CHAPTER 3

PREPARATION OF MWCNT NANOFLUIDS

3.1 INTRODUCTION

The most economic and widely used method to prepare nanofluids in large scale production is the two-step method. In this method, nanoparticles are synthesized and then dispersed in base fluid. An important problem that needs to be solved in the two-step synthesis methods is the stabilization of the suspension prepared. Ultrasonication was one of the dispersion methods used to avoid the agglomeration of nanoparticles and to produce well-dispersed stable suspension.

During the procedure of two-step technique, the dispersed nanoparticles were prepared by chemical and physical methods first, and then the nanoparticles were added into a specified base fluid, with or without pretreatment and surfactant based on the need. Severe aggregation always takes place in the as-prepared CNTs (pure CNTs) because of the non-reactive surfaces, intrinsic Van der Waals forces, and very large specific surface areas, and aspect ratios.

The surfactant-free CNT nanofluids preparations include disentangling the nanotube entanglement and introducing hydrophilic functional groups on the surfaces of the nanotubes by chemical treatments. Chemical functionalization generally involves treating CNTs with acids at high temperature, either at their top or sidewall. This results in the addition of polar groups at defect sites on nanotube surface, thus making CNTs more hydrophilic in nature. The important technique to enhance the stability of nanoparticles in base fluids is the surface modification.
In the present work, MWCNT-nanofluids were prepared using the two-step method of dispersing MWCNTs in Silicone oil and Dowtherm A base fluids. In the prepared nanofluids, stability was maintained with the help of ultrasonication and by using carboxyl (-COOH) and hydroxyl (-OH) functionalized MWCNTs. MWCNT nanofluids made in this way were found to be very stable for months without visually observable sedimentation.

3.2 STRUCTURE AND PROPERTIES OF BASE FLUIDS

3.2.1 Structure of Silicone oil

Structure of silicone oil used in the present study is shown in figure 3.1.

Figure 3.1 Structure of Silicone oil (polydimethyl siloxane)

Polar inorganic groups consist of long and strong Si-O bond with open Si-O-Si angle. It has low rotation energy and low barrier to rotation. The siloxane backbone's high bond energy of ~445 kJ/mol along with its "inert" methyl (CH$_3$) functional groups combine to make polydimethylsiloxane (PDMS) a very chemically stable material. Typical use of temperatures for PDMS can range from below -40 to above 150°C. The presence of groups other than methyl along the polymer chain enables silicone properties to be modified.

Polydimethylsiloxane (PDMS) has outstanding flexibility, internal mobility, and large free volume. This property enables functional groups to
align efficiently to the most compatible interface, reduces competition among functional groups, and lowers functionality requirements. As a result, PDMS polymers are able to perform in applications where rigid organic polymers would require higher concentrations of expensive functional groups.

The unique properties of Si-O bond over C-O bond are as follows: (i) Si-O bond has higher bond energy than the C-O bond. (ii) Si-O bond is longer and flatter than the C-O bond. (iii) Si-O bond has a lower barrier to rotation than the C-O bond and higher free volume. All of these factors contribute to silicone’s open, flexible structure and low glass transition temperature.

3.2.2 Properties of Silicone oil

Table 3.1 Properties of Silicone oil

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity</td>
<td>43.5 cP</td>
</tr>
<tr>
<td>Density</td>
<td>0.968-1.29 g/cm³</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>74</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>2.9</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.399-1.403</td>
</tr>
<tr>
<td>Dipole moment</td>
<td>12-14D</td>
</tr>
<tr>
<td>Appearance</td>
<td>Pale yellow</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.1 W/mK</td>
</tr>
</tbody>
</table>

3.2.3 Dowtherm A or biphenyl and diphenyl oxide (C₆H₁₀ and C₆H₁₀O)

Dowtherm A is a mixture of special fluids that have the higher stability needed to collect, transport and store heat, and is ideal for systems
that use liquid or vapour phase heating. At each of the solar plants, Dowtherm A is used to collect heat energy and transport it to a power generating station. The transported heat converts water to steam, which in turn drives turbines to make electricity.

### 3.2.4 Structure of Dowtherm A

The structure of Dowtherm A used in the present study is shown in Figure 3.2.

![Structure of Dowtherm A](image)

**Figure 3.2 Structure of Dowtherm A**

### 3.2.5 Properties of Dowtherm A

**Table 3.2 Properties of Dowtherm A**

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity</td>
<td>3cP</td>
</tr>
<tr>
<td>Density</td>
<td>1.056 g/cm³</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>166</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>3.4</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.590</td>
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<tr>
<td>Dipole moment</td>
<td>10D</td>
</tr>
<tr>
<td>Appearance</td>
<td>clear to light yellow</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.139 W/mK</td>
</tr>
</tbody>
</table>
3.3 ULTRASONIC PROCESSOR

The ultrasonic processor UP400S (400 watts, 20 kHz) which is shown in figure 3.3 is the most powerful laboratory device. The device is suited for the sonication of sample with sonotrodes of a diameter range from 3 to 40 mm. The UP400S is mainly used for the preparation of samples in bigger volumes. It is suited for the development of ultrasonic applications in the laboratory.

Liquids can also be sonicated at elevated temperatures and pressures with special flow cells and flange connections. High power generates the intensive cavitation required, but this result in unwanted noise. For operating the UP400S we recommend to use the sound protection box. Typical applications include homogenization, de-agglomeration and the emulsification of liquids.

![Figure 3.3 Ultrasonic processor (UP400S)](image)

The effects of dispersing energy (ultrasonication) ultrasonic waves were used to efficiently disperse and breakdown agglomerated nanoparticles in the base fluids. The utilized device was probe kind sonicator. The ultrasonic dismembrator uses ultrasonic vibrations to thoroughly blend and suspend the
nanoparticles in the base fluid. The power supply for the sonic dismembrator converts the power from AC line voltage to 20 kHz electrical energy.

The energy is then fed to another converter, consisting of a lead zirconate titanate electrostrictive element, which expands and contracts with alternating voltage producing mechanical vibrations in the longitudinal direction. This travels to the horn tip and creates cavitations in the nanofluid and this causes the suspension to become energized. The Ultrasonic wave’s produced electrostatic repulsive forces have to be established between nanotubes.

3.4 PREPARATION OF MWCNT NANOFLOIDS

Nanofluids are widely prepared by two-step method and it is the most economic method to have nanofluids in large scale production. The present work follows the two-step method. In this method, pure and functionalized MWCNTs were commercially purchased and then dispersed in base fluids. The general problem encountered in the formulation of nanofluid is that simple mixing cannot achieve a stable nanotubes suspension. Therefore, in the present study, an ultrasonic processor was employed for that purpose.

The process of preparation of MWCNTs/Silicone oil and Dowtherm A nanofluids are as follows: (1) weigh the mass of MWCNTs by a digital electronic mass balance with an accuracy of 0.1 mg (model: AY220, SHIMADZU); (2) put MWCNTs in to the weighed Silicone oil / Dowtherm A and prepare the MWCNTs/ Silicone oil and Dowtherm A mixture; (3) sonicate the mixture continuously for 30 minutes with Cuphorn sonicator to obtain uniform dispersion of nanotubes in Silicone oil and Dowtherm A. Through this preparation, the temperature of nanofluids increases up to 55ºC. The prepared nanofluids with sonication processing have a more uniform and stable dispersion than a mixture without sonication processing.

The commercially purchased MWCNTs with purity >95% were used in our study. The purchased nanotubes (Pure MWCNTs, OH-MWCNTs and
COOH-MWCNTs) of five different concentrations (0.001 g, 0.002 g, 0.003 g, 0.004 g and 0.005 g) were mixed with any one of the measured quantity of base fluids (Silicone oil or Dowtherm A). Then this mixture was subjected to intensive ultrasonication using Cuphorn sonicator for 30 minutes with the working frequency of 20 KHz at an output amplitude of 100% (Heilscher UP 400S) to ensure better and stable suspension of nanofluids.

The sonication was performed in an ice bath to maintain a constant temperature in the suspension. The sonication time is an important parameter for dispersing the aggregated nanoparticles. Therefore, after several tests, the time of sonication was selected as 30 min for this study. In order to avoid the agglomeration of nanotubes and to produce well-dispersed stable suspension ultrasonication was mainly used. The suspensions were found to be stable and there was no observable sedimentation over a period of 1 month.

The schematic representation of nanofluid preparation is shown in figure 3.4.

![Schematic representation of nanofluid preparation](image)

**Figure 3.4** Schematic representation of nanofluid preparation

The following six Silicone oil and Dowtherm A based nanofluids with different MWCNTs concentrations (0.001 g, 0.002 g, 0.003 g, 0.004 g and 0.005 g) were prepared for the analysis.

1. Pure MWCNT + Silicone oil
2. Hydroxyl (-OH) MWCNT + Silicone oil
3. Carboxyl (-COOH) MWCNT + Silicone oil
4. Pure MWCNT + Dowtherm A
5. Hydroxyl (-OH) MWCNT + Dowtherm A
6. Carboxyl (-COOH) MWCNT + Dowtherm A