Study on the Effect of Nano-Silver on the Properties of Nanocomposite Based on Unsaturated Polyester

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Abstract

The masterbatch of unsaturated polyester (UP)/nano-silver obtained by using the Unidrive X1000 CAT mixer at 14000 rpm in 50 mins. The field emission scanning electron micrograph showed the flock of nano-silver has burst into smaller clusters and dispersed evenly in UP. The viscosity of matrix resin containing different nano-silver contents was almost unchanged except 100 ppm. Moreover, the presence of nano-silver has prolonged the gel and curing time but increased maximum exothermal temperature of emission. In general, the presence of nano-silver improved strongly in mechanical properties of composite especially nano-silver content of 60 ppm. Two bacterial strains: gram-positive bacterial (S.aureus) and gram-negative bacterial (E.coli) were used to evaluate the antibacterial property of sample. The results showed matrix resin without nano-silver possessed antibacterial property with both strains. The presence of nano-silver raised the gram-positive antibacterial property but reduced gram-negative antibacterial property of matrix resin.

Keywords: Nano-silver, nanocomposite, antibacterial, unsaturated polyester

1. Introduction

Although the technologies of conventional composites materials have peaked in most areas of application, scientists are constantly looking for more advanced materials and technologies to serve for commercial interest [1-3]. Polymer nanocomposites-modern materials are opening up a new generation of macromolecular materials with low densities and multifunctional properties [4]. Unlike conventional composites with microscale reinforcement, nanocomposites are a class of material in which the size of the reinforcement is nanometers. Because of the dramatic interfacial area in polymer nanocomposites and a higher influence of interfacial adhesion on final properties, polymer nanocomposites achieve the desired requirements even at rather low filler loading [1,3-5].

Among the numerous nanoparticles that have been used as antimicrobial filler in polymer nanocomposites, silver nanoparticles represent the most sought-after nanomaterials [2,5]. The excellent antibacterial activity of these nanocomposites has been demonstrated and it strongly depends on the nanoparticle size as this parameter changes the surface area that is in contact with the bacterial species [4].

Among various thermoset resins, unsaturated polyesters are the most widely used resins in polymeric composites because they are relatively cheap [3,6]. Many types of nanoparticles have been dispersed in unsaturated polyester resin to make nanocomposite like clay [1,6-8], carbon nanotube [9] graphene [10], silica [3], and Fe_2O_3 [11].

However, so far, there has been no report on the investigation of the unsaturated polyester/nanosilver-based nanocomposite. Therefore, this word focuses on assessing the effect of nano-silver on the properties of nanocomposite based on unsaturated polyester.

2. Materials and methods

2.1. Materials

The unsaturated polyester (UP) was purchased by Eternal Materials Co., Ltd., Taiwan. Catalyst as trigonox 93 (tert-butyl peroxy-benzoate) and cobalt accelerator NL-53 (cobalt (II) 2-ethylhexanoate) were manufactured in Akzo Nobel Chemincaks SA, Belgium. Silane was introduced by Evonik Resourece Effciency GMBH, Germany. Nano-silver powder 50K-HF (Na-Ag) Guard, Poland.

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2.2. Methods

2.2.1. The dispersion nano-silver

The 600 ppm of nano-silver, 2% of silane, and UP were mixed in Unidrive X1000 CAT mixer at 14000 rpm in 50 mins at National Key Laboratory for Polymer and Composite Materials, Hanoi University of Science and Technology to obtain masterbatch (fig.1).

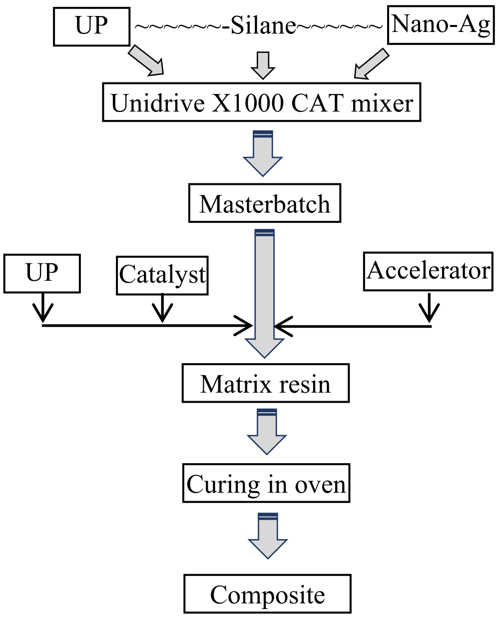


Fig. 1. The diagram of dispersion nano-silver and producing composite

The UP, catalyst and accelerator were added to obtain matrix resin with a defined nano-silver content. In which, the weight ratio of UP to catalyst and accelerator as 100/1/0.01. Then, the matrix resin was cured in oven at 40ºC in one hour to have composite (fig.1). With the goal of putting nano silver into engineered stone to create antibacterial materials, the nanocomposite was fabricated at R&D centers in accordance with the engineered stone manufacturing process of Vicostone Company in Vietnam (fig.1).

2.2.2. The study of viscosity of matrix resin

The viscosity of matrix resin with different nano-silver content was measured on Brookfield equipment at temperature of 20ºC

2.2.3. The analysis of morphologies of samples

The morphologies of nano-silver powder and nanocomposite were studied by a field emission scanning electron microscope (FeSEM, JSM-7600F, USA).

2.2.4. The study of curing reaction

The heat of curing reaction was determined by using the Testo 176T4 instrument (Germany). The gel time, curing time, and peak exothermic temperature of reaction of thermosetting resin were measured according to ASTM D 2471 standard.

2.2.5. The antibacterial property

The antibacterial test was evaluated in the School of Biotechnology and Food Technology, Hanoi University of Science and Technology based on published documents [12-14].

The antibacterial test was conducted by using standard disc diffusion assay on LB agar medium contained 10 g/l of peptone, 5 g/l of yeast, and 10 g/l of NaCl. In this process, two kind of bacterial, *Stanphylococcus aureus* - gram-positive bacterial (ATCC 25923), *Escherichia coli* - gram-negative bacterial (ATCC 25922) of 10^6 CFU/ml were used as indicators. An autoclave was used to sterilize all disc and materials before experiments. After sterilization, the bacterial solution was poured in plates, then the plates were set at room temperature for 24 hours to enable the surface to dry. The disc diffusion assay was determined by placing a 6 mm disk saturated by 50 µl of matrix resin slurry onto an agar plate inoculated with various microorganisms. The diameters of the inhibition zones were measured after 24 hours of incubation. The bigger diameter of inhibition zone means better antibacterial property.

2.2.6. Evaluating of properties of composites

Tensile and flexural strength were determined according to ASTM D638 and D790 standard, respectively by Instron equipment, USA. Impact strength was evaluated according to ASTM D256 standard by Tinius Olsen, USA.

3. Results and Discussion

3.1. The effect of nano-silver on the viscosity of matrix resin

UP, catalyst and accelerator were added to masterbatch to obtain matrix resin with nano-silver content varying from 0 to 100 ppm. The viscosity of matrix resin was reported in table 1.

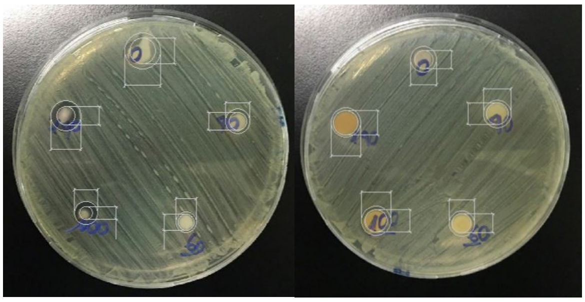
Table 1. The viscosity of matrix resins

Na-Ag, ppm	0	10	20	60	100
Viscosity, cP	422	430	433	430	460

The table 1 showed the viscosity of matrix resin did not change with small nano-silver content but increased lightly at 100 ppm of nano-silver content.

3.2. The effect of nano-silver on antibacterial property of matrix resin

All test samples showed the inhibition zone with different diameters (fig. 2). That means, the matrix resin possessed antibacterial property with both gram negative and positive bacterial even without nano-silver. The diameter of inhibition zone was determined by using Parallel Dimension tool in CoreDraw-2018 software. The result was shown in fig. 3.



E.coli strain *S.aureus* strain

Fig. 2. The picture of test disc after 24 hours of incubation

Without nano-silver, diameter of the inhibition zone of matrix resin with both bacterial strains were equal means their antibacterial property were the same. With gram-positive bacterial, the diameter of the inhibition zone raised from 14 to 15.67 mm when the nano-silver content increased to 100 ppm. The result showed an increase in nano-silver content lead to an improvement in inhibitory ability with gram-positive bacteria of *S.aureus*. While, the inhibitory activity of the sample with the gram-negative strain increased very little to 14.1 mm when the nano-silver content increased from 0 to 20 ppm and then reduced. At 20ppm nano-silver, the diameter of inhibition zone varied insignificantly compared to that of the sample without nano-silver. Thus, the presence of nano-silver has a negative impact on inhibitory activity against gram-negative strain of *E.coli* (fig. 3).

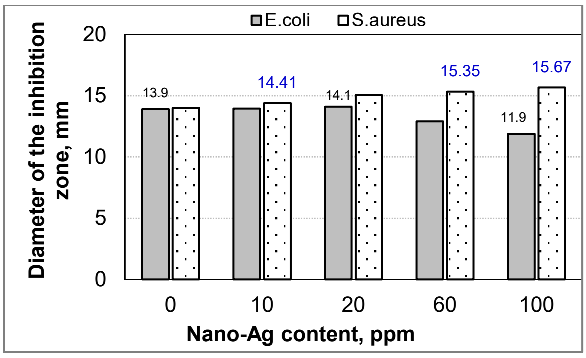


Fig. 3. The effect of nano-silver content on the diameter of inhibition zone

The fig. 3 also showed that the antibacterial ability of nano-silver for gram-negative strain of *E.coli* was less than gram-positive bacterial of *S.aureus*. This contrasts with the result reported by Huynh Nguyen Thanh Luan [15] but consistent with the result published by Giovani Pavoski [16].

3.3. The effect of nano-silver on characteristics of curing of matrix resin

The six curing reactions were carried out at the temperature of 40ºC. The nano-silver content changed from 0 to 100 ppm. The progress of reaction was monitored by measuring the exothermal heat of curing reaction. The results were shown in fig.4 and table 2.

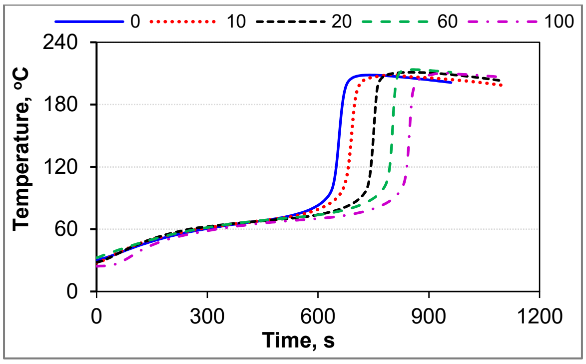


Fig. 4. The effect of the nano-silver content on the heat of curing reaction

It can be noticed from fig.4, the temperature of the system increased versus time to the peak exothermic temperature and then decreased with the prolonging curing time. Curing reactions of all test samples had a similar trend. The first phase of curing reaction (about the first 600 seconds), the temperature of the system increased slowly to about 80ºC but suddenly raised to over 200ºC due to the intense curing reaction. The peak exothermic temperature grew up with increasing the nano-silver content and then fallen down if the nano-silver content was bigger than 60ppm. The biggest exothermal heat of curing reaction was 173.7ºC at nano-silver content of 60 ppm, that means the curing reaction at nano-silver of 60 ppm occurred more intensely (table 2).

Table 2. The effect of nano-silver content on the highest exothermic temperature, gel and curing time

Na-Ag, ppm	T_{max}, ºC	Exothermal heat, ºC	Gel time, mins	Curing time, mins
0	208.5	168.5	4.92	11.00
10	209.3	168.3	7.17	11.83
20	211.1	171.1	7.42	12.83
60	213.7	173.7	7.67	13.33
100	210.5	170.5	7.83	13.58

The table 2 showed that, the presence of nano-silver has prolonged both the gel time and the curing time. Therefore, the presence of nano-silver slowed down the gelation process, whereas the curing reaction occurred more strongly due to more heat emission. A curing reaction was more intense with the presence of nano also received by the research results of Manila Chieruzzi when the temperature at the peak of in DSC analysis increased [1].

3.4. The effect of nano-silver on mechanical properties of composite

It is found that, the presence of nano-silver improved both flexural strength and flexural modulus. It has been observed in fig.5 that the flexural strength of composite increased significantly to 154.23 MPa with nano-silver loading until 60 ppm. The adding of nano-silver after this point lead to the decrease in flexural strength not much. That means, when the nano-silver content was large enough, the flexural strength depended not much on the nano-silver loading. On the contrary, the more raised the nano-silver content, the more grew up flexural modulus. The flexural modulus of composite was improving 6% with the presence of 100 ppm nano-silver, whereas, the highest flexural strength reached 154.23 MPa, 23% improvement when using 60 ppm nano-silver.

As can be seen from fig.6, both the tensile strength and tensile modulus of composite increased with nano-silver loading until an optimum point was achieved. The adding of nano-silver after this point caused the decrease of them. The highest tensile strength of composite with 20 ppm nano-silver were 68.12 MPa, 14% improvement, while the highest tensile modulus was 2.12 GPa, 16.5% improvement for composite containing 60 ppm nano-silver.

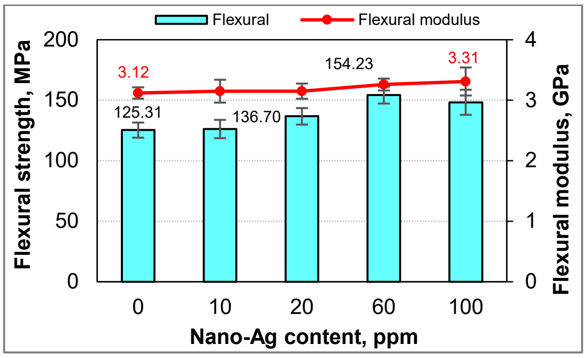


Fig. 5. The effect of the nano-silver content on the flexural properties of composite

The results of flexural and tensile strength received in this work are consistent with the published research results [3, 6]. In these documents, the flexural and tensile strength of nanocomposite based on UP and a suitable nano content increased.

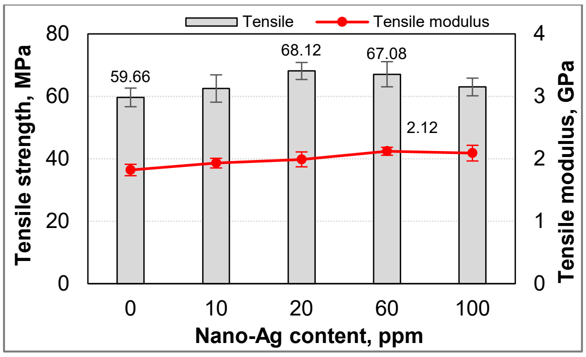


Fig. 6. The effect of the nano-silver content on the tensile properties of composite

The fig.7 showed that, the presence of nano-silver in composite brought an increase in an impact strength except for 100 ppm nano-silver content. The impact strength increased with nano-silver loading until an optimum point was achieved. The adding of nano-silver after this point caused the strong decrease in impact strength. The impact strength of composite containing 10 ppm nano-silver was only 7% higher than that of sample without nano-silver, but the impact strength raised drastically if the higher nano-silver content. The impact strength of composite was improved by 46.8% from 4.87 to 7.15 KJ/m^2, with the presence of 60 ppm nano-silver. This result indicated 60 ppm was sufficient for better interactions between the UP and nano-silver.

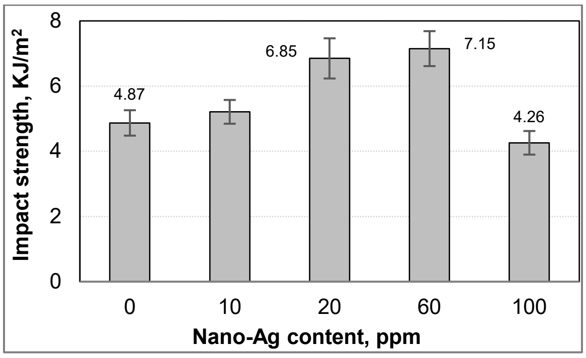


Fig. 7. The effect of the nano-silver content on the impact strength of composite

The impact fractured surface micrograph of nano-silver and composite containing 60 ppm nano-silver were displayed in fig. 8. It can be confirmed from fig.8a that the nano-silver itself with a size of 5 to 15nm exists in the agglomerated state as a flock. Under the Unidrive X1000 CAT mixer, this flock was burst into smaller crowds of 100 nm in size and dispersed evenly in unsaturated polyester resin. However, the field emission scanning electron micrograph also showed that it has not been separated into individual nanoparticles (fig.8b). This may be the reason for the poor antibacterial properties of matrix resin in section 3.2 because the antibacterial activity depends very much on the size of the nanoparticles that exist in the matrix resin [4].

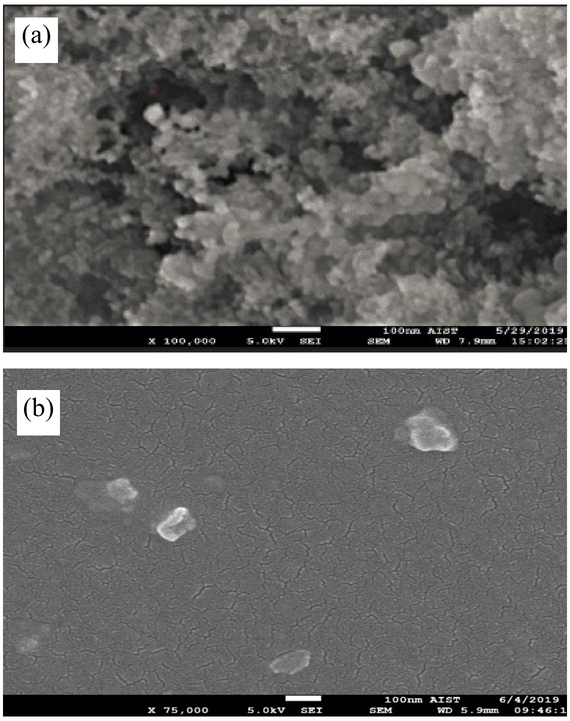


Fig. 8. The field emission scanning electron micrograph of nano-silver (a) and nanocomposite (b)

Overall results showed that, the composite containing 60 ppm nano-silver had the high mechanical properties. The tensile, flexural and impact strength of this composite were 67.08 MPa, 154.23 MPa and 7.15 KJ/m^2, improving in 12.4, 23 and 46.8%, respectively compared to the sample without the nano-silver.

4. Conclusions

The flock of nano-silver was dispersed in unsaturated polyester resin by using Unidrive X1000 CAT mixer at speed of 14000 rpm in 50 mins. The field emission scanning electron micrograph was evidence that the flock of nano-silver has burst into smaller clusters and dispersed evenly in unsaturated polyester resin. The matrix resin without nano-silver itself possessed the antibacterial property with both gram positive and negative strain. The presence of nano-silver reduced the gram-negative antibacterial property, whereas increased the gram-positive antibacterial property of matrix resin. The viscosity of matrix resin containing different nano-silver contents was unchanged except 100 ppm. Moreover, the presence of nano-silver has prolonged the gel and curing time but increased the maximum exothermal temperature of emission. In general, the presence of nano-silver improved in the mechanical properties of composite especially the nano-silver content of 60ppm. The tensile, flexural and impact strength of this composite were 67.08 MPa, 154.23 MPa and 7.15KJ/m^2, improving in 12.4, 23 and 46.8%, respectively compared to the sample without the nano-silver.

Acknowledgements

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