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Influence of nanosilica on the properties of nanocomposite based on K-153 epoxy resin

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Abstract

This article presents the effects of nanosilica content on some properties of nanocomposite based on K-153 epoxy resin (K-153 epoxy resin was made by modifying ED-20 epoxy resin with thiokol and oligomer acrylate, simultaneously) and polyethylene polyamine (PEPA) (as a hardener). Results show that nanosilica of lower than 1.5 weight percent (wt%) was suitable for K-153 epoxy resin in manufacturing polymer composite. At 80 ºC, gelation of K-153 epoxy resin with 1.5 wt% was 79,15 % in comparison to 75,28 % of K-153 neat epoxy. Tensile strength and flexural strength of nanocomposite with 1.2 wt% of nanosilica were 79.81 MPa and 98,14 MPa higher than those of K-153 respectively (53.30 MPa and 60.81 MPa). Besides that, thermal oxidation resistance and remaining ash of nanocomposite also increased in comparison to K-153 epoxy resin.

Keywords: Polymer composite, K-153 epoxy resin, nanosilica, nanocomposite, mechanical properties, thermal oxidation resistance.

1. Introduction

Epoxy resins were widely used in coating, polymer composite because of their good mechanical, thermal and chemical properties. They were also compatible with a variety of reinforcement materials. Those excellent properties made epoxy resin as a choice resin for many high-performance engineering applications. Despite their high performances, there are many opportunities to further performance and durability improvements of epoxy composites (Goodman, 1998; Liang & Pearson, 2009; Morsch, Liu, Greensmith, Lyon, & Gibbon, 2017; Park, Lee, & Lee, 2017). Some authors used nanoclay, nanographene, carbon nanotube with different contents to investigate flexural strength, tensile strength, thermal performance of epoxy nanocomposite (Li, Liu, Fang, Liu, & Liu, 2018; Papadopoulos, Gkikas, Paipetis, & Barkoula, 2016; Potts, Dreyer, Bielawski, & Ruoff, 2011; Radhi, Mohamad, Abdul Rahman, Abdullah, & Hasan, 2021). Nanocomposite materials based on epoxy resin and nanosilca, rubber particles, glass fiber cured with accelerated methylhexdrophthalic acid anhydride or modified cycloaliphatic amine (H-100), attracted many scientists in order to improve properties such as elasticity, hardness, or fracture toughness of epoxy resins (Blackman et al., 2007; Manjunatha, Taylor, Kinloch, & Sprenger, 2009; Tsai, Huang, & Cheng, 2011). K-153 epoxy resin (K- 153) was produced by modifying ED-20 epoxy resin simultaneously with thiokol and acrylate oligomer (TU 6-05-1584-85) so it is flexible and has a lower viscosity than common epoxy resins and it is easy to use as a composite matrix. In my previous research, the author had investigated the effect of drying temperature on curing and structural morphology of polymer composite based on K-153 with glass fiber (Thanh, 2019, 2020). Current paper presents the influence of nanosilica on some properties of nanocomposite based on K-153 and PEPA as a hardener. In this resaerch, the effect of nanosilica content on epoxy- nanosilica mixture viscosity and some mechanical properties of the final nanocomposite were studied to find the suitable content for manufacturing nanocomposite. In addition, the article also shows results of FT-IR infrared spectroscopy analysis to demonstrate curing reaction of epoxy resin with PEPA and investigate the thermal oxidation resistance of nanocomposite in comparison to K-153.

2. Materials and methods

2.1. Chemicals

- K-153 epoxy resin (Russia):
+ Epoxy content: 19- 22 %.
+ Molecular weight: 390 g/mol.
- Polyethylene polyamine supplied by Chimex

Ltd (Russia):
+ Molecular weight: 230- 250 g/mol.
+ Third amin group: 5- 9.
- Nanosilica, Sigma-Aldrich:
+ Fine powder.
+ Purity: 99.8%.
+ Average size: 12nm,
+ Specific surface area: 175- 225 m^2/g (according to BET method).

2.2. Sample preparation

- Mixing well K-153 and nanosilica of 0- 2 wt% until getting homogenous mixture. Making nanocomposite samples of above mixtures by adding PEPA as 100 wt% of K-153 with 10 wt% of PEPA repectively (Thanh, 2019, 2020).
- Preparing mold.
- Pouring the above mixture into the mold.
- Getting samples and drying at 50 °C, 60 °C, 70 °C, 80 °C, 90 °C, 100 °C in 6 hours (Thanh, 2020).
- Keeping samples for 07 days at room temperature before testing machenical properties.

2.3. Analysis methods

- Determining degree of curing: Preparing soxhlet device, extracting soluble components in filter paper with acetone on soxhlet device for about 3 hours. Then, drying filter paper to constant weight, weighing filter paper (g_0). Spreading on filter paper a quantity of cured K-153 or nanocomposite, this value was g_1. Samples were dried at 50 °C, 60 °C, 70 °C, 80 °C, 90 °C, 100 °C for 6 hours, cooled and extracted in acetone at room temperature for 20 hours. Then, taking samples out, drying until sample weight was constant, weighing to determine value g_2.

Degree of curing (G) was determined by:

$$G = \frac{g_2 - g}{g_1 - g_0}.100\%$$

Where:
G: Curing degree, %
g_0: Weight of dried filter paper, g
g_1: Weight of dried filter paper + unextracted sample, g
g_2: Weight of dried filter paper + unextracted sample, g

- Infrared spectroscopy (FT-IR) on the Fourier FTIR-8700 series converter.
- Thermal oxidation resistance: Thermal gravimetric analysis (TGA) was analyzed by NETZSCH TG 209F1 LIBRA in air condition with temperature rate of 10 °C/minute from room temperature to 600 °C.
- Tensile strength was determined as ISO 527-1:2012 on Zwick device with sample pulling speed of 5 mm/minute, at temperature of 25 °C, humidity of 70 %.
- Flexural strength was determined as ISO 178:2010 on Instron 5582-100 kN device, bending speed at 5 mm/minute.
- Viscosity of K-153 and K-153/nanosilica was determined by Brookfield Model RVT- Series 93412, at 25 °C.
- Hardness of material was determined as ISO 7619-1:2010 by TECLOCK- Jisk 6301A.
- Material abrasion was determined by ISO 4649: 2002.

3. Results and discussion

3.1. Effect of nanosilica content on physical state and viscosity of K-153 epoxy resin

Dispersion of nanosilica particles strongly effected on properties and fabricating of nanocomposite, when nanoparticles were well dispersed in polymer matrix, they would give good reinforcement effect. Influence of nanosilica content on physical state and viscosity of K-153 epoxy resin at 25 °C was shown in table 1.

Table 1. Physical state and viscosity of K-153 with different nanosilica content.

No.	K-153, Wt%	Nanosilica, Wt%	Physical state	Viscosity, Cp
1	100	0	Liquidity, transparence	35
2	100	0.5	Liquidity, transparence	73
3	100	1	Liquidity, opaque	217
4	100	1.5	Liquidity, opaque	589
5	100	2	Gel	-

Table 1 showed with nanosilica content up to 1.5 wt%, mixture remained its viscous liquid state; when nanosilica content reached to 2 wt% then mixture became gel. Nanosilica with a small content (0.5 wt%), viscosity of mixture increased slightly compared to the epoxy resin. When nanosilica content was increased continuously, the viscosity of the mixture increased sharply. It reached maximum value when nanosilica was about 1.5 wt% with viscosity of 589 cP. When nanosilica content reached 2 wt%, the mixture became gel state, which could not be used to make composite. This could be explained with silanol groups (Si-OH) on the surface of nanosilica, when nanosilca in the mixture was high enough, many silanol groups would interact with hydroxyl groups in epoxy resin therefore, leading to gelation. Besides that, nanosilica particles in epoxy resin were too high that they would agglomerate themselves and cause gelation (Ghaemy, Bazzar, & Mighani, 2011).

3.2. Effect of nanosilica content on curing reaction of K-153

Effect of nanosilica content on curing reaction of epoxy was determined by curing temperature and gel content. Samples were investigated with nanosilica content of 1.5 wt%, curing time was 6 hours at temperature of 50 ºC, 60 ºC, 70 ºC, 80 ºC, 90 ºC, 100 ºC (Thanh, 2020). Results were shown in figure 1, in which, M1 was for K-153 and M2 was for nanocomposite.

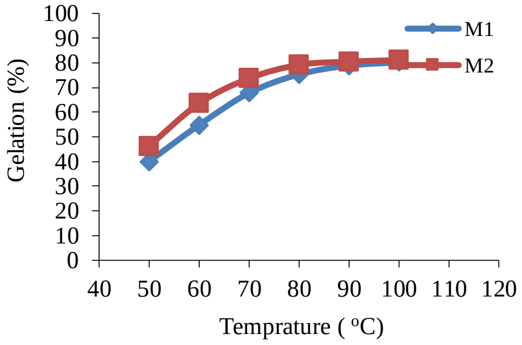

Figure1. Effect of nanosilica content on curing temperature of K-153 and nanocomposite.

Figure 1 showed that, in the investigated temperature range, with nanosilica content of 1.5 wt%, gel concentration of K-153 changed significantly compared to K-153 without nanosilica. For example, at 80 ºC, gel concentration of K-153 with nanosilica was 79.15 %, which significantly increased compared to neat K-153 of 75.28 %. This could be explained that, when adding nanosilica to epoxy resin, nanosilica had played as a catalyst and reduced activation energy of composite, leading to curing reaction of epoxy with PEPA strongly at lower temperatures (Ghaemy et al., 2011).

3.3. Effect of nanosilica content on abrasion and surface hardness of nanocomposite

Abrasion resistance and surface hardness are important information of material applicability. To study the influence of nanosilica content on abrasion resistance and surface hardness of nanocomposite, samples with nanosilica content of 0.5- 1.5 wt% were prepared and cured at 80 ºC in 6 hours (Thanh, 2020). Keeping samples for 07 days at room temperature before determining abrasion resistance and surface hardness. Results were shown in figure 2 and figure 3.

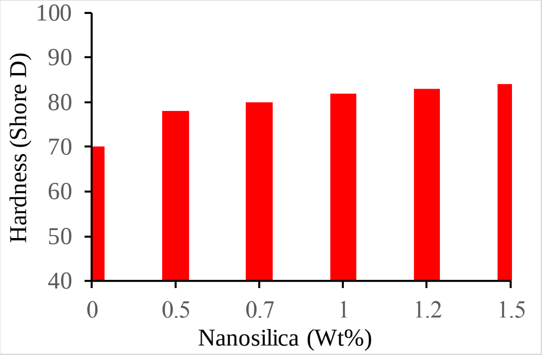

Figure 2. Effect of nanosilica content on surface hardness of nanocomposite.

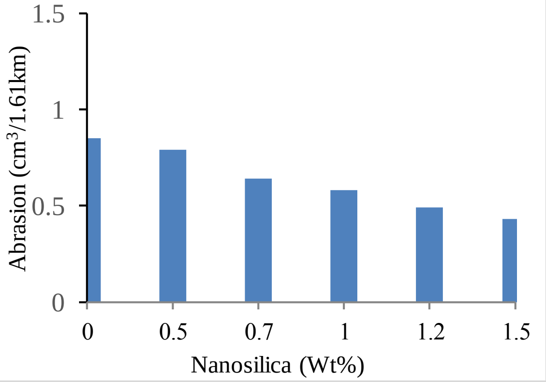

Figure 3. Effect of nanosilica content on abrasion of nanocomposite.

Figures 2 and 3 showed that, surface hardness of nanocomposite increased by nanosilica content. When nanosilica content was 1.5 wt%, surface hardness of nanocomposite reached 84 Shore D (much higher than that of K-153, 70 Shore D). It can be explained that, in this case, epoxy resin played the role of dispersing force applied to nanocomposite material, meanwhile, nanosilica worked as the corresponding force phase and that improved its resistance to deformation due to external forces to nanocomposite. In addition, nanosilica particles have much higher hardness than epoxy resin, so nanosilica content increases hardness of nanocomposite would be increased accordingly. Similarly for abrasion resistance of nanocomposite, when nanosilica content increased, abrasion resistance of material improved significantly or in other words, loss of material after testing decreases (Ghaemy et al., 2011; Li et al., 2018; Manjunatha et al., 2009).

3.4. Effect of nanosilica content on tensile strength and flexural strength of nanocomposite

To study the influence of nanosilica content on tensile strength, flexural strength of nanocomposite, samples with nanosilica content of 0.5- 1.5 wt% were prepared and cured at 80 ºC in 6 hours (Thanh, 2020). Keeping samples 07 days at room temperature before determining tensile strength, flexural strength of material. Results were shown in Figure 4.

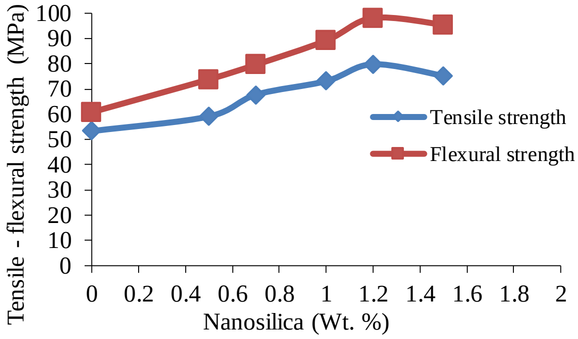

Figure 4. Effect of nanosilica content on tensile strength and flexural strength of nanocomposite.

Figure 4 showed that, when nanosilica content increased from 0.5- to 1.2 wt%, tensile and flexural strength of nanocomposite were significantly improved compared to K-153 (without nanosilica). Maximum tensile strength of nanocomposite was 79.81 MPa when nanosilica content was 1.2 wt%, compared to 53.30 MPa of K-153. Meanwhile, flexural strength of nanocomposite reached maximum value of 98.14 MPa when nanosilica content of 1.2 wt% compared to this value of 60.81 MPa of K-153. Improvement in tensile strength and flexural strength of nanocomposite can be explained that, nanosilica is uniformly dispersed in epoxy matrix up to 1.2 wt% without agglomeration. Due to close interaction between nanosilica surface and epoxy matrix, stress would transfer between two phases. In addition, nanoparticles could act as a agent to prevent crack propagation during the destruction of nanocomposite. Besides that, nanosilica particles had much greater hardness than epoxy, so when nanocomposite was loaded, deformation between two phases would be delayed, leading to more energy absorption and mechanical strength increases. However, if nanosilica content would increase continuously, nanoparticles tend to agglomerate into larger particles to release surface energy with bond between them was relatively weak (hydrogen bond) that was easily broken, so tensile and flexural strength of nanocomposite would decrease (Liang & Pearson, 2009; Papadopoulos et al., 2016; Tsai et al., 2011).

3.5. FT-IR of epoxy resin, PEPA, cured epoxy and nanocomposite

To investigate curing reaction of K-153 epoxy resin with PEPA and indetify the presence of nanosilca in nanocomposite, FT-IR was used for K-153, PEPA, cured K-153 and nanocomposite. Results were shown in figures 5a, 5b, 5c, 5d.

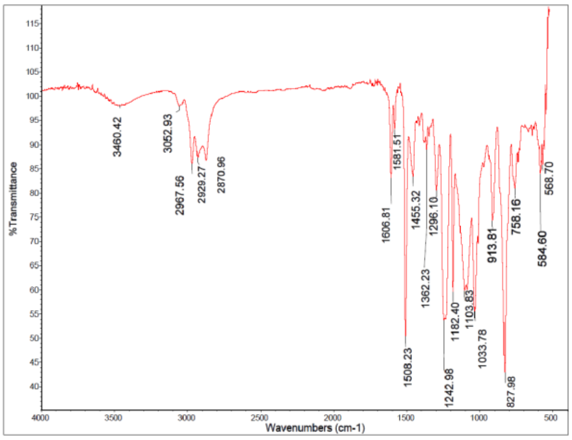

Figure 5a. FT-IR of K-153.

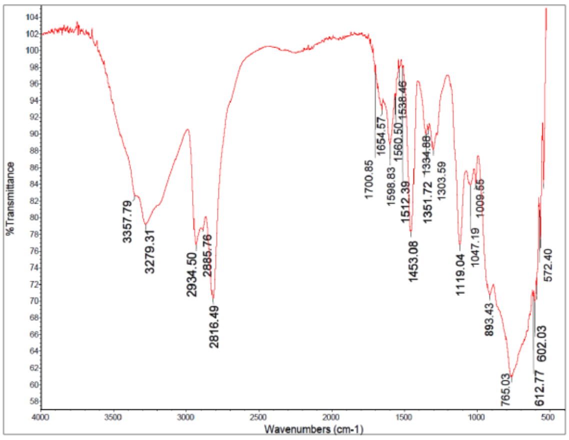

Figure 5b. FT-IR of PEPA.

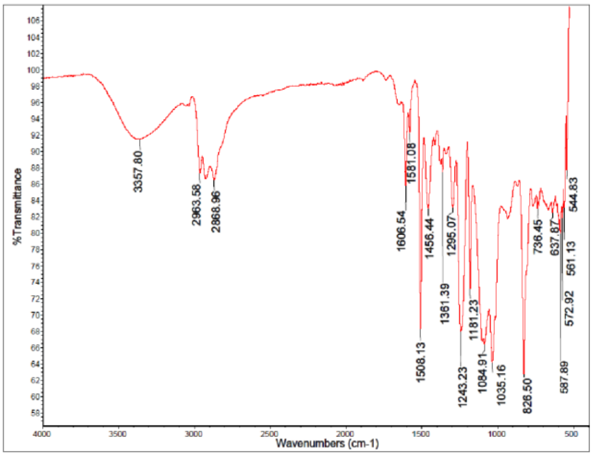

Figure 5c. FT-IR of cured K-153.

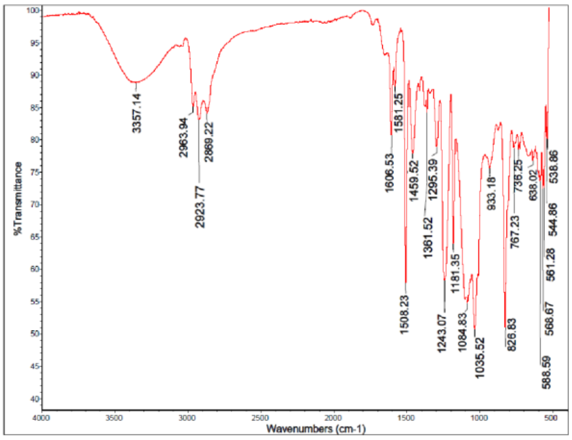

Figure 5d. FT-IR of nanocomposite.

Figures 5a, 5b, 5c, 5d showed that (Moore, 2017), peak 913.81 cm-1 of the oxiran group in epoxy resin (figure 5a) could not be observed at figure 5c and figure 5d. Besides that, peak 3279.31 of the NH group in figure 5b could also not be seen at figure 5c and figure 5d. This indicated that, epoxy ring- opening reaction with PEPA had completely occurred. There were some new peaks on figure 5d, in which, peak 933.18 cm-1 represented the vibration of Si-OH bond, and peak 767.23 was typical for the vibration of the Si-O-C bond, which proved in the captured sample FT-IR spectrum with silica.

3.6. Thermal oxidation resistance of K-153 and nano composite

To investigate thermal oxidation resistance of cured K-153 epoxy and nanocompsite, Thermogravimetric analysis (TGA) was used. Samples were cured K-153 epoxy and nanocompsite with nanosilica of 1.2 wt% . Results were shown in table 2 and figures 6a, 6b.

Table 2. Thermal oxidation resistance of epoxy resin and composite epoxy/nanosilica.

Samples	Weight loss (%)	
	300 ºC	600 ºC
K-153	16.53	94.81
Nanocomposite	3.16	86.09

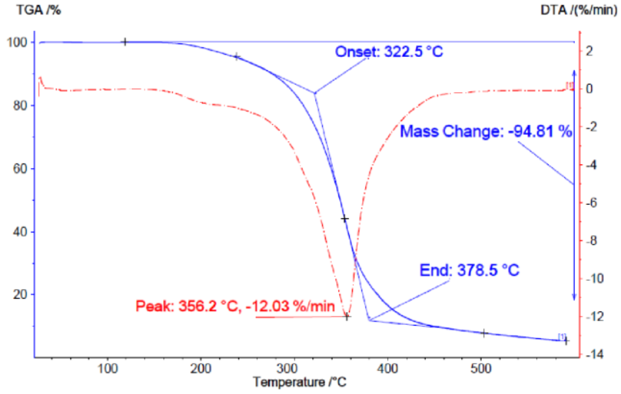

Figure 6a. TGA of K-153.

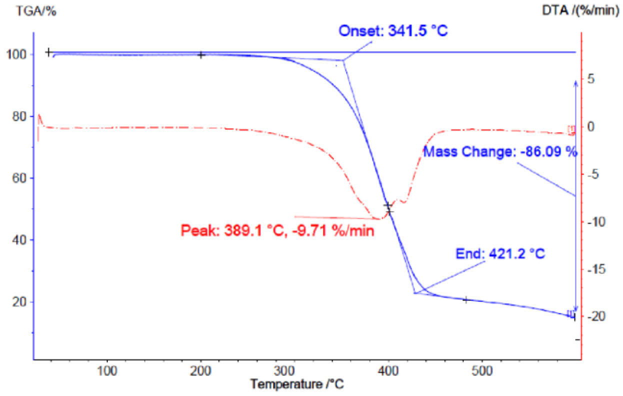

Figure 6b. TGA of nanocomposite.

Figures 6a, 6b and table 2 showed that, compared with K-153, thermal oxidation resistance of nanocomposite increased significantly. Besides that, K-153 had an ash content of 5.19 % and in the presence of nanosilica, ash content of nanocomposite was much higher, up to 13.91 %. Thus, it showed that nanosilica had improved thermal oxidation resistance of epoxy resin. In conditions of high temperature and oxygen, polymer chains were cut and oxidation of organic substances by oxygen also occurred. At that time, oxygen promoted the formation of free radicals, causing polymers to degrade deeply, forming lower molecular compounds containing oxygen. For nanocomposite, nanosilica particles prevented penetration of heat and oxygen into the structure of epoxy, in addition, thermal decomposition of nanosilica would coke to form a stable structure like ceramic (Huang, Xu, Du, Lee, & Wang, 2017).

4. Conclusions

- Nanosilica is strongly affected by the physical state and viscosity of K153 epoxy resin. Nanosilica content of less than 1.5 wt% was suitable for K153 in manufacturing polymer composite.

- Nanosilica greatly affected the curing temperature of K153, at 80 ^oC, gel content was 79.15%, significantly increased compared to K-153 without nanosilica of 75.28 %.

- Nanocomposite’s tensile strength was 79.81 MPa and flexural strength was 98.14 MPa with nanosilica of 1.2 wt%, those significantly increased in comparison with those of K-153 were 53.30 MPa and 60.81 MPa respectively.

- Nanosilica with content up to 1.5 wt% enhanced surface hardness of nanocomposite (increased from 70 Shore D to 84 Shore D). Regarding other properties of nanocomposite, nanosilica content of 1.2 wt% was suitable for manufacturing nanocomposite.

- Thermal oxidation resistance of polymer composite was higher than epoxy resin and ash of K-153 epoxy resin was 5.19 % but of nanocomposite was 13.91 %.

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