

Chapter 2

MATERIAL DESCRIPTION AND SAMPLE PREPARATION

In this chapter, we will discuss the synthesis of neat epoxy and epoxy-based nanocomposites samples. Additionally, this chapter discusses in detail how to quantify the dispersion of nanofillers in polymer matrices.

2.1 MATERIAL USED

2.1.1 Host material

Epoxy resin (LY556 Bisphenol-A, density 1.17 g/cm³ at 25°C) supplied from Huntsman used as a host material. It was decided to use epoxy resins for the current investigation because they are non-toxic, easy to handle, and can be cured at room temperature. More importantly, they are potential insulating materials for electrical equipment, and their electrical, thermal, and mechanical properties are still being investigated. Due to their light weight, flexibility, and hydrophobic properties, epoxy-based composites are being considered as a new class of insulators to replace porcelain and glass. Their design, on the other hand, is the subject of considerable research, particularly from an electrical, thermal, and mechanical standpoint, as their properties must be enhanced to achieve greater reliability.

The chemical structure of the epoxy resin is given in Figure 2.1. In epoxy, the end group contains the three-member epoxide rings. Because of the equilateral triangle formed by the atoms and the consequent intermolecular interactions, the epoxide rings are stretched, making the epoxy group highly reactive. Due to the high chemical

reactivity and large number of epoxide rings, an extensive network of connections can form, providing excellent electrical insulation, mechanical strength, and rigidity.

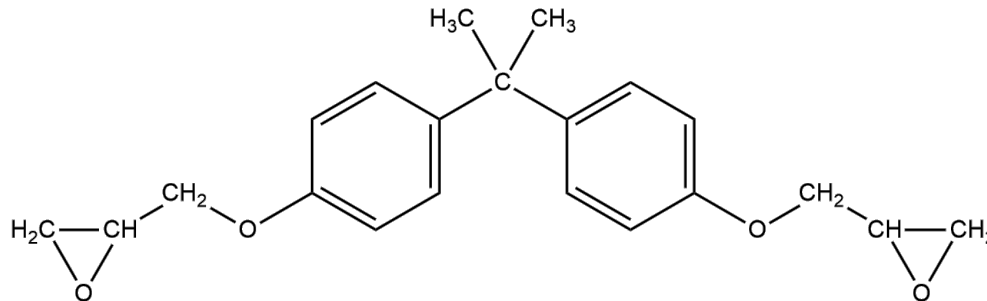


Figure 2.1 Chemical structure of uncured epoxy



Figure 2.2 Epoxy resin (LY556) and hardener (HY951) supplied from Huntsman

2.1.2 Filler material

Aluminum oxide Al₂O₃ nanopowder from Sigma Aldrich (average particle size = 50nm, spherical in shape, density 3.97 g/cm³ at 25°C) is used as filler. Because alumina nanoparticles have strong dielectric, mechanical, and thermal qualities, they were chosen as the filler material for the electrical insulation system. Furthermore, alumina's

excellent mechanical and thermal capabilities complement the material qualities of the host polymer.

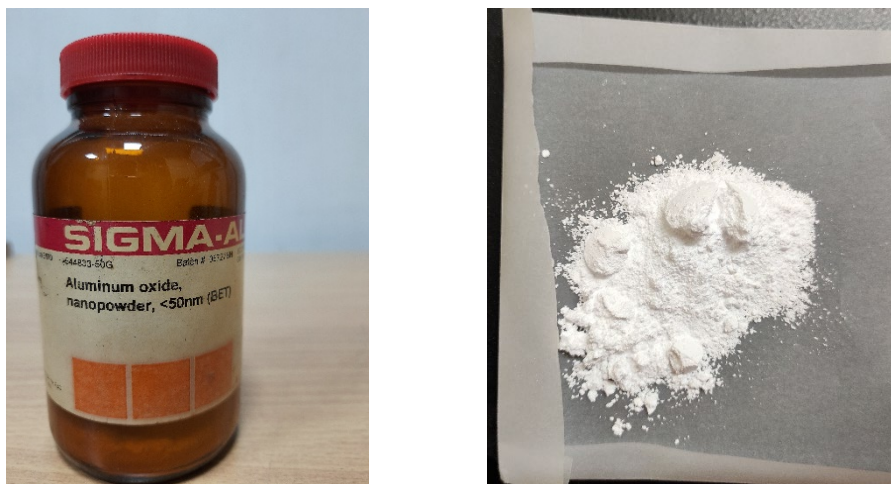


Figure 2.3 Aluminum oxide (Al_2O_3) nanopowder supplied from Sigma Aldrich

2.1.3 Coupling Agent

The dispersion of nanoparticles is one of the most difficult aspects of nanocomposites synthesis. For nanodielectrics to reach their full potential, nanoparticle dispersion in the host material is critical. The agglomeration of nanoparticles, if they are not distributed, causes them to behave like larger particles, as a result benefits of nanoparticles would be negated. The use of an appropriate surfactant to treat nanoparticle surfaces improves filler matrix interaction and aids in the uniform dispersion of nanoparticles. The coupling agent utilized in this study is 3-Glycidoxypropyl trimethoxy silane (GPS) supplied from Sigma Aldrich. This coupling agent's chemical structure is depicted in Figure 2.4. The GPS consists of a linker, a silicon atom, and hydrolyzable groups. The organofunctional group is an epoxy group that can link to the host material, whereas the hydrolyzable group can bond to hydroxyl groups on nanoparticle surfaces.

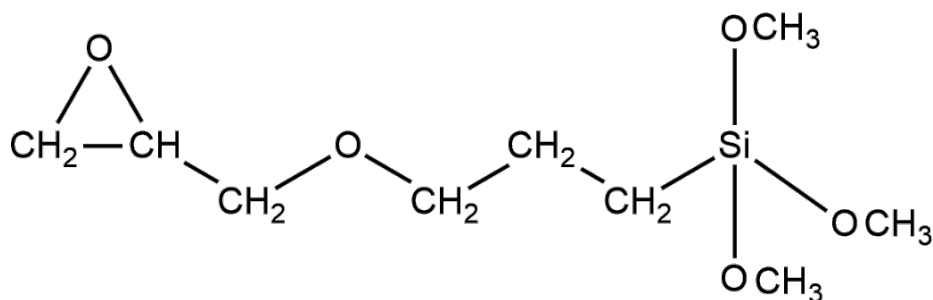


Figure 2.4 Chemical structure of coupling agent



Figure 2.5 3-Glycidyloxypropyltrimethoxysilane (GPS) supplied from Sigma Aldrich

2.1.4 Curing agent

The curing agent (commonly called ‘hardener’) is used to open the epoxide ring and interconnects the polymer chains. Triethylenetetramine (HY951, density 0.98 g/cm³ at 25°C) supplied from Huntsman used the curing agent. The chemical structure of the hardener is shown in Figure 2.6.

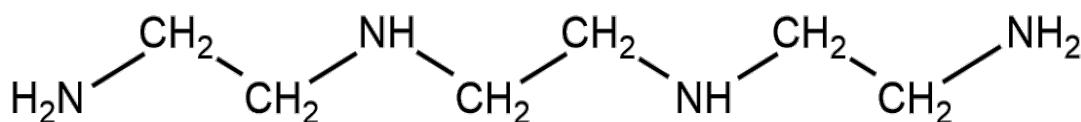


Figure 2.6 Chemical structure of hardener

2.2 SAMPLE PREPARATION

The following types of specimens were prepared and used in subsequent chapters for research:

1. Neat epoxy
2. Epoxy nanocomposites synthesized with as-received (or untreated) alumina nanofillers
3. Epoxy nanocomposites synthesized with surface treated alumina nanofillers

The synthesis procedure for various kinds of samples is detailed in the following subsections.

2.2.1 Synthesis of pure epoxy samples

To synthesize pure epoxy samples, epoxy and hardener are carefully mixed in a 10:1 ratio. To remove entrapped gas bubbles, the mixture is subsequently placed in a desiccating chamber. The solution is put into the mould once it has been degassed. The mixture is cured for 24 hours at ambient temperature before being post-cured for 12 hours at 100°C.

2.2.2 Synthesis of nanocomposites with untreated nanofillers

For the formation of nanocomposites samples with untreated nanofillers, moisture absorbed by hydrophilic alumina nanoparticles is removed using a heat treatment procedure at 200°C. Following that, alumina nanoparticles (1 vol.%) are suspended in ethanol and probe sonicated. A magnetic stirrer is subsequently used to mix this solution with epoxy resin. The solvent is eliminated by slightly raising the temperature of the solution over the ethanol's boiling point. After the ethanol is removed,

nanocomposite samples of desired thickness are prepared using the molding and curing technique outlined in the synthesis of pure epoxy.

2.2.3 Synthesis of Nanocomposites with surface-treated nanoparticles

For the synthesis of nanocomposites samples with surface-treated nanoparticles, a process described in [84], [85] is followed. In this process, first, a solution containing 95% ethanol and 5% distilled water is prepared. By adding acetic acid to the solvent, the pH is first adjusted to 4.5. A preset amount of 3-Glycidoxypropyl trimethoxy silane (GPS) is slowly injected into the solution during sonication. The silane is allowed to hydrolyze entirely after 30 minutes of sonication. Untreated alumina nanoparticles are added to the hydrolyzed GPS solution at regular intervals to achieve uniform dispersion and proper coating of the nanoparticles. Afterward, the mixture is sonicated for an additional hour. After the solvent has evaporated, the functionalized nanoparticles are washed with hexane to remove any excess GPS. Additionally, the Fourier transform infrared spectroscopy (FTIR) is used to confirm the surface functionalization of the nanoparticles. To prepare nanocomposite samples, a predetermined amount of surface-functionalized alumina nanoparticles were introduced to ethanol, and the particles were dispersed uniformly using ultrasonication for 60 minutes. The epoxy resin was added to the ultrasonicated ethanol solution in a pre-calculated amount and stirred well with a magnetic stirrer. Nanocomposites samples were prepared using the same process as pure epoxy samples after the ethanol was removed. Figure 2.7 depicts the synthesis of epoxy alumina nanocomposites, whereas Figure 2.8 depicts the various apparatus utilized to make epoxy alumina nanocomposites.

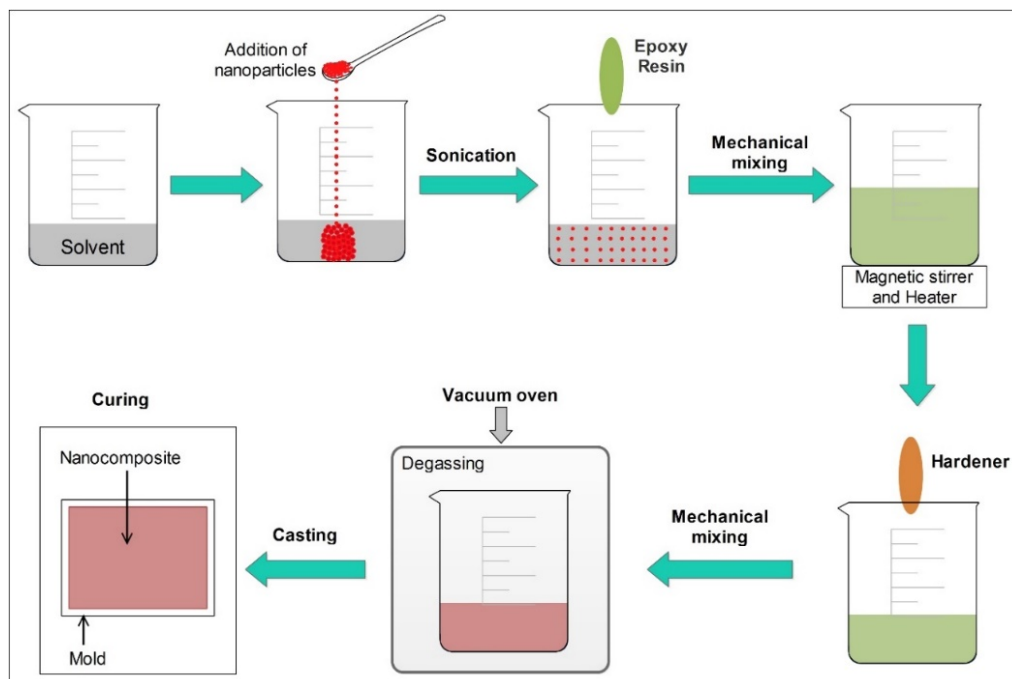


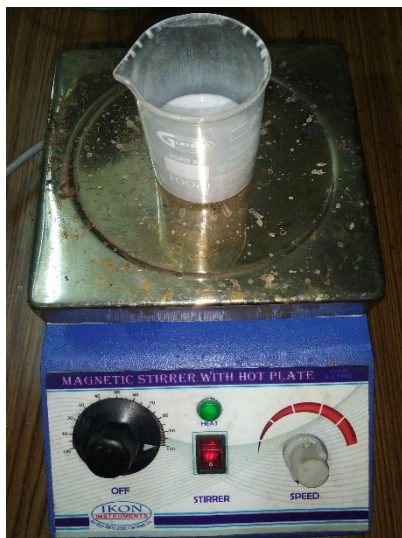
Figure 2.7 Schematic diagram for synthesis of epoxy alumina nanocomposite



(a)



(b)



(c)



(d)

Figure 2.8 Apparatus used for synthesis of epoxy alumina nanocomposite (a) Weighing machine, (b) Ultra-sonicator (c) Magnetic stirrer with hot plate, and (d) Vacuum pump.

2.3 DISPERSION OF NANOFILLERS

Particle dispersion in nanocomposite samples is qualitatively examined using images produced using a Field Emission Scanning Electron Microscope (FESEM) available at central instrument facility IIT (BHU). The FESEM setup is shown in Figure 2.9.



Figure 2.9 ZEISS SEM apparatus at CIF, IIT (BHU)

FESEM (Field Emission Scanning Electron Microscopy) images only provide a qualitative assessment of dispersion homogeneity. Understanding the relationship between dielectric characteristics and other control parameters such as filler concentrations, filler size, and interfaces necessitates quantifying the degree of dispersion and level of agglomeration. In this work, the filler dispersion in a polymer matrix is quantified using a method [14]. Computer-generated samples shown in Figure 2.10 is used to illustrate a concise overview of the method. Filler particles with square cross sections are employed to demonstrate the notion because their area fraction and volume fraction are the same. In Figure 2.10, filler particles of size d are uniformly distributed inside a square of size $2000 \text{ nm} \times 2000 \text{ nm}$, with the volume fraction of dispersed particles being v_0 . A sample square of length L is used to calculate the volume

fraction within this square at N random spots. The average of all such squares' values is used to calculate the effective volume fraction.

Figure 2.11 depicts three sampling squares with different length scales (L=a, L=b, L=c), with D representing the inter-particle distance. As the length of the sampling square is reduced, the estimated volume fraction (v_f) changes, but the difference is negligible as long as $L \gg D$. The estimated volume fraction deviates from the expected values in the extreme cases (i.e. L=b or L=c). If v_f^i is the computed volume fraction at the i^{th} position of the sampling square, and v_0 is the desired volume fraction, the variance for such N instances is given by:

$$\sigma^2(L) = \frac{1}{N} \sum_{i=1}^{i=N} (v_f^i - v_0)^2 \quad (2.1)$$

The length scale at which the variance shows a sharp increase in its value corresponds to the average inter-particle distance.

Figures 2.11a and 2.11b depict two computer-generated samples with a 1 vol.% filler loading and particles (size=50 nm) dispersed uniformly and non-uniformly, respectively. At several window lengths (L) ranging from 2000 nm to 100 nm, the volume percentage of particles is calculated. The volume fraction is determined at 100 random places for each window length while maintaining the particle distribution. The estimated variance at various window lengths of the sample square is shown in Figure 2.12. At a window length of 500 nm, a sharp spike in variance is observed for the sample with uniform distribution. The variance in the sample with agglomerated particles, on the other hand, begins to rise at a window length of 1000 nm. The average inter-particle distances are represented by these numbers. As a result, the inter-particle distance rises as agglomeration progresses. Table 2.1 shows the inter-particle distances for two computer-generated samples with similar filler concentrations but varied

particle dispersions. The inter-particle distance (D') differs from the expected ideal value (D) in the sample with agglomeration, and the ratio of the two can be used to characterize the degree of homogeneity.

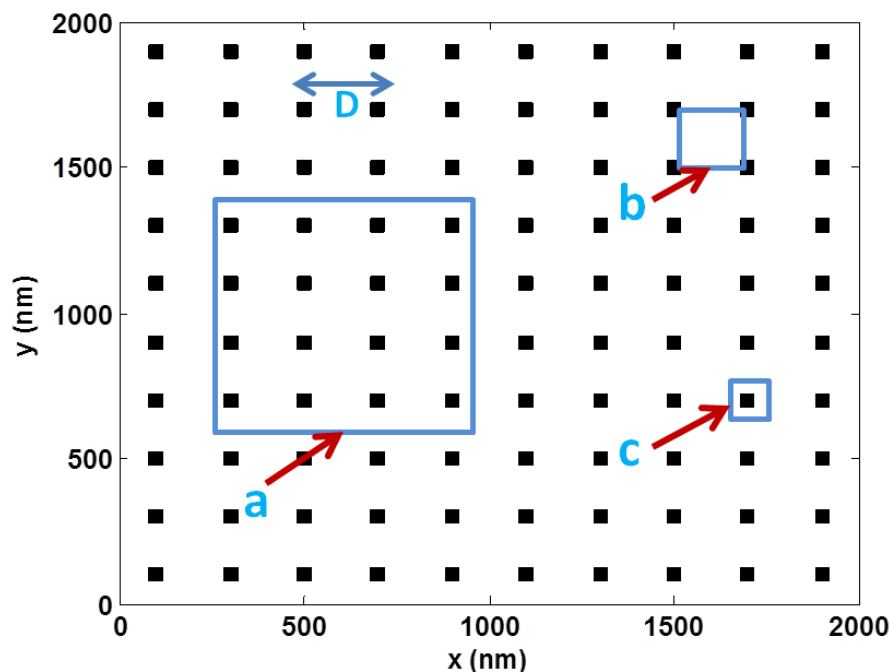


Figure 2.10 Schematic showing particle vol.% within sampling square of different length

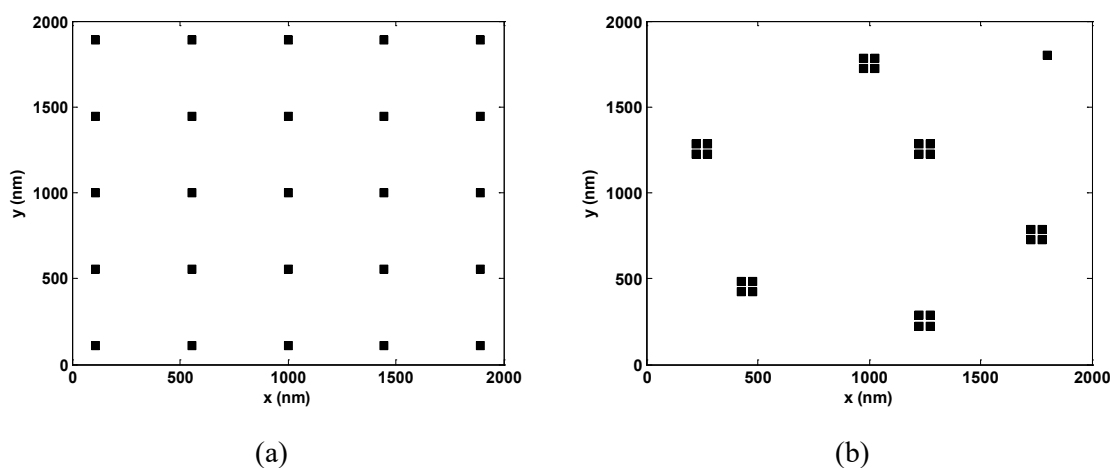


Figure 2.11 Filler particles of 50 nm diameter and with a concentration of 1 vol.% (a) uniformly distributed (b) agglomerated

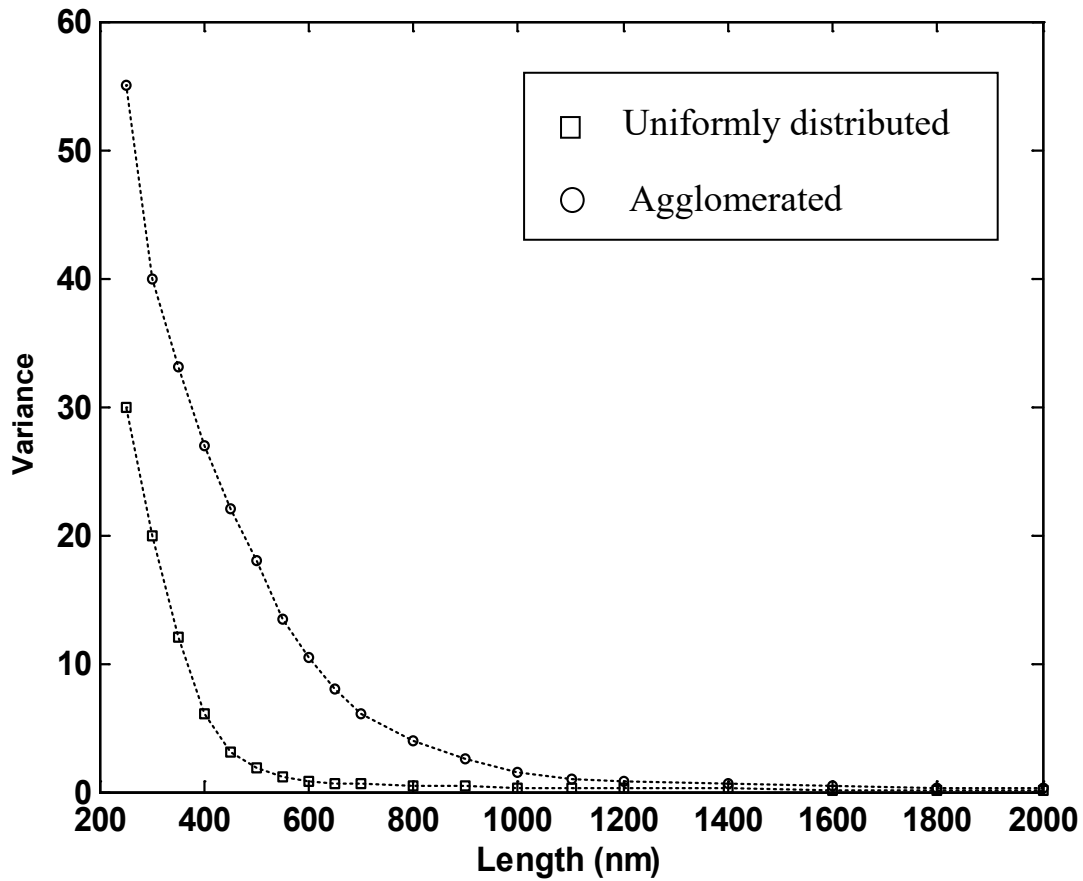


Figure 2.12 Variance (σ^2) vs. window length (L) for dispersion in Figures 2.11

Table 2.1 Quantification of particle dispersion in Figure 2.11

Inter particle distance with uniformly distributed particles (D)	Inter particle distance with agglomerated particles (D')	Degree of uniformity (D/D')
500 nm	800 nm	0.63

In a composite sample with evenly distributed particles, the inter-particle distance (D) can be calculated using the following formula:

$$D = d \sqrt{\frac{1}{v_f}} \quad (2.2)$$

where, d and v_f are the size and volume fractions of the fillers, respectively. It's worth

noting that the area and volume fractions in the equation above are the same. The computed inter-particle distance with a filler loading of 1 vol. % and particles (size=50 nm) is 500 nm, which matches the computed inter-particle distance in Table 2.1 quite well. As a result, the methodology for measuring filler dispersion has been proven to be accurate.

2.4 SUMMARY

This chapter provides a complete description of the materials utilized in this study (matrices, fillers, surfactants, and curing agents). We also briefly discussed the synthesis of neat epoxy and nanocomposites samples (with untreated and surface-treated nanofillers). In order to improve characteristics, nanofiller dispersion in the host material is crucial. FESEM is used to investigate filler dispersion in a polymer matrix qualitatively. In addition, a method for quantifying nanofiller dispersion in the polymer matrix is demonstrated. The following chapter discusses several characterization methodologies as well as investigations into electro-thermal characteristics and other important issues associated with polymer nanocomposites.