mater. Interfaces* **2013**, *5*, 8897–8906. [CrossRef] [PubMed]
8. Jang, J.S.; Bouveret, B.; Suhr, J.; Gibson, R.F. Combined numerical/experimental investigation of particle diameter and interphase effects on coefficient of thermal expansion and young's modulus of SiO_2/epoxy nanocomposites. *Polym. Compos.* **2012**, *33*, 1415–1423. [CrossRef]
9. Chen, K.; Tian, C.; Lu, A.; Zhou, Q.; Jia, X.; Wang, J. Effect of SiO_2 on rheology, morphology, thermal, and mechanical properties of high thermal stable epoxy foam. *J. Appl. Polym.* **2014**, *131*. [CrossRef]
10. Liu, M.; Jia, Z.; Jia, D.; Zhou, C. Recent advance in research on halloysite nanotubes–polymer nanocomposite. *Prog. Polym. Sci.* **2014**, *39*, 1498–1525. [CrossRef]
11. Copuroglu, M.; Sen, M. Synthesis and characterization of a Zr-containing silicate-based epoxy-functional polymer nanocomposite system. *Polym. Eng. Sci.* **2015**, *55*, 792–798. [CrossRef]
12. Halder, S.; Ahmed, S.; Das, S.; Wang, J. Epoxy/glass fiber laminated composites integrated with amino functionalized ZrO_2 for advanced structural applications. *ACS Appl. Mater. Interfaces* **2016**, *8*, 1695–1706. [CrossRef] [PubMed]
13. Lu, Q.; Guo, F.; Sun, L.; Li, A. Surface modification of ZrO_2:Er^{3+} nanoparticles to attenuate aggregation and enhance upconversion fluorescence. *J. Phys. Chem. C* **2008**, *112*, 2836–2844. [CrossRef]
14. Kim, T.H.; Kim, D.; Lim, C.S.; Seo, B. Studies of the physical properties of cycloaliphatic epoxy resin reacted with anhydride curing agents. *Key Eng. Mater.* **2017**, *737*, 248–255. [CrossRef]
15. *ASTM D790M Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials (Metric)*; ASTM International: West Conshohocken, PA, USA, 2010.
16. Sohn, J.R.; Lee, D.G. Characterization of zirconium sulfate on TiO_2 and activity for acid catalysis. *Korean J. Chem. Eng.* **2003**, *20*, 1030–1036. [CrossRef]
17. Imai, T.; Sawa, F.; Nakao, T.; Ozaki, T.; Shimizu, T.; Kozako, M.; Tanaka, T. Effects of nano- and micro-filler mixture on electrical insulation properties of epoxy based composites. *IEEE Trans. Dielectr. Electr. Insul.* **2006**, *13*, 319–326. [CrossRef]
18. Giddappanavar, S.V.; Pol, A.S.; Shikkeri, S.B. Study of thermal properties by influence of filler material on carbon-epoxy composites. *Int. Res. J. Eng. Technol.* **2015**, *2*, 836–842.
19. Ash, B.J.; Rogers, D.F.; Wiegand, C.J.; Schadler, L.S.; Siegel, R.W.; Benicewicz, B.C.; Apple, T. Mechanical properties of Al_2O_3/polymethylmethacrylate nanocomposites. *Polym. Compos.* **2002**, *23*, 1014–1025. [CrossRef]