Effect of TiO2 Nanofluid and Hybrid TiO2 Nanofluid on Mechanical Properties of Steels for Automotive Applications

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Abstract. Quenching is a process involving rapid cooling in quenching media and hardening of steels. The effect of quenching process on the microstructure and mechanical properties (hardness) are studied and elaborated in this thesis. The quenching media uses including conventional fluid (distilled water and mineral oil), nanofluid (TiO2 nanofluid), and hybrid-based nanofluid (TiO2 hybrid nanofluid). Thermal conductivity and microstructure development are closely-linked to each other. Conventional fluids as quenching media have low thermal conductivity thus limiting the development of desired microstructure in the steels. The thermal conductivity and stability of nanofluid and hybrid-based nanofluid are studied to enhance the thermal properties of the quenching media.

1. Introduction
Quenching is a process that involves rapid cooling in medium of quenching and hardening of steels or other metal alloys. It helps to improve the mechanical and physical properties such as microstructure and hardness of steels or other metal alloys [1]. The role of quenching application can be seen in industrial areas such as nuclear reactor safety, the cooling of superconductor, metal forming, automotive and flash freezing [2].

During the past decade, the research on nanofluids has been increasing rapidly as it has beneficial value in terms of engineering applications. Metal oxides such as Al2O3 [2,3], CuO [3–5], Fe2O3, Fe3O4, SiO2 [6], TiO2 [4,7,8], and ZrO2; metal carbides such as SiC [9], metal nitrides such as AlN, and SiN; and carbon materials such as carbon nanotubes [10–12], graphite, and diamond are usually used as nanoparticles in the researches of nanofluid. In this experiment, TiO2 nanoparticles and C-TiO2 hybrid nanoparticles will be synthesized alongside with the conventional fluids to determine their effects on the quenching process. The mechanical and physical properties of heat treated high carbon steel and medium carbon steel will also be investigated by immersing both steels into conventional fluids (i.e. water, mineral oil, ethylene glycol, silicon oil and methanol), TiO2 nanofluids and C-TiO2 hybrid nanofluids.

2. Materials and Method

2.1. Synthesis of TiO2 Nanofluid and Hybrid TiO2 Nanofluid
Different particle size of TiO2 and C nanopowders are used for synthesis process of different volume fraction of 0.1% TiO2 nanofluid (100 nm), 0.5% TiO2 nanofluid (30 nm), and 0.1% TiO2 - 0.9% C hybrid nanofluid (30 nm). Both nanopowders are weighed accordingly using the equation 1 and 2.
respectively;

\[
\varphi = \left[ \frac{(\frac{W}{\rho})_{TiO_2}}{(\frac{W}{\rho})_{TiO_2} + (\frac{W}{\rho})_{water}} \right] 
\]

\[
\varphi = \left[ \frac{(\frac{W}{\rho})_{C}}{(\frac{W}{\rho})_{C} + (\frac{W}{\rho})_{water}} \right] 
\]

(1)

(2)

Table 1: Volume fraction of TiO$_2$ nanofluid and C-TiO$_2$ hybrid nanofluid

| Volume fraction of TiO$_2$ (%) | Mass of TiO$_2$ (g) | Volume fraction of C (%) | Mass of C (g) | Mass of distilled water (g) |
|-------------------------------|---------------------|--------------------------|----------------|-----------------------------|
| 0.1                           | 0.064               | -                        | -              | 15.000                      |
| 0.5                           | 0.320               | -                        | -              | 15.000                      |
| 0.1                           | 0.064               | 0.9                      | 0.576          | 15.000                      |

Table 1 shown the volume fraction of TiO$_2$ nanofluid and C-TiO$_2$ hybrid nanofluid. The table indicated the mass of TiO$_2$ and C are required to produce different volume fraction of TiO$_2$ nanofluid and C-TiO$_2$ hybrid nanofluid. Next, the TiO$_2$ nanopowder and C nanopowder are grinded using mortar and pestle to breakdown the aggregated nanopowder respectively. Then, by using magnetic stirrer, both TiO$_2$ and C nanopowders are poured slowly into distilled water and stirred for 3h.

2.2. Stability Analysis

The TiO$_2$ nanofluid and C-TiO$_2$ hybrid nanofluid prepared are sonicated using ultrasonication water bath in 3 different time (1h, 3h, and 5h) and their stability are evaluated after sonication process. The optimum sonication time (the most stable TiO$_2$ nanofluid and C-TiO$_2$ hybrid nanofluid) is evaluated and used for quenching process.

2.3. Thermal Conductivity Analysis

Thermal conductivity analysis is carried out by using C-Therm equipment. Different type of quenching media such as conventional fluid (i.e. distilled water and mineral oil), different volume fraction of 0.1% TiO$_2$ nanofluid (100 nm), 0.5% TiO$_2$ nanofluid (30 nm), and 0.1% TiO$_2$ - 0.9% C hybrid nanofluid (30 nm) are evaluated and compared in term of thermal properties.

2.4. Heat Treatment

A long rod of high carbon steel is cut into same size with dimension 1 cm depth and 1 cm wide using the manual abrasive cutting machine. The various type of specimens is prepared through heating process. The specimens are heated in the furnace until 950 °C for 90 minutes and hold for 20 minutes. Then, the specimens are quenched immediately into the different type of quenching media respectively. One of the specimens heated is allowed to cool down in room temperature.
2.5. Microstructure Analysis
The specimens are mounted using acrylic and undergone grinding and polishing processes by using different emery paper (200, 400, 600, and 800) of roll grinder and polish disc to achieve mirror finished specimens. Then, the specimens are dipped into nital solution for 7 secs before conducting microstructure analysis. The microstructure is observed under optical microscope.

2.6. Hardness Analysis
Hardness analysis is carried out by Vickers hardness testing. 30 N of load are applied onto the various specimens and the hardness value at 3 different spots are evaluated including inner, middle, and outer part of the specimens.

3. Result and Discussion

3.1. Thermal conductivity of different quenching media
Figure 1 shown the thermal conductivity of different quenching media. The thermal conductivity of 0.5% volume fraction of TiO₂ nanofluid (30 nm) shows the highest thermal conductivity with 0.631 W/m.K based on figure 1. The result is followed by 0.1% TiO₂-0.9% C hybrid-based nanofluid with 0.623 W/m.K and 0.1% volume fraction of TiO₂ with 0.620 W/m.K (100 nm). The thermal conductivity of the TiO₂ nanofluids and C-TiO₂ hybrid-based nanofluid are compared with the conventional fluids used during quenching process. Distilled water has a higher thermal conductivity with 0.620 W/m.K compared to mineral oil with 0.139 W/m.K. It is proven that both nanofluids and hybrid-based nanofluid have higher thermal conductivity compared to the conventional fluids. Based on the previous studies made by many researchers, hybrid-based nanofluid has a better thermal properties’ performance compared to nanofluid. However, there is an anomaly found based on the data chart shown in figure 1. The thermal conductivity of 0.5% volume fraction of TiO₂ nanofluid is higher compared to 0.1% volume fraction of TiO₂ hybrid-based nanofluid. Therefore, different methods of thermal conductivity measurement should be considered and carried out to ensure the accuracy of the results.

3.2. Stability of nanofluid and hybrid nanofluid
The synthesis of nanofluids and hybrid-based nanofluid with volume fractions of 0.1% TiO₂ nanofluid (100 nm), 0.5% TiO₂ nanofluid (30 nm), and 0.1% TiO₂ - 0.9% C hybrid-based nanofluid are carried out with different sonication times of 1h, 3h, and 5 h. Figure 2 shows the most stable TiO₂ nanofluids and C-TiO₂ hybrid-based nanofluid with sonication time of 1 h.
3.3. Microstructure of the quenched sample

The microstructure of the specimens is observed under an optical microscope. Figure 3 shows the microstructure of high carbon steel before heat treatment process. Based on the result shown, fine mixture of ferrite, iron carbide, and pearlite are observed on the specimen. Based on figure 3(b), martensite or needle-like structure is observed in quenched samples of distilled water. The quenched sample of 0.1% TiO$_2$ nanofluid (figure 3d) is made up of mostly martensite and bainite, and a few pearlite structures. Martensite and bainite structures are observed in the quenched samples of 0.5% TiO$_2$ nanofluid (figure 3e) and 0.1% C-0.9% of TiO$_2$ hybrid nanofluid (figure 3f). The least martensite with abundant pearlite structures are observed in mineral oil quenched sample (figure 3c). It can be concluded that the thermal conductivity in different quenching media affects the changes in microstructure. The rapid cooling due to the high thermal conductivity of quenching medium allows the formation of martensite structure in the high carbon steel specimen.

3.4. Hardness analysis

The hardness value at three different spots of heat treated and quenched samples are measured and
The hardness value of heat treated high carbon steels are taken in three different spots (i.e. inner, middle, and outer). The highest hardness value measured is the quenched sample of 0.1% TiO\textsubscript{2} - 0.9% C volume fraction of hybrid-based nanofluid which is 1677.77 HV. The least hardness value measured is the normalized sample (without quenching process) which is 710.37 HV. Furthermore, the outer spots of the quenched samples (i.e. distilled water, mineral oil, 0.1% and 0.5% volume fractions of TiO\textsubscript{2} nanofluids, and 0.1% TiO\textsubscript{2} - 0.9% C volume fraction of hybrid-based nanofluid) compared to the inner and middle spots of quenched samples. In essence, the hardness values in the quenched samples are influenced by the microstructure. For instance, 0.1% TiO\textsubscript{2} - 0.9% C volume fraction of hybrid-based nanofluid consists of martensite and bainite structure, thus it will improve the material strength as it is extremely hard and brittle. Plastic deformation may occur as well due to the slip mechanism in the quenched sample.

### Table 2: Hardness value of heat treated and quenched samples at three different spots

| Type of Quenching Media | Type of Spots | Hardness Value (HV) | Average Hardness Value (HV) |
|-------------------------|---------------|---------------------|-----------------------------|
| Distilled water         | Inner         | 708.3               | 1015.43                     |
|                         | Middle        | 662.7               |                             |
|                         | Outer         | 1675.3              |                             |
| Normalising             | Inner         | 483.7               | 710.37                      |
|                         | Middle        | 416.1               |                             |
|                         | Outer         | 351.1               |                             |
| Mineral Oil             | Inner         | 880.2               | 839.00                      |
|                         | Middle        | 489.3               |                             |
|                         | Outer         | 1147.5              |                             |
| 0.1% TiO\textsubscript{2} nanofluid | Inner | 557.7               | 954.77                      |
|                         | Middle        | 594.4               |                             |
|                         | Outer         | 1712.2              |                             |
| 0.5% TiO\textsubscript{2} nanofluid | Inner | 1095.8              | 1275.73                     |
|                         | Middle        | 1571.4              |                             |
|                         | Outer         | 1160.0              |                             |
| 0.1%TiO\textsubscript{2}-0.9% C hybrid nanofluid | Inner | 1750.3              | 1677.77                     |
|                         | Middle        | 1501.2              |                             |
|                         | Outer         | 1781.8              |                             |

### 4. Conclusions
Throughout the experiment conducted in this project, there were four different aspects of analysis can be concluded in terms of thermal conductivity, stability, microstructure, and hardness, of the heat treated samples in different quenching media.
i) **Thermal conductivity:**
The thermal conductivity of TiO$_2$ nanofluids are influenced by the different size of TiO$_2$ nanoparticles. For example, the size of TiO$_2$ nanoparticle in 0.5% volume fraction of TiO$_2$ nanofluid is smaller compared to 0.1% volume fraction of TiO$_2$ nanofluid, resulting to a higher thermal conductivity. The C-TiO$_2$ hybrid-based nanofluid showed the lower thermal conductivity compared to 0.5% volume fraction of TiO$_2$ nanofluid. Both nanoparticles size used for synthesis are 30 nm. This could indicate that there were abnormalities of data collected from C-Therm equipment. The value of thermal conductivity of C-TiO$_2$ hybrid-based nanofluid should be higher than TiO$_2$ nanofluids. Hence, an improvement of methods of thermal conductivity analysis should be considered, carried out, and evaluated to obtain the most accurate and precise data.

ii) **Stability:**
The stability of the different type of nanofluids’ synthesized showed that 1 h sonication time was the optimum time to achieve the stability. The high time leads to deterioration of the stability of nanofluid.

iii) **Microstructure:**
Microstructure of quenched samples are affected by the thermal conductivity of different quenching media (conventional fluids such as distilled water and mineral oil, and different type of nanofluids such as TiO$_2$ nanofluids and C-TiO$_2$ hybrid-based nanofluid). The martensitic structure is observed under microscope on quenched samples of both TiO$_2$ nanofluids, TiO$_2$ hybrid-based nanofluids, and distilled water. These quenching media showed the significant values of thermal conductivity that enable the transformation of austenitic structure to martensitic structure.

iv) **Hardness:**
The hardness value is influenced by the microstructure observed on the surface of quenched samples. The highest hardness value measured is the C-TiO$_2$ hybrid-based nanofluid quenched sample. There were abundant of martensite and bainite structure causing the great enhancement of the hardness of the heat treated quenched sample. The plastic deformation in the quenched sample may occur due to the slip mechanism develop because of the quenching process.

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