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Evaluate the Effectiveness of some Homopolymers as Lube oil Additives

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Abstract

Some lube oil additives increase the basic oil performance, for example, such as improving the viscosity index and depression pour points, the most important type of additives. In the present work, some homopolymeric additives have been prepared with different alcohols. (1-dodecyl,1-tetradecyl, 1-hexadecyl and 1-octadecyl) by esterification of acrylic acid and then homopolymerization of prepared esters with different catalyst ratios of benzoyl peroxide (0.25%& 0.5 % and 1%). Infra-red spectroscopy confirmed the structure of the prepared esters. By using a gel permeation chromato-graph, molecular size of prepared homopolymers were determined. In order to improve the viscosity index and pour point depressants for lube oil, the quality of prepared home polymers was studied. All prepared homopolymers were found to work as an improvement as viscosity index improvers and pour point depressants for lube oil at the percentage 0.25%. of catalyst, Thermal stability is present, and the fluid behavior is non Newtonian.

***Keywords**: Homopolymerization; Improving viscosity index; Non Newtonian; Pour point depressants; Lube oil additives.*

1. Introduction

Lubrication is the operation by which friction and wear are reduced between contact surfaces of solids moving in relation to each other by applying a substance with appropriate characteristics [1]. Lubrication can decrease friction, wear and stop seizure, thus prolong the machine life and save power [2]. Over the years, the use of lube oil is not enough but must add some additives to lube oil. Oil additives are dissolved or suspended organic or inorganic compounds. Depending on the machine, they usually vary between 0.1 and 30% of the oil volume. Additives have three fundamental functions. A) Improve the current base oil characteristics as antioxidants, corrosion inhibitors, anti-foam agents and demulsifiers. b) eliminate undesirable base oil characteristics as viscosity index (VI) improvers and pour-point (PP) depressants. c) Give the base oils new characteristics as detergents and extreme pressure(E.P) additives [3-4]. The viscosity index (VI) expresses oil change in viscosity when the temperature varies, i.e. the smaller these changes, the higher the viscosity index, different compounds, usually polymeric compounds, were proposed as lubricating oil additives, with the aim of enhancing viscosity index and thus extending their field of use. Viscosity Index (VI) improvers are chemical products used in lubricating oil to adhere with the ideal lubricant [5]. In general, polymer solubility increase when temperature rises and the polymer modules shift from tight to enlarged because the interaction between the polymer chain and the solvent molecules is increased. This increase in volume results in a greater blend viscosity, which compensates with a higher temperature for the standard decrease in oil viscosity. Increasing the polymer's molecular weight also increases the quantity of polymer micelle in an oil solution [6-8]. The pour point of lube oil is the lowest of the 5°F (or 3°C) values when the oil is cooled and checked in prescribed circumstances. oil is not flowing.. Lubricating oil may be cooled to low temperatures, undergoing several changes: (i) solidification; (ii) solidification with the creation of microcrystals swelling to give the remaining oil its crystalline structure [4,9]. Pour point depressants (PPDs) are polymers intended to monitor the production of wax crystal in lubricants which result in reduced pour point and improve the performance and quality at lower temperature.. The resulting surface layer of the pour point depressant prevents the growth and ability of wax crystals to absorb oil and gel. Oil can move freely through any solid wax particles present in the absence of large, interlocking crystals or floated particles [10-12].

In this work we have prepared several homopolymers to be used as lube oil additives based on acrylic acid esterification with dodecyl alcohol, tetradecyl alcohol, hexadecyl alcohol and octadecyl alcohol then polymerization by using benzoyl peroxide catalyst with different ratios (0.25 percent & 0.5 percent and 1 percent), then study prepared compounds performance for lube oil as viscosity index improvers and pour point depressants.

2. Experimental

2.1. Ester preparation

The esters were prepared through reacting to 1 mole acrylic acid with 1 mole of various alcohol types (l- dodecyl , tetradecyl, hexadecyl and octadecyl). The reactions were done in a resin kettle flask with 0.25wt % hydroquinone the inhibitors of acrylic acid polymerization and with 0.5wt % as a catalyst, add p-toluene sulfonic acid and xylene as a solvent as well. Under slow deoxygenated nitrogen stream the esterification reactions were done; the preparation reactions were exhausted in 500 rpm mechanic mixer. Mixed reactants with the same xylene weight then heated progressively from room temperature to 130°C ± 0.5°C using a well monitored thermostat. Monitoring of the amount of liberated water followed the extent of the reaction to give products dodecyl acrylate, tetradecyl acrylate, hexadecyl acrylate and octadecyl acrylate.

$CH_3(CH_2)_nOH + H_2C{=}CHCOOH \rightarrow CH_3(CH_2)_nOOCHC{=}CH_2 + H_2O$

where n= 11, 13 and 15.

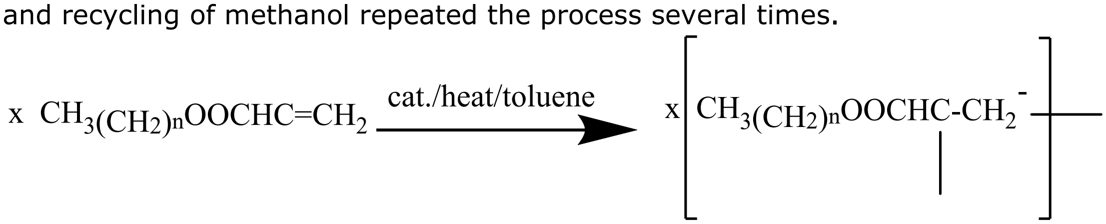
2.2.The IR analysis

IR spectra of the prepared esters have been established by utilizing FTIR spectrometer Model Type Mattson Infinity Series Top 961

2.3. Preparation of homopolymers

In three-neck flask nitrogen-controlled inlet valve, condenser and a temperature controller. The monomer dodecylacrylate was placed with different ratio of benzoyl peroxide (0.25%, 0.5 % and 1%) used as an initiator and toluene used as a solvent the reaction at 60°C -80°C was continued for 8h. Study the efficiency of each one as viscosity index improvers (VII) and pour point depressants (PPD), then repeat the reaction with different acrylate (tetradecyl acrylate, hexadecylacrylate and octadecylacrylate).

The purification process of the homopolymer is carried out in the following steps (1): Precipitation and then separation in an excess volume of methanol. (2) The process was repeated several times by dissolution in acetone and recycling with methanol, (3) Dissolution of acetone and recycling of methanol repeated the process several times.



2.4. Determination of the molecular weights

The molecular weights of preparation homopolymers were determined by using gel permeation chromatography (GPC), the Water 600E.

2.5. ¹HNMR Spectroscopic analysis

The 1HNMR spectra of prepared compounds were measured by Magnet: 400 Megahertz, console (Spectrometer): Varian model mercury plus, probe: Varian 5 millimeter.

2.6. Thermal analysis

The structural changes of the prepared thermal treatment samples were investigated by thermogravimetrical analysis (TGA). 10 mg sample was chalked up to 700◦C and the thermo balance instrument TA-USA (SDTQ-600) was heated at a heating rate of 10◦C in air or N_2 in flow rates of 100 mL/min^{-1}.

2.7. Study of rheological properties

The compounds prepared were examined by means of a modular type compact rheometer 502 for rheological properties (Anton Paar) [13].

2.8. Photo micrographic analysis

Photomicrographs declare the independent action for wax crystallization of the attended and unattended lube oil sample with the prepared additives at different ratios.

2.9. Evaluation of the prepared homopolymers as lube oil additives

A. As viscosity index improvers (VII)

The prepared homopolymers have, in accordance with ASTM D2270-87, been assessed as viscosity index improvers using base oil (SAE 30). The kinematic viscosity of the oil has been determined at 40°C and 100°C with the compound being tested. The effect of lube oil VI concentration was studied in a variety of concentrations between 0.25 wt % - 3.0 wt % [14].

B. As pour point depressants

Printed homopolymers have, through the point test ASTM-97-87, been assessed as point depressants using base oil (SAE 30). Cryostat apparatus for point measurement was the instrument used for measuring the pour point [15-16].

3. Results and discussions

Dodecyl, tetradecyl, hexadecyl and octdecyl alcohols were esterified by using acrylic acid and The completion of the esterification reactions was explained by IR spectroscopy, All esters have the same range of IR spectrum give in Fig. 1 which indicate the absence of strong absorption broad band at (3000 cm^{-1}- 3400 cm^{-1}) for OH group of the carboxylic acid which indicate that esterification reaction take place completely and presence of (C=O) ester group Table 1 .Preparation of different type of homopolymers, the percentage component of each homopolymer which are given in Table 2 and also all the prepared homopolymer are similar in ¹HNMR Spectrum Analysis for example Fig 2 which indicates to explained in Table 4. The homopolymer A, B and C group have the same dodecyl acrylate but different percentage of catalyst (1, 0.5 and 0.25%) that causes the Inverse relationship between the percentage of catalyst and the molecular weight which are given in Table 3, this result because of each molecule of the catalyst began the polymer chain so the less percentage of catalyst (0.25%) give increasing in the molecular weight.

Table 1. IR spectrum of dodecylacrylate

Compound	Peak position	Indication
A	absence of strong absorption broad band at (3000-3400cm^{-1})	Aliphatic (v OH) group of the characteristic absorption bands of the carboxylic acids.
	2840cm^{-1} & 29508cm^{-1}	(v C–H) aliphatic
	1465cm^{-1}	(v CH=CH) for methylene
	1720cm^{-1}	(v C=O) for ester
	1250cm^{-1}	(v C-O-C) for ester

Table 2. The percentage component of each homopolymer

Designed polymer	Monomer	% of used catalyst
A	Dodecyl acrylate	1%
B	Dodecyl acrylate	0.5%
C	Dodecyl acrylate	0.25%
D	Tetradecylacrylate	0.25%
E	Hexadecyl acrylate	0.25%
F	Octadecyl acrylate	0.25%

Table 3. The mean molecular weight of designed homopolymers

Designed polymer	Mean molecular weight	Designed polymer	Mean molecular weight
A	10 928	D	15 745
B	12 330	E	16 985
C	14 571	F	17 189

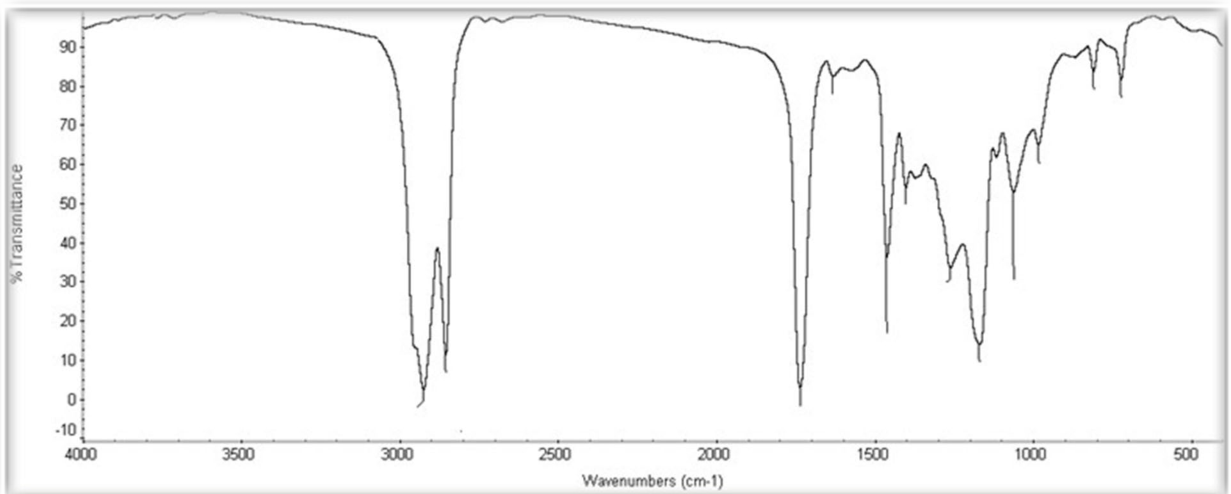


Fig. 1. IR spectrum of dodecylacrylate

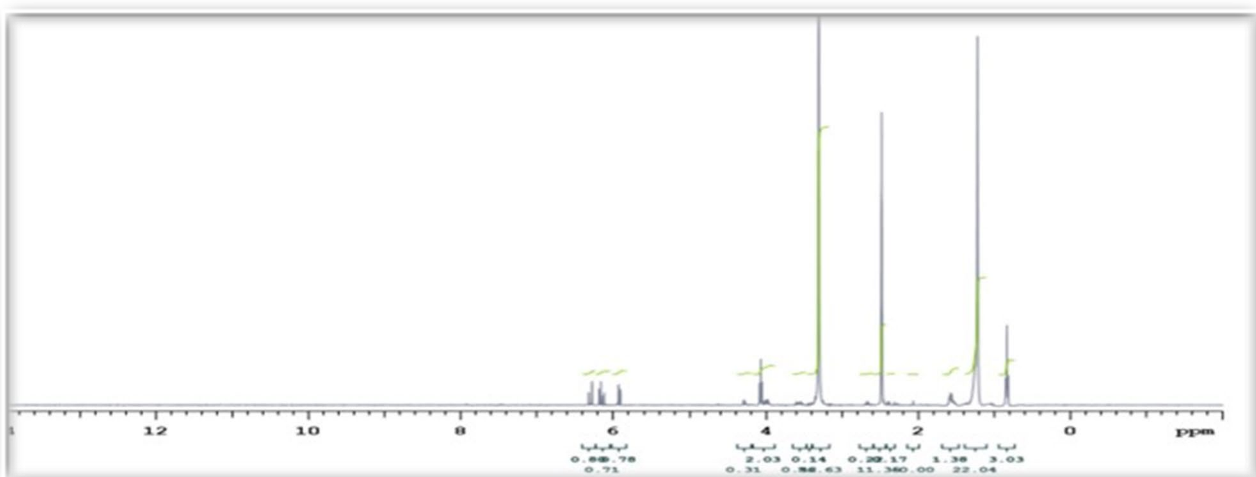


Fig. 2. [1]HNMR spectrum of prepared compound (A)

3.1. Effect of catalyst ratio on viscosity index

By homopolymerization of dodecyl acrylate with different catalyst ratio from 1% to 0.25% (A, B, and C) it was found that the viscosity index of homopolymer C give best result as given in Table 5. This may be due to increase in the molecular weight of polymer by decreasing the ratio of catalyst.

Table 4. ^{1}HNMR spectrum of the prepared compound (A)

Compound	δ Value	Splitting	Indication
	δ 0.88	triplet	Terminal CH_3
	δ 1.26	multiplet	Alkyl H
A	δ 1.43	pentiplet	CH_2 at β- to ester
	δ 4.3- δ 3.8	triplet	CH_2 at α- to ester
	δ 5.83-6.12	triplet	ethylene H

Table 5. Concentration effect on the viscosity index

Conc. x10^{-3} ppm	A	B	C	D	E	F
30.00	110	112	116	120	124	126
20.00	100	102	106	110	114	116
10.00	98	98	99	102	105	106
5.00	96	97	98	98	99	102
2.50	94	96	97	98	98	100
0.00	90	90	90	90	90	90

The homopolymer D, E and F group have the same percentage of catalyst 0.25% but different in alkyl chain length that causes the positive relationship between alkyl chain length and the molecular weight Table 2) the alkyl chain length increase cause increasing in the molecular weight and give best efficiency as viscosity index improvers.

The structural changes in the prepared samples were studied using thermal treatment with a thermogravimetric analysis (TGA). It was found that the samples have very high thermal stability so it is suitable to use as lube oil additives which is shown in Fig 3.

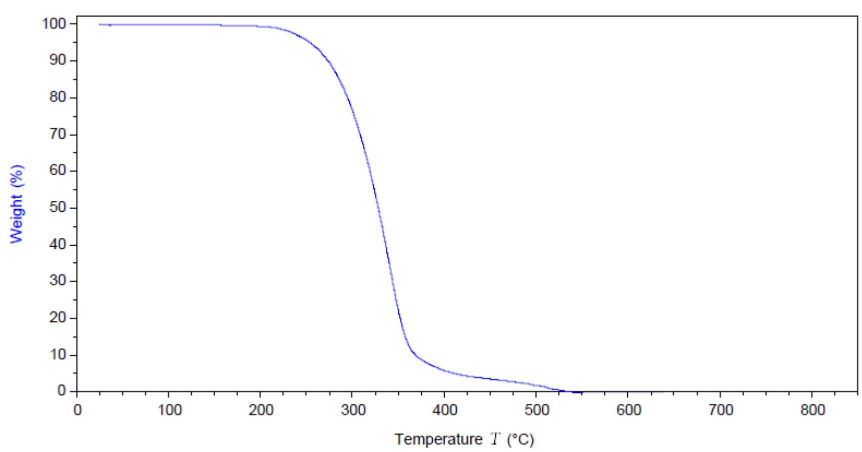


Fig. 3. TGA analysis of the prepared compound (C)

3.2. Effect of catalyst ratio on pour point

It was found that the pour point efficiency increase by decreasing the catalyst ratio as given in Table 6 as polymer (C) given the highest efficiency as pour point depressant for lube oil and by homopolymerization of tetradecyl (D), hexadecyl (E) and octadecyl acrylate (F) it was found that the pour point efficiency decrease . and by study the Photomicrographs analysis it was found that lube oil untreated photo has many accumulation of wax in cold flow condition but the other one which is lube oil +300ppm (C) the prepared homopolymer additives absorbed on the wax crystal and inhibition the wax crystal accumulation so the photo is clear which is shown in Fig 4.

Table 6. Effect of concentration on the pour point

Conc. $x10^{-3}$ ppm	A	B	C	D	E	F
30.00	-12	-15	-18	-12	-12	-9
20.00	-12	-15	-15	-12	-12	-9
10.00	-12	-12	-15	-12	-9	-6
5.00	-12	-12	-12	-9	-6	-6
2.50	-9	-9	-12	-9	-6	-3
0.00	-3	-3	-3	-3	-3	-3

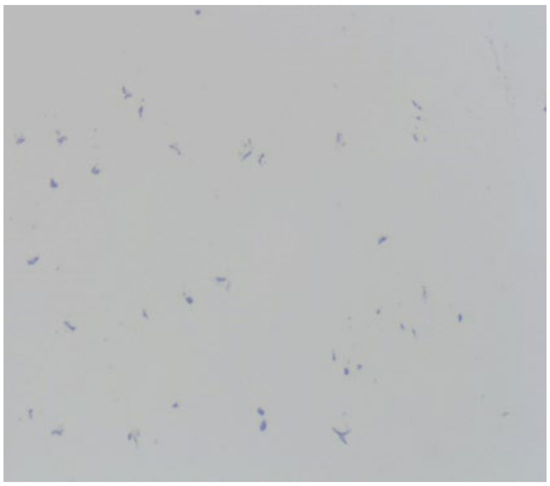


Fig. 5a. Photomicrographs of untreated lube oil

Fig. 5a. Photomicrographs of lube oil+300ppm (C)

Study lube oil (SAE-30) rheological behavior with and without prepared additives, and it was found that they behave as non Newtonian fluid which shown in Fig. 5, that’s mean Their viscosity depends on the rate of shear (shear thinning). Fluids are shear thinning because of the Inverse relationship between the viscosity and the shear rate. Shear thinning fluids also known as pseudo-plastics [17].

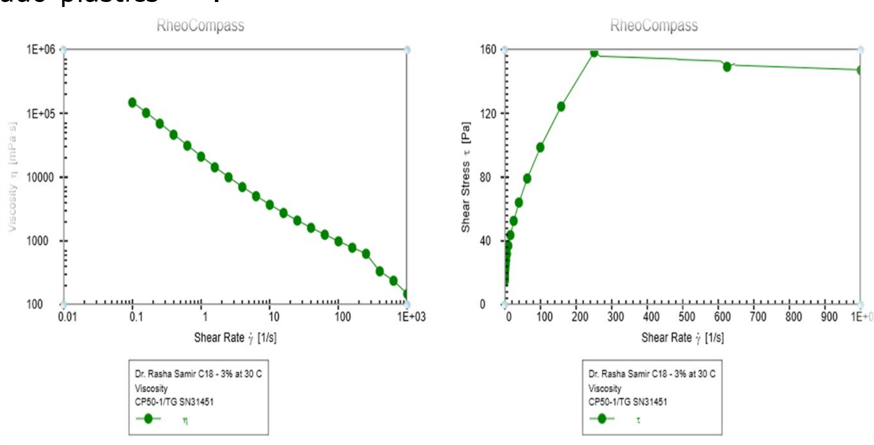


Fig. 5. The rheological behavior of homopolymer additives (C)

A number of factors, all related to the structural reorganization of fluid molecules as a result of flow, may contribute to non-Newton's behavior. The alignment of highly anisotropic chains in polymer melting and solutions leads to a reduced viscosity. So the best viscosity index is 126 at octadecyl acrylate homopolymer [18].

4. Conclusion

The preparation of all homopolymers are influential as improving viscosity index and depressing pour point. The efficiency of the prepared homopolymer as viscosity index and pour point increases by decreasing the concentration of catalyst used.

The efficiency of the prepared homopolymers as viscosity index and pour point increase by increasing the additive concentration. The best result for viscosity index of the prepared homopolymer is when the percentage of the catalyst is 0.25% in case of using octadecyl acrylate homopolymer.

The best result of the pour point for the prepared homopolymer is when the percentage of catalyst is 0.25% in case of using dodecyl acrylate homopolymer. All the prepared homopolymer have thermal stability and they are Non Newtonian fluid behavior.

References

[1] Maione R, D'Elia L. Lubrication and lubricants. Encyclopaedia of Hydrocarbons, New Developments: Energy, Transport, Sustainability 2007; III: 751-772.

[2] Hori Y. Hydrodynamic lubrication. Yokendo Ltd., 2006: 2-22.

[3] Kamal RS, Ahmed NS, and Nasser AM. Study the efficiency of some compounds as lubricating oil additives. Journal of Applied Petrochemical Research,(2013; 3: 1-8.

[4] A-AA Abdel Azim, AM Nassar, Ahmed NS, El Kafrawy AF, Kamal RS. Multifunctional Additives Viscosity Index Improvers Pour Point Depressants and Dispersants for Lube Oil. Petroleum Science and Technology, 2009; 27(1): 20–32.

[5] Kamal RS, Nassar AM, Ahmed NSAbdel Azim., A-AA. Preparation and Evaluation of Acrylate Polymers as Viscosity Index Improvers for Lube Oil. Petroleum Science and Technology, 2005; 23(5): 537 – 546.

[6] Hus SM. Molecular basis of lubrication. Tribology International, 2004; 37: 553.

[7] Rundnick LR. Lubricant Additives: Chemistry and Applications. Marcel Dekker, New York, 2003: 1-293.

[8] Pirro DM, Wessol AA. Lubrication fundamentals. Marcel Dekker, Inc., New York and Basel 2001; 3: 37.

[9] A-AA Abdel-Azim, AM Nassar, NS Ahmed, RS. Kamal Preparation and Evaluation of Acrylate Polymers as Pour Point Depressants for Lube Oil. Petroleum Science and Technology, 2006; 24(8): 887 – 894.

[10] Zhang J, Wu C, Li W, Wang Y and Cao H. DFT and MM calculation: The performance mechanism of pour point depressants, Fuel, 2004); 83: 315.

[11] Zhang J, Wu C, Li W, Wang Y, and Han Z. Study on performance mechanism of pour point depressants with differential scanning calorimeter and X-ray diffraction method. Fuel, 2003; 82: 1419

[12] Nasser AM, Ahmed NS, and Kamal RS. Preparation and Evaluation of Some Terpolymers as Lube Oil Additives. Journal of Dispersion Science and Technology, 2011; 32: 616 – 621.

[13] Simpson MM, and Janna WS. Newtonian and Non-Newtonian Fluids: Velocity Profiles, Viscosity Data and Laminar Flow Friction Factor Equations for Flow in A Circular Duct. Conference: ASME 2008 International Mechanical Engineering Congress and Exposition, (2008).

[14] Nassar AM. Synthesis and Evaluation of Viscosity Index Improvers and Pour Point Depressant for Lube Oil", Petroleum Science and Technology, 2008; 26(5): 523-531.

[15] Al-Sabagh AM, Sabaa MW, Saad GR, Khidr TT, Khalil TM. Synthesis of polymeric additives based on itaconic acid and their evaluation as pour point depressants for lube oil in relation to rheological flow properties. Egyptian Journal of Petroleum, 2012; 21(1): 19-30.

[16] El-shazly RI, Kamal RS, Nassar AM, Ahmed NS, and Sayed GH. The behavior of some terpolymers as lubricating oil additives. Applied Petrochemical Research, 2020; 10: 115-123.

[17] Joseph DD. Steep wave fronts on extrudates of polymer melts and solutions: lubrication layers and boundary lubrication. Journal of Non-Newtonian Fluid Mechanics, 1997; 70(3): 187-203.

[18] Sarlak A, Ahmadpour A, and Hajmohammadi MR. Thermal design improvement of a double-layered microchannel heat sink by using multi-walled carbon nanotube (MWCNT) nanofluids with non-Newtonian viscosity. Applied Thermal Engineering, 2019; 147: 205-215.

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