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Effect of Multi-walled Carbon Nanotube and Polyethylene Glycol Addition in Nanofluid Quench Medium for Steel Heat Treatment Application

Wahyuaji Narottama Putra[1*], Myrna Ariati[1], Bambang Suharno[1], Alfian Noviyanto[2,3], I Made Riko[4]

[1]Department of Metallurgical & Materials Engineering, Faculty of Engineering, Universitas Indonesia, Kampus Baru UI, Depok, 16424, Indonesia
[2]Nano Center Indonesia, Jl. Puspiptek, South Tangerang, Banten, 15314, Indonesia
[3]Department of Mechanical Engineering, Mercu Buana University, Kebun Jeruk, Jakarta, 11650, Indonesia
*[4]Institute of Materials Research and Engineering, A*Star Singapore, 2 Fusionopolis Way, 138634, Singapore*

Abstract. In the steel heat treatment industry, quenching is a critical stage for enhancing the characteristics of steel. However, the lack of adherence to appropriate procedures, especially in quenchant selection, can lead to cracks or distortion. Quenchant selection is based on the required cooling rate for the specific steel being quenched. Cooling rate of the quenchant is primarily determined by the thermal conductivity of the fluid. This conductivity can be modified by dispersing stabilized solid particles, typically in the nano-scale range, thus forming a nanofluid. It is important to note that a higher conductivity will increase the heat transfer characteristic and vice versa, hence, cooling rate can be controlled by adjusting the amount of the dispersed particle. In this study, the dispersed particle and surfactant used was multi-walled carbon nanotube (MWCNT) and polyethylene glycol (PEG), respectively. The concentrations of the dispersed particle were 0.1, 0.3, and 0.5 weight%. Furthermore, the surfactant was added at 3 – 30% on each particle variation. The results showed that the highest thermal conductivity of 0.68 W/mK was achieved at 0.5% MWCNT and 5% PEG. This translated into better steel properties, as it led to a hardness of 48 in Hardness Rockwell C-scale (HRC) compared with the water-quenching technique. A higher percentage of PEG surfactant decreases the thermal conductivity of the quenching medium and steel hardness. This decrease was attributed to the high viscosity of the medium. In conclusion, adjusting the particle and surfactant concentration allows for the optimal quenching medium, offering enhanced steel properties.

Keywords: Heat treatment; MWCNT; Nanofluid; PEG; Quench medium; S45C carbon steel

1. Introduction

Nanofluid is a fluid containing nano-sized particles suspended in a base fluid. These nanoparticles serve to improve thermal conductivity. It is important to note that solid particles generally have higher conductivity compared to any fluid (Ali and Salam, 2020). The extensive surface area in nanoparticles contributes to even higher conductivity. Therefore, nanofluid is commonly used in heat transfer-intensive processes, such as coolant systems (Septiadi *et al.,* 2020), or quenching mediums in heat treatment (Radhiyah and Nurziela, 2020; Yahya *et al.,* 2018; Babu, Arularasan, and Ramkumar, 2017).

*Corresponding author's email: wahyuaji@ui.ac.id, Tel.: +62-21-7863510; Fax: +62-21-7872350
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Several types of solid particles can be added to nanofluid, including metals, metal oxides such as CuO, TiO_2, and Al_2O_3, as well as carbon-based particle (Arularasan and Babu, 2021; Ramadhani *et al.,* 2019; Xia *et al.,* 2014). Carbon-based particle, specifically advanced types such as MWCNTs, has garnered increased attention due to the significantly higher thermal conductivity (Chen, Zeng, and Yuan, 2017). Therefore, a small addition of this particle has the potential to substantially increase the thermal conductivity of nanofluid (Hamidi and Putra, 2023).

In the base fluid, nanoparticles were dispersed, but a challenge, namely agglomeration, arises with the particle dispersion (Ilyas, Pendyala, and Marneni, 2014). Fine particles are prone to easy agglomeration, leading to inhomogeneous nanofluid. This problem also impacted the stability of nanoparticles, as they tend to settle at the bottom of nanofluid container (Ilyas, Pendyala, and Marneni, 2014). To overcome the challenge, a surfactant was added to improve the dispersion inside the fluid (Jehhef and Siba, 2019; Adiwibowo, Ibadurrohman, and Slamet, 2018). Several types of these surfactants were categorized as anionic, cationic, non-ionic, and zwitterionic. The classification was based on the charge type of the molecule. Surfactants modify the surface of nanoparticles by decreasing the surface tension, thereby enhancing stability and dispersion, leading to higher thermal conductivity (Qadariyah *et al.,* 2022; Kusrini *et al.,* 2019; Asadi *et al.,* 2017; Paramashivaiah and Rajashekhar, 2016).

Nanofluid application is primarily applied in heat transfer fluid due to the superior thermal conductivity. A specific application of the heat transfer fluid is in the quenching medium during the heat treatment of steel (Agboola *et al.,* 2020; Kresnodrianto *et al.,* 2018; Ikubanni *et al.,* 2017). Improving steel properties, particularly hardness, can be achieved by quenching it from the austenitizing temperature, transforming the microstructure from Austenite to the Martensite phase. The cooling rate plays a crucial role in the transformation, with a slower rate resulting in a phase other than Martensite.

Rapid cooling leads to cracks and distortion in the steel, necessitating the need for appropriate quench medium with better cooling rate (Fredj *et al.,* 2017). The use of nanofluid offers a distinct advantage as cooling rate can be adjusted based on the quantity of nanoparticles added to the base fluid. This adjustability makes the quenchant highly versatile in the heat treatment industry.

This study aimed to provide a more comprehensive experimental analysis of the effect of combining MWCNT and PEG in nanofluid, which is to be used specifically as a quenchant in a steel heat treatment process. The difference in the thermal conductivity of the quenchant was compared directly to the hardness of the quenched steel. A direct relationship between the thermal conductivity and cooling rate could be used to design a better quenchant. In summary, a nanofluid with an adjustable cooling rate may provide an appropriate solution in a thermal-sensitive heat treatment process to prevent defects.

2. Experiment Setup

MWCNT used in this study was a laboratory grade purchased from Sigma Aldrich. According to the datasheet, MWCNT particle had a diameter ranging from 50 – 90 nm, with an average of 65 nm. To explore deeper into the particle characteristics, a Scanning Electron Microscope (SEM), specifically FEI Inspect F50 with integrated Energy Dispersive Spectroscopy (EDS) from EDAX, was applied for observation. Nanotube was used to synthesize a nanofluid with distilled water as the base fluid. Finally, the particle concentration was varied at 0.1, 0.3, and 0.5 % w/v.

To improve the dispersion of MWCNT in the base fluid, Polyethylene Glycol (PEG) surfactant was used as a stabilizer. PEG, purchased from Sigma Aldrich as a liquid with an average molecular weight of 200, was added at concentrations ranging from 3 – 30 % v/v for each MWCNT percentage variation. To study nanofluid characteristics, zeta potential and thermal conductivity were conducted. Zeta potential was performed using the Horiba SZ-100 series machine to observe the stability of the particle in the fluid. Meanwhile, KD2 Pro Thermal Properties Analyzer was adopted to examine the thermal conductivity based on the transient heat transfer principle.

The synthesized nanofluid was used as a quench medium in the steel heat treatment process to enhance the characteristic, particularly hardness. A medium carbon steel S45C was used as the sample for the heat treatment. The chemical composition was verified using Optical Emission Spectroscopy (OES) with the Foundry-Master Xpert equipment. The dimension of the steel is shown in Figure 1a. This sample was austenized at 900°C for 60 minutes to achieve a complete Austenite phase. However, to prevent cracking or distortion due to thermal shock, preheating at 540°C was conducted (Mochtar, Putra, and Abram, 2023). The complete thermal treatment cycle is presented in Figure 1b. After austenitization, the steel was quenched in nanofluid to obtain a Martensite phase. Microstructure observation and hardness test were performed to confirm the phase transformation in the sample.

In this study, the microstructure was observed using Olympus Inverted Metallurgical Microscope BX41M-LED. The steel sample was prepared beforehand by etching in 2% Nital solution. The etchant duration was varied from 3 – 10 seconds. For hardness measurement, Rockwell and Vickers hardness tests were performed with the application of Qualirock Digital Hardness Tester and Micromet 5100 series micro-indentation tester, respectively.

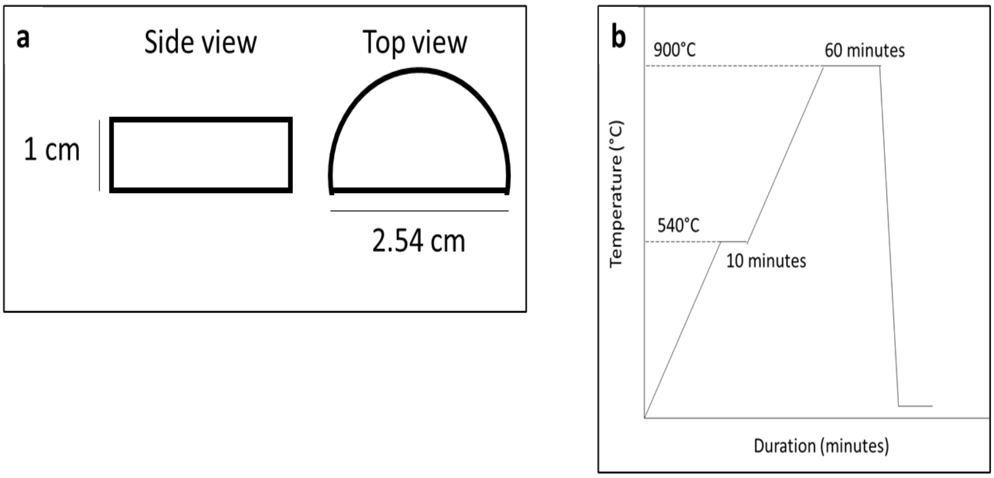

Figure 1 (a) Steel sample dimension, (b) Thermal cycle for steel heat treatment

3. Result And Discussion

3.1. Preliminary Observation on the Multiwalled Carbon Nanotube and S45C Steel Sample

MWCNT was examined using SEM to observe the morphology. Figure 2 presents the electron microscope imaging of MWCNT particle, showing a length of more than 1 μm.

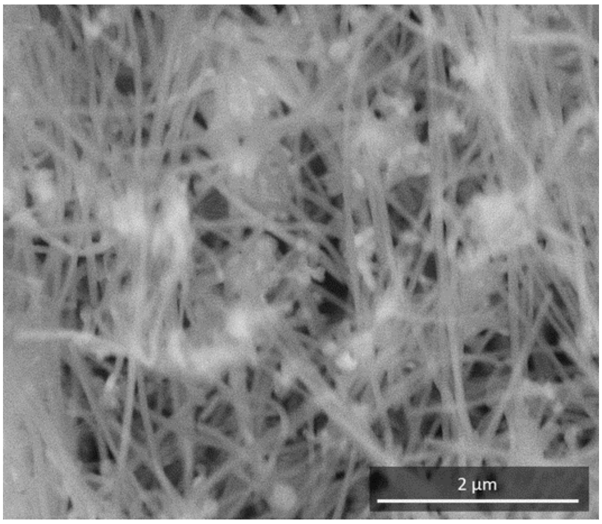

Figure 2 Electron microscope image of Multiwalled Carbon Nanotube

The sample used for quenching was S45C medium carbon steel. Furthermore, the chemical composition was verified using OES and the result is presented in Table 1.

Table 1 S45C chemical composition by OES

Element	Weight %
Fe	98.2
C	0.42
Si	0.26
Mn	0.68
P	0.008
S	0.006

Based on the result, the steel sample conformed to the S45C standard (Otai, 2015)

3.2. Multiwalled Carbon Nanotube Stability of Nanofluid in Various Surfactant Concentrations

Zeta potential was used to assess the stability of MWCNT inside nanofluid. The measurement specifically targeted the concentration of 0.5% MWCNT, with the addition of 3, 7, 10, and 30% of surfactant. Table 2 shows the result of the measurement.

Table 2 Zeta potential measurement of nanofluid

MWCNT (%)	PEG (%)	Zeta Potential (mV)
0.5	3	-37.2
	7	-25.5
	10	-23.4
	30	-23.2

The result showed that the introduction of additional PEG enhanced stability by increasing zeta potential to -37.2 mV. Nanofluid with a zeta potential of more than ± 30 mV was considered to the moderately stable (Ghadimi, Saidur, and Metselaar, 2011). On the other hand, less than ± 30 mV implied suboptimal stability, potentially leading to sedimentation. The augmentation of PEG contributes to stability improvement by modifying the surface tension on the particle. During absorption, the particle will have lower surface tension and create a layer to avoid agglomeration with similar particles. Therefore, the addition of 3% PEG yielded the most favorable zeta potential in this investigation. A decrease in stability was observed with higher PEG concentration, attributable to the formation of micelles from the bulk surfactant (Zhang *et al.*, 2021;

Paramashivaiah and Rajashekhar, 2016). The formation of micelle reduces the ability to modify the surface tension of the particle, resulting in lower stability.

3.3. Thermal Conductivity Evaluation of MWCNT-based Nanofluid with Different Concentrations of Particle and Surfactant

An examination of the effect of additional MWCNT and surfactant on thermal conductivity was also conducted. Figure 3a shows the measurement result on all nanofluid variables. The inclusion of MWCNT increased the thermal conductivity of the quenchant, even without surfactant. Increasing the percentage of nanotube and PEG could enhance conductivity. The highest thermal conductivity of 0.68 W/mK was obtained after 0.5% MWCNT and 5% PEG were added. For comparison, distilled water had a conductivity of 0.59 W/mK, which was improved by approximately 15%. The results suggested that the optimum surfactant concentration was 5%.

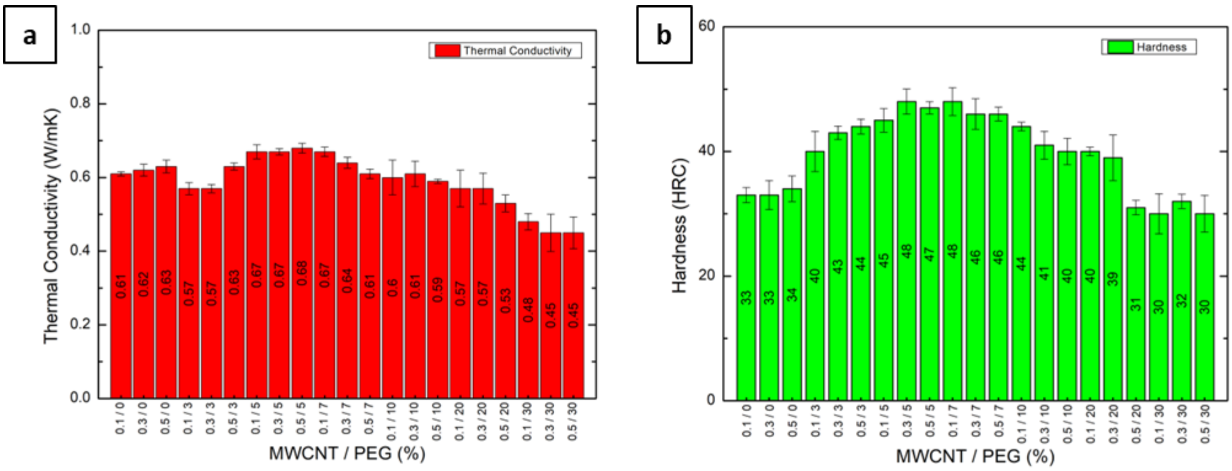

Figure 3 (a) Thermal conductivity measurement result, (b) Steel hardness measurement result

The thermal conductivity decreased at a higher percentage of PEG surfactant. The poorest conductivity was observed after the addition of 30% PEG, yielding a value of 0.45 W/mK, even lower than distilled water. This decline could be attributed to the formation of surfactant micelles, as explained previously. Higher surfactant concentration may compromise stability and create agglomeration of MWCNT. This results in an inhomogeneous nanofluid and reduces the effective transfer of heat.

3.4. Improvement of S45C Steel Hardness after Quenching Process in Various MWCNT-based Nanofluid Quenchant

Nanofluid was used as a medium to quench austenized S45C medium carbon steel. After quenching, the sample hardness was measured and presented in Figure 3b. The hardness value trend was similar to the thermal conductivity. The variable with the highest thermal conductivity (0.5% MWCNT and 5% PEG) also had the highest hardness at 48 Rockwell hardness C scale (HRC). For comparison, S45C steel sample had a value of 12 HRC before any heat treatment process, then escalated to 43 HRC after being quenched with distilled water. Therefore, the increase in hardness achieved through nanofluid was up to 11% compared to distilled water quenching. S45C steel sample after being treated with nanofluid was nearly identical to the expensive high alloy tool steel SKD 61 (Kosasih, Priadi, and Suliyanti, 2023).

The same trend was followed for the sample with higher surfactant concentrations. Hardness decreased quite significantly after the addition of 20% and 30% surfactant. The decrease has a strong relation with the lower thermal conductivity. In heat treatment, a high cooling rate was needed for the transformation from the Austenite to the Martensite phase. Therefore, a quench medium with high thermal conductivity was essential to obtain a high cooling rate and vice versa (Aziz and Zaharudin, 2020). Based on the result, it was concluded that higher thermal conductivity could provide a faster cooling rate, resulting in higher steel hardness.

3.5. Microstructure Evolution of S45C Steel after Quenching Process

Microstructure observation was conducted to support the steel hardness result. Figure 4a and 4b shows the microstructure before and after heat treatment, respectively.

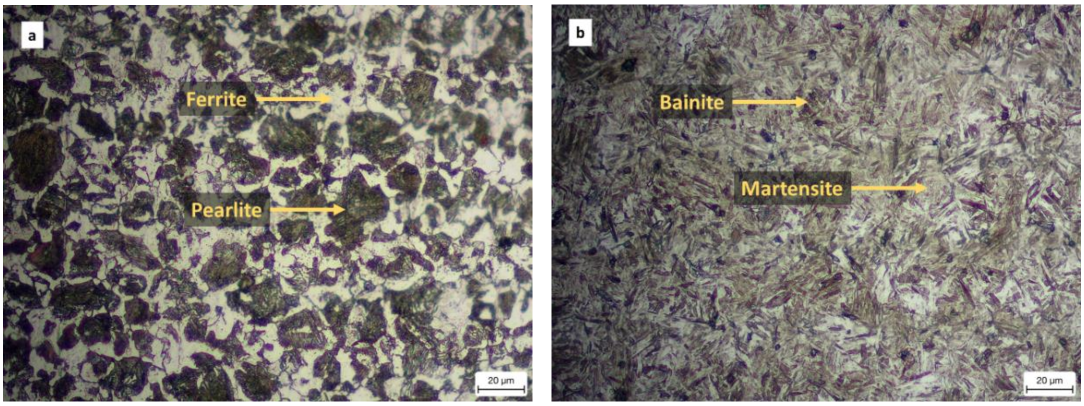

Figure 4 Microstructure of S45C (a) before heat treatment, (b) after quenched in distilled water

In Figure 4b, distinguishing between Bainite and Martensite phases in microstructure after quenching proved challenging. A Vickers Hardness was used to discriminate between the two phases, based on their hardness, as shown in Table 3. Microhardness result suggested that the brighter area was the Martensite phase, while the darker area was the Bainite phase. This interpretation was in line with a similar microstructure reported by Nishimoto (Nishimoto *et al.*, 2022).

Table 3 Vickers microhardness results in quenched microstructure

Area	Vickers Hardness Number (HV)
Brighter phase	743 ± 15
Darker phase	563 ± 17

For comparison, the microstructure of the steel with the lowest and highest hardness after quenched in nanofluid are presented in Figure 5a and 5b, respectively. Figure 5a showed that the microstructure was dominated by Ferrite and pearlite phases, with some Martensite phases in certain areas. Due to the presence of Ferrite phase, hardness was low. Meanwhile, Figure 5b showed only Martensite and Bainite phases, contributing to significantly higher steel hardness. Comparing Figure 4b (quenched in distilled water) and 5b (quenched in nanofluid), it was observed that the amount of Martensite was slightly higher in 5b, hence, hardness was also higher.

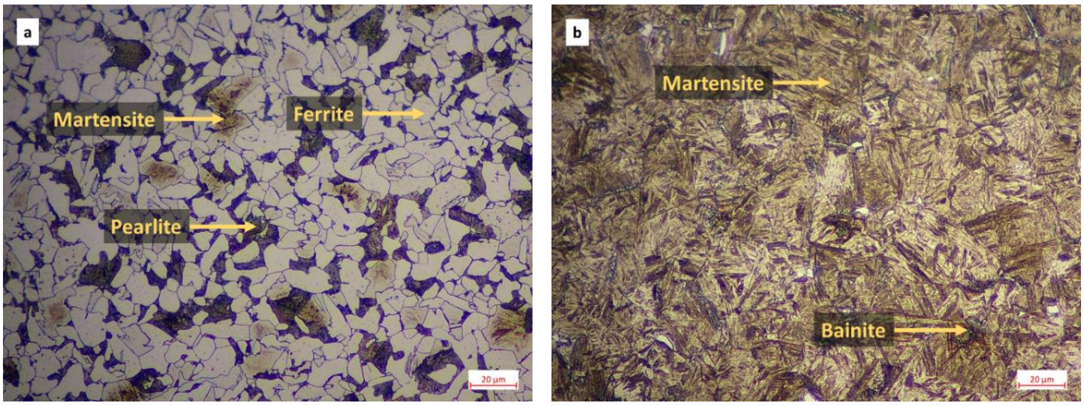

Figure 5 Microstructure of S45C quenched in nanofluid with (a) 0.5% MWCNT and 30% PEG, (b) 0.3% MWCNT and 5% PEG

4. Conclusions

In conclusion, the integration of MWCNT as nanoparticle and PEG surfactant improved the performance of quenching medium by enhancing thermal conductivity. The superior thermal conductivity of nanoparticles contributed to enhanced nanofluid conductivity. The results showed that in the absence of a surfactant, the inclusion of MWCNT alone elevated water conductivity to 0.63 W/mK. Significantly, the introduction of 5% PEG concentration led to further refinement, thereby increasing the value to 0.68 W/mK. This refinement resulted from the improved dispersion and stabilization of MWCNT particles facilitated by PEG. Zeta potential analysis showed that the addition of 3% surfactant led to an increase, reaching -37.2 mV. This showed a moderate level of nanofluid stability. The pursuit of higher thermal conductivity translated into a faster cooling rate and increased steel hardness. Experimental results substantiated this notion, as steel sample subjected to quenching in nanofluid with high conductivity showed hardness level of 48 HRC. The excessive addition of surfactant adversely affected thermal conductivity and steel hardness post-quenching. At higher concentrations, micelle formation occurred, diminishing the efficacy of modifying surface tension and leading to particle agglomeration. Consequently, thermal conductivity was reduced to 0.45 W/mK, and steel hardness decreased to a minimum of 30 HRC due to a slower cooling rate. This study explored the development of an adaptable cooling rate quenchant based on nanofluid, offering a potential solution for steel heat treatment industry, particularly for products sensitive to thermal variations. The determination of an optimal ratio between particle and surfactant concentration was a critical factor in achieving the desired objectives.

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