

# INVESTIGATING ULTRASONIC DISPERSION OF NANOSTRUCTURED SILICA FOR NANOCOMPOSITE MATERIALS APPLICATION

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**Abstract** - This article presented the results of investigating the influence of ultrasonic dispersion of nanostructured silica that has been referred to nanosilica ( $n\text{-SiO}_2$ ) into unsaturated polyester (UPE) resin for nanocomposite materials application. Scanning electron microscopy (SEM) method was employed to analyze the dispersion characteristics in this work. The optimally suitable ultrasonic factors have been identified including ultrasound frequency amplitude of 60%, ultrasound time of 120 minutes. Also, the bending strength measurement results of nanocomposite samples have shown that nanosilica material addition has increased significantly the mechanical properties of the nanocomposite material based on UPE resin. This also has shown the possibility of using  $n\text{-SiO}_2$  as a reinforcing agent for nanocomposite materials applications.

**Key words** - Nanosilica ( $n\text{-SiO}_2$ ); unsaturated polyester (UPE) resin; nanocomposite materials; ultrasonic frequency; ultrasonic frequency amplitude

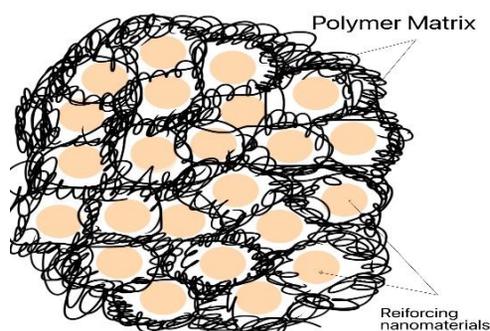
## 1. Introduction

In recent years, nano-sized inorganic fillers have been widely applied in polymers. Various fillers have been used to design suitable properties in the UPE matrix, such as nano-silica [1]. In there, we have expected to use the advantages of silica nanomaterials in material technology for contributing to grow the value of natural materials sources such as white sand, waste from agricultural products such as rice husks. Unsaturated polyester resin (UPE) is a thermosetting resin with many advantages such as high mechanical and physical strength, heat resistance, good chemical resistance, ease of processing, and relatively low price [2].

A polymer or copolymer with nanoparticles or nanofillers distributed in the polymer matrix is called a polymer nanocomposite. These may be of different shapes (platelets, fibers, spheroids), but at least one dimension must be in the range of 1–50 nm. The addition of nanoparticulates to a polymer matrix can enhance its performance (these materials are better described by the term nanofilled polymer composites) [3]. The incorporation of polymers can contribute to improving the durability and mechanical properties (especially flexural, tensile strength) of composites materials, high thermal resistance [4]. By uniformly dispersing the fillers into the matrix properties of the matrix can be enhanced also, it for effective performance and high yield this strategy is effective. There are several polymeric nanocomposites used for bone tissue engineering applications such as carbon nanotubes, molybdenum disulfide, graphene, and tungsten disulfide [3].

Nanosilica are silica particles ranging in size from 1-

100 nm. It is an inert, non-toxic substance with dose-dependent on cumulative silica dust in air less than  $0.01 \text{ mg/m}^3$  [4] and has high thermal resistance. The nanosilica material has many functional groups, such as silanol groups ( $\text{Si-OH}$ ), which can interact with other molecules. This allows nanosilica to bind to other substances, such as drugs, pigments or other nanoparticles [1, 5]. Nanosilica is applied in many different fields, including building materials, paints, plastics, rubber, cosmetics, healthcare,...



**Figure 1.** Typical structural of nanoparticles-reinforced polymer nanocomposites

Therefore  $n\text{-SiO}_2$  materials have chose to reinforce for UPE resin with many superior and potential properties for a lot of application areas for the study. Furthermore, it is important that influence factors of dispersion when using nanostructured materials for manufacturing composite materials [4, 5]. Investigations at various dispersions of nanoparticulate agglomerates with a variable solid content have demonstrated the considerable advantage of ultrasound when compared with other technologies, such as rotor stator mixers, piston homogenizers, or wet milling methods. The most obvious is the dispersing of materials in liquids to break particle agglomerates. Generally, this leads to smaller particles and increased size uniformity. The ultrasonic breakup of the agglomerate structures in liquid allows utilizing the full potential of nanosized materials [6]. Hence the application of ultrasonic dispersion of nanoparticles has been used for this research.

## 2. Experiment

### 2.1. Experimental materials, chemicals

- The nanosilica materials have been produced in the Institute of Materials Sciences, Vietnam Academy of Science and Technology.

- T101E commercial UPE resins were made in Thailand.

- The other chemicals (Methyl ethyl ketone peroxide (MEKP) initiator, Cobalt accelerator for curing UPE, xylene solvent) were made in China.

## 2.2. Laboratory equipments and instruments

- The used experimental devices and instruments are in the laboratories of Faculty of Chemical Engineering in the University of Danang - University of Science and Technology, including the ultrasonic device 750 WATT Model with the maximum ultrasonic frequency of 200 MHz; Analytical balance Ohaus PA 214, made in USA; rying cabinet UNB 500, made in Japan; glass stirring rods, glass experimental tubes, plastic cups, mold...

- The JSM-6010PLUS/LV (JEOL) SEM device was used for this work in the Petrochemical laboratory in The University of Danang - University of Science and Technology.

## 2.3. Experimental and research methods

### 2.3.1. Method of dispersing n-SiO<sub>2</sub> into UPE resins

- Used ultrasonic method to disperse n-SiO<sub>2</sub> into UPE resin.  
- Investigated ultrasonic factors: ultrasonic frequency amplitude (45%, 60%, and 75%) and ultrasound duration (from 15 minutes to 120 minutes with jumps of 15 minutes, respectively).

### 2.3.2. Nanocomposite samples preparation

The samples were prepared to the experimental process is described in Figure 2. There are main steps, including:

- The 1st step: dispersing n-SiO<sub>2</sub> into UPE resin by ultrasonic device (with a content of 0.6wt% of polymer content for all samples).

- The 2-nd step: blending the n-SiO<sub>2</sub> dispersed UPE resin with the other ingredients (content of 1wt% of initiating agent MEKP, content of 0.1wt% of curing accelerator Cobalt for all samples) by glass stirring rods until becoming a homogeneous mixture.

- The 3rd step: pouring the blended mixture into the prepared the molds and curing the resin mixture at room temperature in 24 hours.

- The final step: removing the samples from molds and proceducing the samples according to the dimensions of the measurement methods.

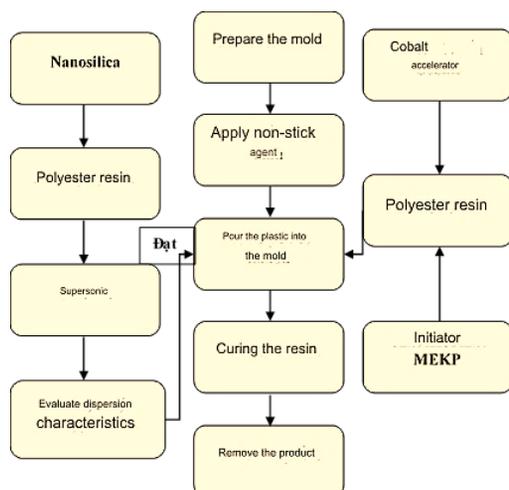


Figure 2. Diagram of nanocomposite samples preparation

### 2.3.3. Dispersion characterization methods

The ultrasonic dispersion conditions for creating the homogeneous mixture, without agglomeration structures have been determined. The two methods were used to evaluate the dispersion characteristics and be considered requirements of homogeneous dispersion.

#### a. Visual method

This method has been considered as a preliminary assessment for dispersion characteristics. The dispersion has been required to be transparent and uniform, without visible white silica particles in the resin mixture [7].

#### b. Scanning electron microscopy (SEM) method

- Scanning electron microscopy (SEM) has used to evaluate the morphology of the n-SiO<sub>2</sub> structure dispersed in the resin matrix.

### 2.3.4. Physico-mechanical properties test method of nanocomposite samples

The three-point bending strength of samples was measured according to ISO 178 standards with sample specimen size 80 x 10 x 4 mm. Each measurement performed 5 samples to get an average value [7, 8].

## 3. Results and discussion

### 3.1. The effects of ultrasonic parameters on the dispersion of n-SiO<sub>2</sub> in UPE resin

Two ultrasonic factors were investigated for the dispersion of n-SiO<sub>2</sub> into UPE resin: ultrasonic frequency amplitude and ultrasonic time. The experiments consisted of 60% and 75% ultrasonic frequency amplitudes respectively and ultrasonic time from 15 minutes to 120 minutes respectively. At 90 minutes the dispersion resin samples have become the transparent liquid and unseeing nanoparticle in the resin (Sample (a)). Therefore, Table 1 presents the results of the dispersion characteristic by visual method and SEM method with different ultrasound durations respectively: 90 minutes (Sample (a)); 105 minutes (Sample (b)), and 120 minutes (Sample (c)).

The results in Figure 3 are commented as follows: Sample (a) was still quite opaque, and white nanoparticles of silica were seen clearly. This can be consisted that white nanoparticles have not completely separated so they have not dispersed between the structures of the resin, so they are not completely dispersed.

This also shown in Figure 4, the SEM figure of silica nanoparticles (a') which have been white points on matrix resin. It can be that the n-SiO<sub>2</sub> particles dispersion has completely separated. Continue to ultrasonic for another 15 minutes (Sample (b)), the resin has become to be more transparent, but there are still white particles at the bottom of the cup. Also, the SEM figure (b') has shown that the white nanoparticles decreased significantly than Sample (a). This indicated that the nanoparticles have interspersed into the UPE resin structure to form a homogeneous dispersion mixture so the polymer molecular chains have covered nearly completely nanoparticle structure that white spots disappeared nearly. While Sample (c) has been more transparent than Sample (b) and unseeing white

nanoparticles at the bottom of the cup. Also, the SEM figure (c') of Sample (c) showed that there are no white spots of nanoparticles. This has proved that enough large ultrasound waves power have broken nanostructure decreasing nanoparticle size resulting in interlayer resin, completely wetting into the dispersed particle structure. These results also showed that the influence of ultrasonic dispersion means of deagglomerating and dispersing are needed to overcome the bonding forces after wetting the powder, that being covered, interlayered, and completely dissolved into the nanoparticle structure to form a homogeneous structure, the dispersed mixture becomes transparent uniformity [1, 6].



Sample (a)

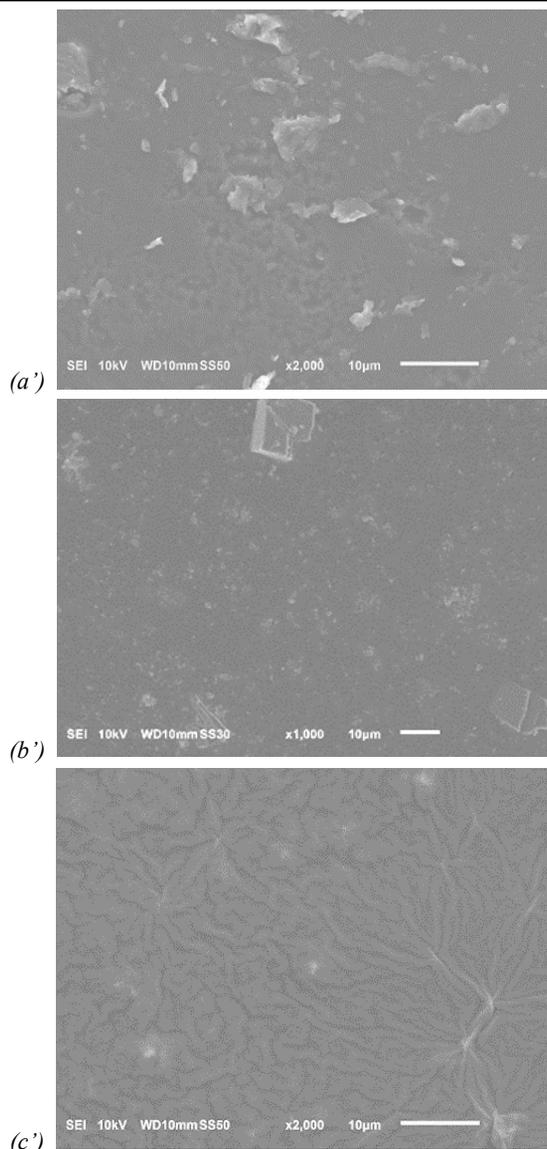


Sample (b)



Sample (c)

**Figure 3.** The results of influence ultrasonic factors on dispersion characterization by visually method of Samples: (a); (b) and (c)



(a')

(b')

(c')

**Figure 4.** SEM images of the dispersion samples: (a') of Sample (a), (b') of Sample (b) and (c') of Sample (c)

When the ultrasonic amplitude was increased by 75% and the investigated ultrasound duration was 30 minutes and 45 minutes, respectively, the results were been indicated in Figure 5.



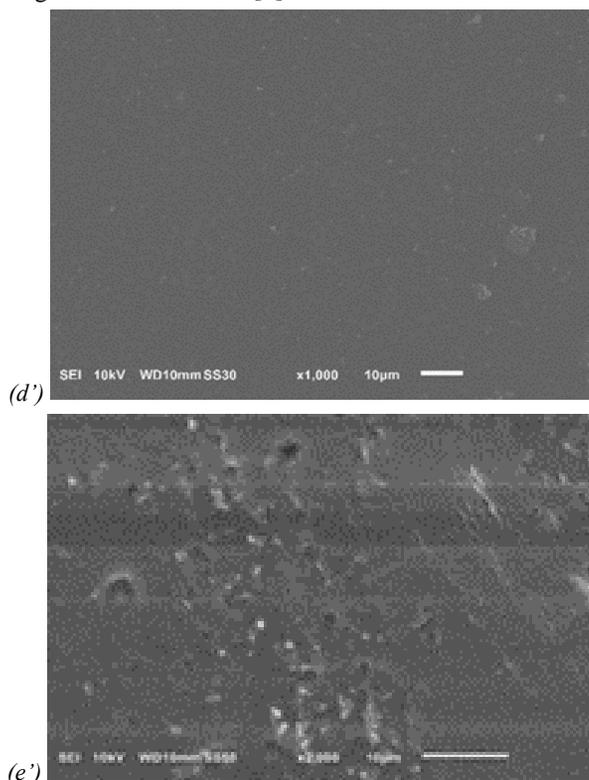
(d)

(e)

**Figure 5.** The results of influence ultrasonic factors on dispersion characterization by visual method of Samples (d) and Sample (e)

Can see the image of Sample (d) has been uniform transparency equivalent to Sample (b, c). This also has been performed in results measured by SEM images in Figure 6. SEM image of Sample (d) was look.

Continuing to increase the ultrasound time, the UPE resin started to become the phenomenon of genetics, that the resin gradually turns dark, the increased viscosity hinders the dispersion. The SEM image (e') presented white clusters of nanodispersed particles appearing, demonstrating that poor dispersion tends to increase markedly when ultrasound is in high amplitude mode and extended duration. This is possible because ultrasound with a large frequency amplitude (75%) means high-intensity ultrasound waves are coupled into a liquid medium, the waves travel through the liquid creating alternating low-pressure and high-pressure (compression) cycles. At the point of maximum bubble growth, the bubble implodes violently during a high-pressure cycle. During the implosive bubble collapse, the phenomenon of cavitation can be observed [6]. Ultrasonic cavitation creates so-called "hot spots" which are characterized by extreme conditions such as increasing temperature, pressures as well as respective temperature and pressure differentials. The dispersed resin has been heavily agitated by liquid jets and shear forces. When the temperature of up to very high heating to leads to too large a dissection force, so that increasing endogenous heat generation strongly [6, 7]. Hence promotions of curing reaction and oxidation of the double bonds in the structure of UPE resins have occurred strongly. This may be the cause of the darkening and gelation of the resin [5].



**Figure 6.** SEM images of the dispersion samples: (d') of Sample (d) and (e') of Sample (e)

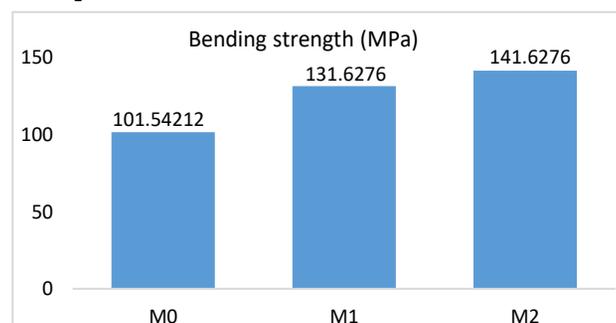
From the obtained results, it can be seen that the corresponding dispersion modes of samples (c) and (d) both achieve satisfactory dispersion characteristics. However, in terms of technological factors, the corresponding mode of lower frequency amplitude (60%)

has higher stability, limiting endogenous thermal phenomena leading to currents affecting the properties of plastics such as color, viscosity, gel oxidation phenomenon... but the dispersion duration is so long (120 minutes). Meanwhile, for the high wave frequency amplitude (75%), the dispersion time is significantly reduced (30 minutes) but the stability is lower, and easy to occur undesirable phenomena that affect the properties of the plastic such as color, viscosity, oxidation [4, 8].

### 3.2. The effects of ultrasonic parameters on the mechanical properties of nanocomposite materials

To assess the stability and effects of undesirable phenomena, the physical and mechanical characteristics of nanocomposite materials were investigated in this study. The prepared samples with ultrasonic dispersion factors included: an ultrasonic frequency amplitude of 75% and ultrasound time of 30 minutes (Sample M1) and the ultrasonic frequency amplitude of 60% and the ultrasound time of 120 minutes (Sample M2). The original samples (without n-SiO<sub>2</sub>) were dispersed with the ultrasonic frequency amplitude of 60% and the ultrasound time of 120 minutes (Sample M0). The bending strength was determined to characterize the mechanical properties of the nanocomposite material based on n-SiO<sub>2</sub> and UPE matrix. The results of the influence ultrasonication on dispersion characterization and mechanical properties of nanocomposite materials are shown in Figure 7.

The results in Figure 7 have presented that the bending strength of the nanocomposite Samples M1 and Sample M2 have been higher significantly than the Sample M0, which increased by 29.6% for the Samples M1 and 39.5% for the Samples M2. This has shown that the samples with n-SiO<sub>2</sub> addition have reinforced the mechanical properties of UPE matrix resin quite well. Besides, the ultrasonic factors also significantly affect the reinforcement degree of n-SiO<sub>2</sub>.



**Figure 7.** Bending strength of M0, M1 and M2 nanocomposite Samples

It may be seen in Figure 8 presented the SEM images (I) of Sample M0 (I) have been performed many porously, with worse tightness than SEM images (II) of Sample M1 and image (III) of Sample M2. This proved that nanoparticles have alternated and dispersed between resin structures, that to masking and filling porous pores that make the matrix resin have become more dense and tight [7, 8]. Thus the nanocomposite materials based on n-SiO<sub>2</sub> and UPE resin have been higher and more mechanical strength.

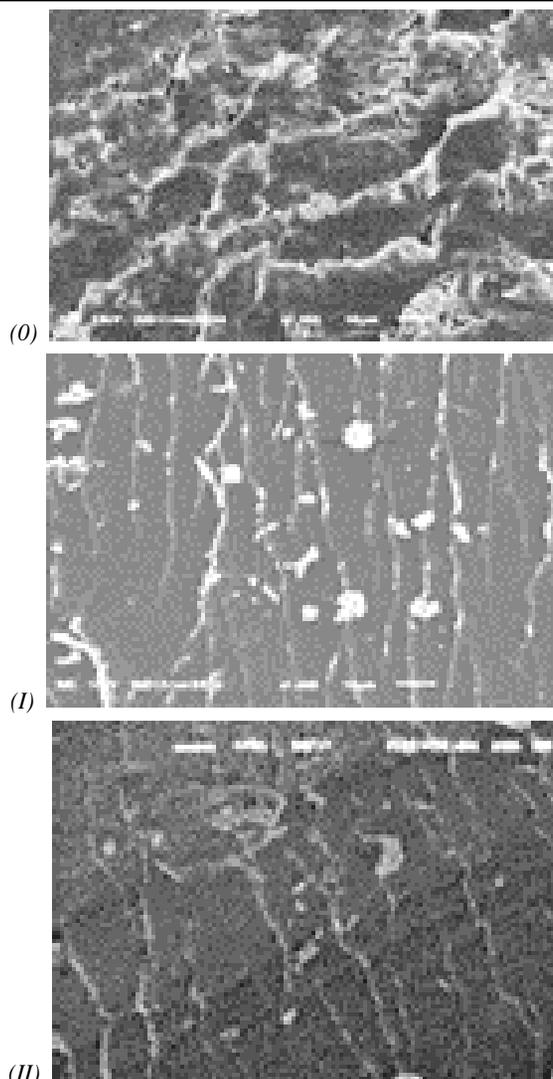


Figure 8. SEM images of Sample M0 (0), Sample M1 (I), Sample M2 (II)

#### 4. Conclusions

The performances of the obtained results may be to get some conclusions as follows:

- Based on two factors: higher stability and better

influence on mechanical properties of nanocomposite materials, the study has chosen the corresponding ultrasonic dispersion mode of the maximum ultrasonic sound wave frequency amplitude of 60% (ultrasonic frequency of 120 MHz) and the duration of ultrasound is 120 minutes.

- The determination of ultrasonic parameters for the dispersion of the nanostructure reinforcement agent into resins is an important element for the application of nanostructured materials to manufacture nanocomposite products.

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