

Mechanism of Nanoparticle Dispersion via Acoustic Cavitation in Highly Viscous Fluid

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Abstract: *Nanoparticles have a strong tendency to agglomerate when used as filler in composites, due to strong van der Waals forces and have adverse influence on property improvement. In this context breaking of agglomerated nanoparticles and their homogeneous dispersion in epoxy adhesive is imperative for enhancement of properties. The nanoparticles can either be dispersed mechanically, with a dissolver or with a bead mill, or by means of ultrasound waves. Present study is primarily concerned with the power required for generation of ultrasonic waves responsible for the dispersion of SiO₂ nanoparticles into epoxy resin. The effect of amplitude is also considered in the present study as higher amplitude includes risk of degradation of the epoxy resin due to localized heat generation at the vicinity of ultrasonic horn. Also in view of the difficulties in the dispersion of nanoparticles in highly viscous fluid, mechanisms of dispersion was studied in the present work and modeled using the experimental results. Experimental results in terms of process parameters such as amplitude, pulsating time, dispersion time etc. were used to determine the mechanisms of Nanoparticle breaking and adequate mathematical expression and compared to Winkler's model. Design of mixing chamber was further studied with regard to the modelled value and experimental process parameters.*

Keywords—*Epoxy; nanocomposites; dispersion; modelling; acoustic Cavitation; scanning electron microscopy*

I. INTRODUCTION

Epoxy is in generally most commonly used matrix material because of various advantages over others [1]. The biggest advantage is that they are light as well as strong. Furthermore, the high performance epoxy adhesives are widely used for advanced applications especially in aerospace and automobile industries because of their outstanding basic properties arising due to highly cross linked network of the epoxy. But, certain complex applications in these industries require epoxy adhesives with high structural, thermal and corrosion resistant properties [2]. Therefore, most of high performance epoxy adhesives are modified by incorporation of fillers resulting in enhanced combination of mechanical and thermal properties [3]. Incorporation of micron size fillers enhances the mechanical properties to some extent but at the cost of other properties like thermal properties and toughness [4]. Epoxy nanocomposites on the other hand is found to overcome all the disadvantages that generally inherently present with micron filler composites primarily because of the high surface to volume ratio of dispersed phases [5]. High

Surface to volume ratio thematically enhances the dominating behaviour of the surface atoms associated with the nanoparticles, there upon results in particle-particle interactions between them within the composites. Because of which properties such as thermal resistance, dielectric constant, strength and even fracture toughness enhances. However, the properties are significantly dependent on the dispersion behaviour and filler morphology in the matrix [6]. Well dispersed nanofiller in epoxy significantly change the bulk property of the composite largely due to the phenomenal variation of the interfacial properties around the nanofiller. However, it is a great challenge to disperse non agglomerated nanofiller evenly in the matrix. To overcome such difficulties acoustic Cavitation has been tried by many researchers worldwide to obtain homogeneous non agglomerated epoxy nanocomposites. Acoustic Cavitation is basically formation of bubbles, which coalescence and grows during several cycles till reaching their critical diameter and implodes. This result in generation of hot spots and which is good enough for breaking the Nanoparticle agglomerates in highly viscous fluid [7]. However, this governed by several other factors such as mixture temperature, surface tension, viscosity etc. [8]. Thus to neglect morphological changes of the base matrix due to heating at degradation temperature it is imperative to cool the base epoxy while processing. [9]. It has been found that entrapment of air during mixing will strongly influence the formation of cavitation bubbles and thus can have influencing effect on dispersion [10]. In the present study experimental results related to epoxy nanocomposites composed of SiO₂ nanoparticles prepared by acoustic cavitation process has been used to determine the mechanisms of Nanoparticle breaking and adequate mathematical expression. Design of mixing chamber was further studied with regard to the modelled value and experimental process parameters. The experimental process parameters were varied accordingly in the mathematical expression derived to obtain the optimum dispersion process parameters. Amplitude is correlated with power input and by considering the value of the power required design of the mixing chamber of higher capacity has been tried.

II. METHODS AND METHODOLOGY

A. Materials and Method

A two component commercially available DGBA based epoxy adhesive and pristine SiO₂ Nanoparticle of 99.5% purity (American Elements) was used for the preparation of

nanocomposite. In mechanical mixing (MM) as well as acoustic cavitation mixing (ACM) SiO₂ Nanoparticle with varying content on weight percent basis was mixed in epoxy resin for the preparation of epoxy nanocomposites slurry. In a stoichiometric ratio 100:80 by weight to the slurry hardener was added followed by mechanical stirring for 10 minutes and degassing at room temperature for the removal of entrapped air during mixing. The resulting epoxy nanocomposites were then poured in moulds coated with a thin layer of paraffin wax, and placed in hot air oven for 16 hours at 40 °C for curing.

B. FESEM studies

The SiO₂ nanoparticles distribution in the epoxy matrix has been examined under field emission scanning electron microscope (FESEM) at an acceleration voltage of 15 kV. The results have been shown in our previous work [11].

C. Calculation Method

Calculation of dispersed agglomerate after sonication of time “t” is determined with the help of Rosin-Rammler-Bennett distribution function [12]. At least nine analyses of the x_D and n have been performed at randomly selected FESEM images of a specimen of SiO₂-epoxy nanocomposites at the same magnification but at different locations to determine particle/cluster size. The results are shown and discussed is described in our previously published work [11].

Studies on the dispersion of SiO₂ nanoparticles into epoxy resin were done by using Winkler’s model to meet the requirement of the present problem. The number of agglomerates at dispersion time “t” was determined using Winkler’s equation by the following approach in consideration of the agglomerate size X with respect to the dispersion time t:

$$X(t) = (X_A - X_E).e^{-\frac{k.V_{eff}.t}{V_T}} + X_E \quad (2.1)$$

Where, X_A is the initial agglomerate size and X_E the final agglomerate size, V_{eff} the effective volume, V_T the total volume of the nanocomposites and k is a (reciprocal) time constant, primarily describing circulation in the mixture. It has been considered that only at the Cavitation zone dispersion occurred. The effective volume was considered in the present study as $V_{eff} = 5.4 \times 10^{-7} m^3$ [9]. Time constant “k” it was obtained from the experimental curve of the agglomerate size with respect to the dispersion time at amplitude of 70% [13]. It has been shown by others that the value of the constant “k” is independent of the amplitude [14]. In this regard the value of k is considered as 220 min^{-1} in the present study. The definite factors primarily influencing X_E is the amplitude or the power input P and strength of the Nanoparticle agglomerates. In view of the above final agglomerate size X_E was determined according to Winkler’s equation [15, 16]:

$$X_E = e^{-\frac{a^*P}{\sigma V_T}} + X_P \quad (2.2)$$

Where, X_P is the primary Nanoparticle size, σ is the agglomerate strength and “a*” is constant describing the power that is transferred to the agglomerates. Substituting Eq. (2.2) into Eq. (2.1) the full expression for determining the Nanoparticle size which is in dependence on the processing parameters is obtained:

$$X(t) = \left(X_A - e^{-\frac{a^*P}{\sigma V_T}} - X_P \right).e^{-\frac{k.V_{eff}.t}{V_T}} + e^{-\frac{a^*P}{\sigma V_T}} + X_P \quad (2.3)$$

Now, we have [9]

$$\begin{aligned} X_A &= 4400 \text{ nm, for 5 wt\% SNC} \\ &= 5000 \text{ nm, for 10 wt\% SNC} \\ &= 6500 \text{ nm, for 20 wt\% SNC} \end{aligned}$$

$$X_P = 10 \text{ nm and volume of epoxy matrix, } V=100 \text{ ml.}$$

Nanoparticle agglomerate strength was estimated by considering, the inter particle forces F, the agglomerate size X and porosity of the powder [17]:

$$\sigma = \frac{1-\varepsilon}{\varepsilon} \frac{F}{X^2} \quad (2.4)$$

The porosity ε was determined by measuring the ratio of bulk density ρ_b to density of the solid material ρ_s [14]:

$$\varepsilon = 1 - \frac{\rho_b}{\rho_s} \quad (2.5)$$

Where, ρ_s is the density of the nanoparticles and ρ_b is the bulk density of the nanoparticles. In the present work $\rho_b = 0.2 \text{ g.cm}^{-3}$ and $\rho_s = 2.4 \text{ g.cm}^{-3}$ thus $\varepsilon = 0.91$.

Inter particle forces was estimated by assuming that the main contribution for particle –particle interaction is London-van-der-Waals forces. It was shown by Hamaker’s equation that, the force can be calculated by considering the agglomerate size X, Hamaker’s constant A and the distance between the agglomerates. The value of Hamaker’s constant A was found from Hamaker’s equation [18]:

$$A = \pi^2 . q^2 . \lambda \quad (2.6)$$

Where, q being the number of atoms per cm^3 and λ is the London-vander Waals constant. For SiO₂, $q = 80 \times 10^{21} \text{ cm}^3$ and $\lambda = 100 \times 10^{-60} \text{ erg.cm}^{-6}$. Putting these values in equation (2.6) we get the value of Hamaker’s constant A which comes out to be $6.31 \times 10^{-19} \text{ J}$. The intermolecular force between nanoparticles is given by

$$F = \frac{A}{24 d^2} \quad (2.7)$$

Where, X is the diameter of the particle and d is inter-particle distance. The inter particle distance was assumed as 0.5 nm and taking into account the Hamaker constant for SiO₂ of $6.31 \times 10^{-19} \text{ J}$ [19], the agglomerate strength σ was estimated to be, $\sigma = 104.1 \text{ N.cm}^{-2}$. The constant a* was determined from the results from Eq. (2.3) so that the measured and calculated final agglomerate sizes are in agreement. The values of a* for amplitudes are listed in Table I.

TABLE I. MEASURED APPROPRIATE TRANSFERENCE CONSTANT FOR VARIOUS AMPLITUDE PERCENTAGES

Amplitude (%)	a* (s)
50	25.6
70	10.9

III. RESULTS AND DISCUSSION

A. Morphology of epoxy nanocomposites

FESEM images of SiO₂-epoxy nanocomposites containing varying Nanoparticle content show no clear evidence of Nanoparticle agglomeration from low magnification as discussed in our previous work [11]. However, high magnification FESEM images of SiO₂-epoxy nanocomposites reveal well dispersed less agglomerated nanoparticles in epoxy matrix. This primarily shows that increasing Nanoparticle content in epoxy matrix does not affect the cluster size. Thus acoustic Cavitation can result in generation of enough energy to deagglomerate the agglomerated of SiO₂ nanoparticles in epoxy matrix.

B. Cluster size

Calculations based on Rosin-Rammler-Bennett model shows that the average cluster size of nanoparticles in SiO₂-epoxy nanocomposites (SNC) processed by ultrasonic process increases more or less linearly with increasing nanoparticles content from 5 to 20 wt%. This shows SiO₂-epoxy nanocomposites containing 20 wt% consists clusters of ~4–6 nanoparticles [11]. Thus, there was considerable amount of de-agglomeration of nanoparticles in 100 ml of epoxy resin primarily due to acoustic cavitation, which is discussed further. The results showing the variation of nanoparticles cluster size with dispersion time are shown in Figs. 1, 2 and 3 respectively for nanoparticles content of 5, 10 and 20 wt%. The graph also shows the effect of amplitude and dispersion time on the breaking of nanoparticles agglomerates. This data was used in the present study for the determination of the power required for breaking the nanoparticles agglomerates and further implemented for the determination of number of ultrasonic probes required in the mixing chamber of capacity 1000 ml.

The variation of power obtained using Winkler's model for SNC 5 at 50% and 70% amplitude is shown in Fig. 4. It was observed that there is negligible variation in power with the increase in dispersion time, but considerably high power is required for the dispersion of the SNC 5 at amplitude 70%. This behaviour is inherent and primarily important for getting higher level of dispersion as described in Fig. 1. From the above graph we also found that the power remains almost constant at a particular amplitude. However, maximum value was 71.4 W at 50% amplitude and 169.83 W at 70% amplitude. The variation of power obtained using Winkler's model for SNC 10 at 50% and 70% amplitude Fig. 5. Similar to the observations for SNC 5 there is negligible variation in power with the increase in dispersion time, but considerably high power is required for the dispersion of the SNC 10 at amplitude 70%, which is inherent and primarily important for getting higher level of dispersion as described in Fig. 2.

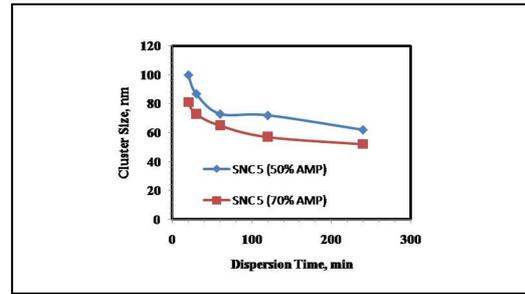


Fig.1 Graph between cluster size and dispersion time for 5 wt% nanoparticles at 50% and 70% amplitude.

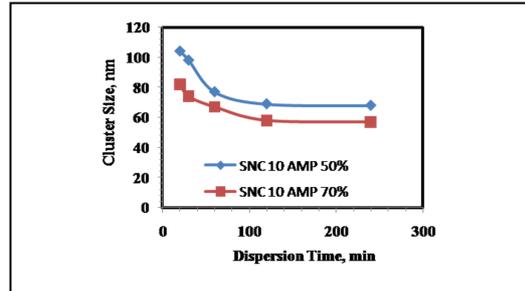


Fig. 2 Graph between cluster size and dispersion time for 10 wt% nanoparticles at 50% and 70% amplitude.

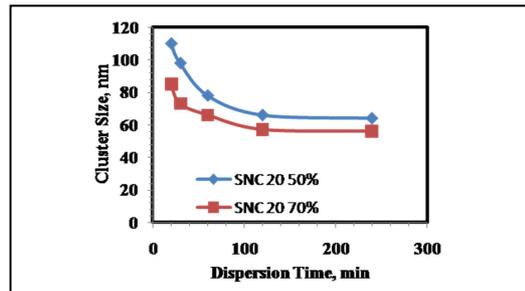


Fig. 3 Graph between cluster size and dispersion time for 20 wt% nanoparticles at 50% and 70% amplitude

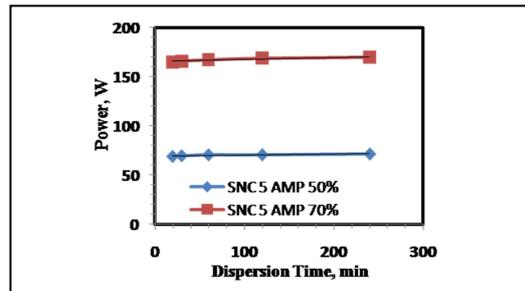


Fig.4 Graph between power and dispersion time for 5 wt% nanoparticles at 50% and 70% amplitude

TABLE II.

TABLE 2 CALCULATION FOR NUMBER OF PROBES REQUIRED IN 1000ML MATERIAL VOLUME

Dispersion time, t (min)	Cluster Size, X(t) (nm)	Porosity of Nanoparticle (ϵ)	Inter particle Distance, d (nm)	Force (N)	Strength σ (N/cm ²)	Transference Constant, a*(s)	Power P(W)
120	60	0.91	0.5	1.05E-09	104.1	10.9	1906.60

It was noted from Fig. 5 that power was almost constant at both the amplitudes with a maximum value of 74.11 W at 50% amplitude and 176.26 W at 70% amplitude. For SNC 20 at 50% and 70% variation of power obtained using Winkler's model is shown in Fig. 6. Similar to the previous cases of SNC 5 and SNC 10 here also there is negligible variation in power with the increase in dispersion time. However, considerably higher power is required for the dispersion of the SNC 20 at amplitude 70% for getting higher level of discussion as described in Fig. 3. The maximum value of power required was observed as 80.81 W at 50% amplitude and 191.62 W at 70% amplitude. Thus interestingly it was observed from Figs. 4, 5 and 6 that power requirement irrespective of nanoparticle content for fixed amplitude. However, power requirement was more for 70% amplitude than 50% amplitude. The variation of power at 50% and 70% amplitudes for 5, 10 and 20 wt% of nanoparticle addition is shown in the form of bar chart Figs 7 & 8 respectively. It was found that maximum power requirement was at 70% amplitude and for SNC 20. This obtained value of power i.e. 191.62 W hence was used for the design of a mixing chamber of 1000ml epoxy nanocomposites. For the design of the mixing chamber of 1000ml the design parameters obtained for the above calculations is shown in Table II. The design was based on constant amplitude of 70% and for optimum cluster size of 60 nm and dispersion time of 120 min, considering the above parameters the total amount of power required is calculated. The total power input was obtained as 1906.6 W. Thus, considering one probe having the generation of 1000 W this will require approximately two probes for the mixing chamber. The various parameters such as amplitude, power, dispersion time and material's volume also influence on the size of nano particle. With increase in the amplitude of sonication, the size of nano particle decreases and its value is minimum in case of 70% amplitude. Amplitude higher than 70% is generally not recommended because it may cause degradation of epoxy mixture near the ultrasonic horn due to high amount of heat generation which subsequently leads to a poor dispersion characteristic. It was also seen that for higher value of power input the final value of dispersed agglomerate is lesser but from power vs. dispersion time curve it is clearly evident that the power required is almost same and does not varies with the dispersion time. This proves that after a certain amount of time the clusters does not break any further and attains a minimum value for that particular power input. It was also found that the particle size is lesser in case of higher amplitude but after some amount of dispersion time the change in cluster size becomes insignificant.

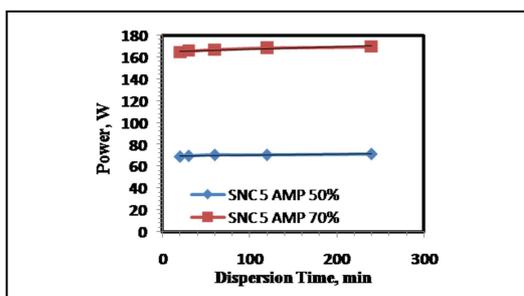


Fig.5 Graph between power and dispersion time for 10 wt% nanoparticles at 50% and 70% amplitude

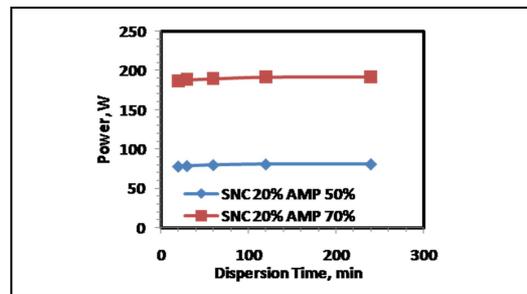


Fig. 6 Graph between power and dispersion time for 20 wt% nanoparticles at 50% and 70% amplitude

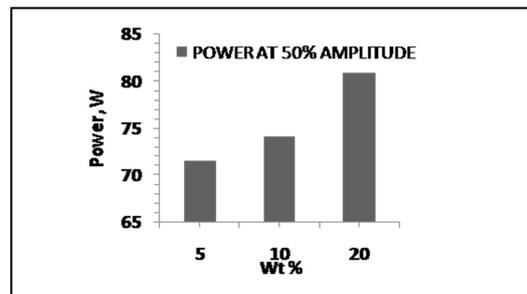


Fig. 7 Bar diagram for power at 5 wt%, 10 wt%, 20 wt% nanoparticles at 50% amplitude

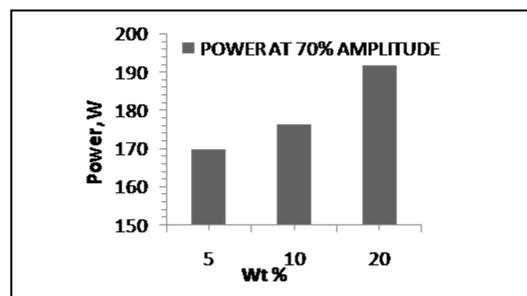


Fig. 8 Bar diagram for power at 5 wt%, 10 wt%, 20 wt% nanoparticles at 70% amplitude

I. CONCLUSION

It was found that as the weight percentage of agglomerated nanoparticles is increased the amount of power required for its dispersion also increases. The power required was minimum in case of 5wt% of nanoparticles and increases as the weight % was increased. Power required was observed maximum in case of 20 wt% of nanoparticles. Again, amount of power required for dispersion of agglomerated nanoparticles increases with the increase in ultrasonic amplitude even when the amount of agglomerated nanoparticles is kept constant. Thus the maximum power requirement is in the case of 20 wt% and 70% amplitude. In all the cases it was evident that as the dispersion time increases first the particle size decreases according to the amount of nanoparticles present and the ultrasonic amplitude. However, after 100 minutes there was no significant variation in agglomerate size. Using the value of maximum power we can design a mixing chamber. To cause dispersion of nanoparticle in a greater volume of epoxy resin the power requirement is obviously higher. Also more number of such ultrasonic probes is required which can generate equal amount of power that is required for successful dispersion of agglomerated nanoparticles. For 100 ml mixture the maximum power

requirement is found to be 191.62 W at 20 wt% SNC at 70% amplitude. Now for 1000 ml mixture the amount of power required is 1906.68 W. Thus to cause proper dispersion of agglomerated nanoparticles in this given condition two number of such probes are required.

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