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Synthesis And Characterization Of Copolymers As Pour Point Depressants And Viscosity Index Improvers For Lubricating Oil

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الخلاصة

تم تحضير poly(1-hexene-co-maleic anhydride) عن طريق بلمرة الجذور الحرة من تفاعل انهيدريد الماليك مع 1-هكسين ، ثم تفاعل البوليمر الناتج مع (1-tetradecanol و 1-hexadecanol) لإنتاج poly(1-hexene-co-ditetradecyl maleate) و poly(1-hexene-co-dihexadecyl maleate) على التوالي ، وكذلك تحضير poly(methyl methacrylate-co-maleic anhydride) من تفاعل انهيدريد الماليك مع ميثيل ميثا اكريلات بواسطة بلمرة الجذور الحرة ثم تفاعل البوليمر الناتج مع (1-tetradecanol) لتكوين بوليمر poly(methyl methacrylate-co-di tetradecyl maleate) وشخصت البوليمرات الثلاثة المحضرة بأستخدام التحليل الطيفي FTIR و HNMR بينما تم قياس الثبات الحراري والوزن الجزيئي بواسطة TGA و GPC . واستخدمت البوليمرات المحضرة لتحسين معامل اللزوجة ومثبطات لدرجة الانسكاب لثلاث أنواع من الزيوت الاساسية من مصفاة الدورة ، حيث اظهرت النتائج فعالية البوليمرات المحضرة ، اما البوليمر poly(1-hexene-co-ditetradecyl maleate) أعطى أفضل نتيجة لتحسين معامل اللزوجة ودرجة الانسكاب للزيوت الاساس المستخدمة.

Abstract

poly (1-hexene-co-maleic anhydride) was prepared by free radical polymerization of maleic anhydride with 1-hexene. 1- tetradecanol and 1-hexadecanol were reacted with the poly(l-hexene-co-maleic anhydride)to produce poly (1-hexene-co-ditetraclecyl maleate) and poly (1-hexene-co-dihexadecyl maleate) respectively . Poly (methyl methacrylate-co-maleic anhydride) was prepared from the reaction maleic anhydride with methyl methacrylate by free radical polymerization, then the resulting polymer was reacted with 1-tetradecanol to give poly(methyl methacrylate-co-maleic anhydride). the three prepared polymers was characterized by FTIR and HNMR spectroscopy, while the thermal stability and molecular weight measured by Thermogravimetric analysis TGA and Gel permeation chromatography GPC. the prepared polymers was used to improves the pour point depressant and viscosity index for three base oils from Dura Refinery. the results show the efficiency of the three polymers to improve the pour point and Viscosity index of the base oil.

Keywords: lubricating oils, viscosity index, Pour Point depressants, TGA and GPC.

Introduction

Lubrication oil was used to reduce friction resulting from the movement of one surface over another, or from the surfaces of overlapping moving parts, which reduces energy loss due to friction. It also reduces the wear of moving parts, and reduces the heat generated during operation. The materials used for this purpose are called lubricating oils. Lubricants are usually gases, liquids, Semi-liquids, solids, or a mixture of liquid, solid and gases. Lubricants contain at least one additive, and sometimes oils contain several different additives to lubricating oils varies, often up to 30% or more [1].Oils often consist of linear or branched alkanes or isoparaffins, cycloparaffins, aromatic rings, and very small amounts of heterocyclic Compounds[2]. Mineral oils have a major problem during low temperatures due to the presence of waxy hydrocarbons whose solubility decreases with decreasing temperature. It crystallizes and separates from the oil, forming a solid three-dimensional crystal network that traps the oil inside and prevents it from flowing or spillings, it expressed as the pour point (PP), which is the lowest temperature at which the oil spills [3]. Viscosity is one of the important Factors that must be taken into account when choosing lubricating oils. When the Viscosity of the oil is very low at the operating temperature, the oil film is not sufficient and therefore corrosion or burning Occurs. If the viscosity is too high, the resistance becomes large loss in Energy and temperature rise between movingparts[4]. Various types of additives are used to lubricating oils to improve some of the existing properties or add new properties to the oil. These additives include corrosion inhibitors, anti-wear, anti-oxidants , anti-friction, pour point depressants (PPP), and viscosity index improver (VI) [5].Pour point depressants (PPD_S) and viscosity index improvers (VIs), sometimes called viscosity modifiers, are among the most important additives to add to lubricants. When the Temperature drops, the polymeric chains shrink and do not affect the viscosity of the oil, while at high temperatures the Polymeric chains relax and expand in the oil, so an increase in viscosity occurs[6]. pour point depressants (PPDs), they are substances added to lubricating oils whose purpose is to effectively improve the fluidity of the oil at low temperatures because the hydrocarbon compounds in the oil crystallize and separate as a result of their low solubility at low temperatures[7].

Experimental

Materials

Maleic anhydride was recrystallized of from chloroform , 1-hexadecanol, 1-tetradecanol , p-Toluenesulfonic acid (P-TSA) ,Benzoyl Peroxide , was purchased from sigma Aldrich company . 1-hexene and methyl methacrylate from Fluke company. three Base oil was supplied from Al-Dora Refinery, (table 1) show It specifications.

Table (1) physical properties of Base oils used

Properties	Base oil 40	Base oil 60	Base oil 150
Viscosity at 40C^0 in cst	14.26	61.74	396.99
Viscosity at 100C^0 in cst	3.35	8.30	29.20
Viscosity index (VI)	105.848	103.232	101.991
Specific gravity at 15.6C^0	0.851	0.832	0.899
Pour point C^0	- 8	-5	0

Instruments

Infrared spectra of as prepared copolymers were recorded using KBr and SHIMADZU FTIR 8400 spectrometer. the structures of the prepared copolymers were also monitored by ^{1}HNMR spectra using Bruker Avance 500 MHZ spectrometer, a solvent (DM SO-d_6) and a reference Material (TMS). molecular weights of the prepared polymers are determined by Gel permeation Chromatography (GPC), by use of tetrahydrofuran as a solvent. thermal analysis were recorded using a TGA Q500 V6.7 device in the presence of argon, with a flow rate of 50 ml/min , heating rate of 10/ min C^0 , and a temperature of (20-900)C^0 .

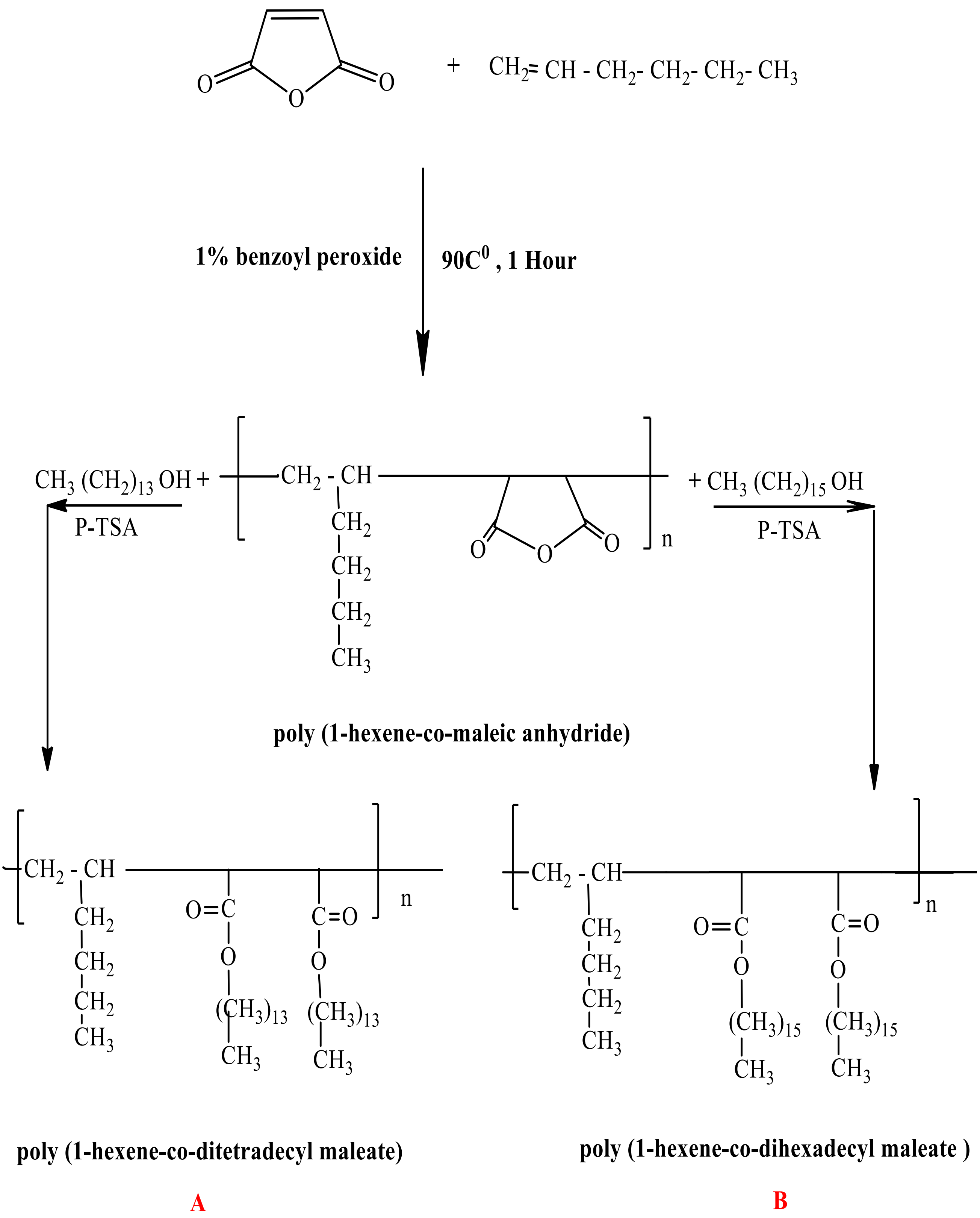
Polymerization and esterification reactions

(1-hexen-co-maleic anhydride) and (methyl methacrylate-co- maleic anhydride) copolymers were prepared by free radical polymerization according to table (2) under argon atmosphere.

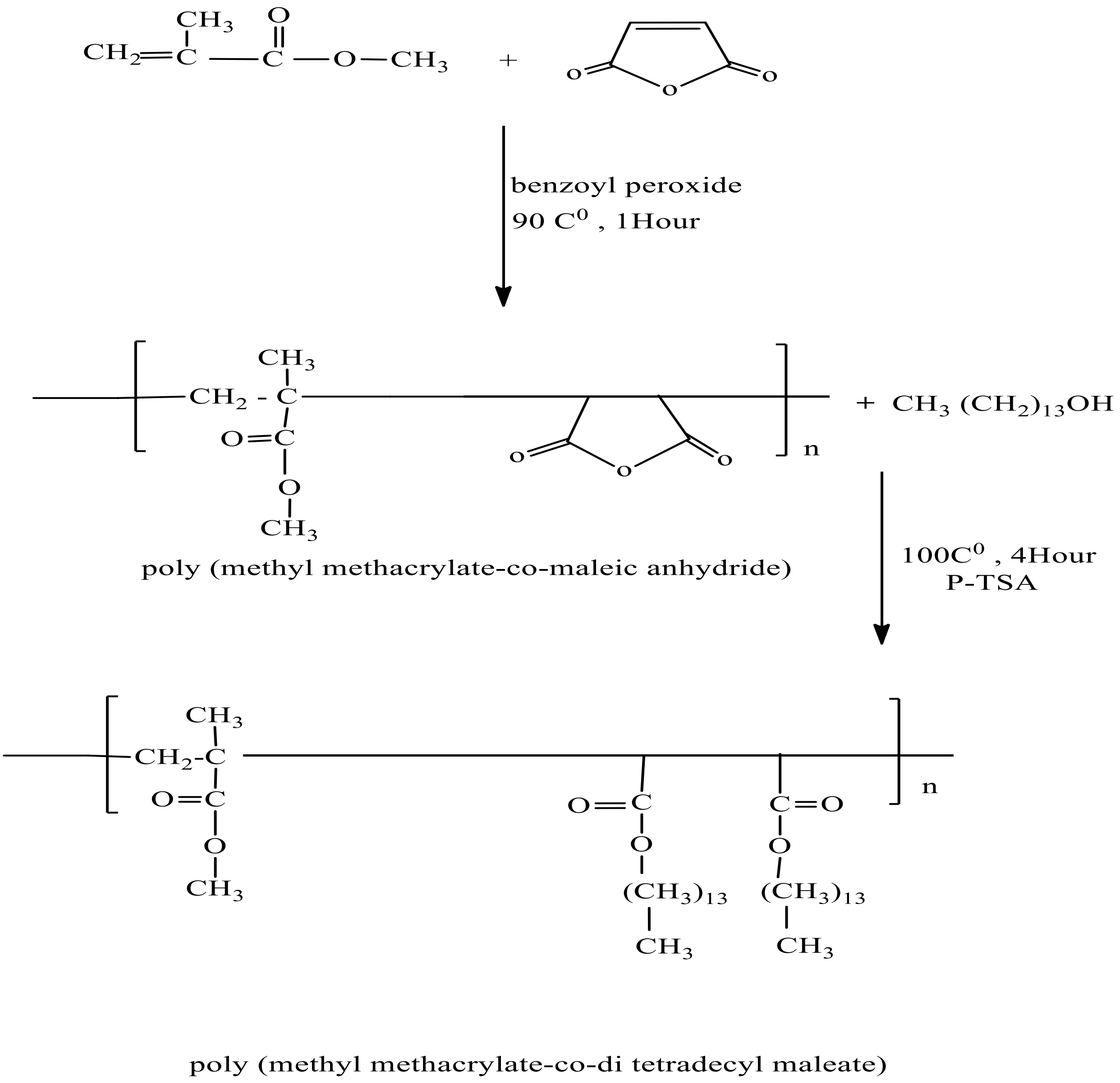
maleic anhydride (mol)	1-hexene (mol)	methyl methacrylate (mol)	Benzoyl Peroxide (w/w)	Temp.(C^0)	Reaction time (h)
0.02	0.06	-	1%	90	1
0.02	-	0.04	1%	90	1

table (2) Basic information on the preparation of maleic anhydride polymers.

The prepared copolymers was isolated from the reaction mixture by precipitation with diethyl ether, washed with benzene and dried at 50C^0. the prepared Poly (1-hexene -co-maleic anhydride) was esterified with two type of alcohol (1-tetradecand) and (1-hexadecanol) with ratio of 1:1 and P-TSA 1% (w/w) as initiator at 100C^0, for three hours, while the poly(methyl methacrylate-co-maleic anhydride) was reacted with (1-tetrade canol) in the same condition the reaction was contained until the theoretical amount of water was collected. Scheme1 Show the reaction mechanism to prepared the Copolymers and it esterification.



Scheme No. (1) Preparation of polymer A [poly (1-hexene-co-ditetradecyl maleate)] and polymer B[poly(1-hexene-co-dihexadecyl maleate)]



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Scheme NO. (2) Preparation of poly (methyl methacrylate-co-di tetradecyl maleate)

Evaluation of prepared Polymers as pour point depressants (PPDs) and viscosity index improvers (VIls)

Copolymers were evaluated as viscosity index improvers in three types of base oils by determining the kinematic viscosity (KV) of oils containing Copolymers at $40C^0$ and $100\ C^0$, using different concentrations (1000-5000) ppm according to ASTM D 2270 method [8]. while for pour point depressants according to ASTM D 97 method[9].

Result and discussion

FTIR

Figure (1) show the FTIR spectra of the Poly(1-hexene -CO-maleic anhydride). from the figure, the two peaks at 1778 cm^{-1} and 1859 cm^{-1} correspond to the absorption of C=O bond of the maleic anhydride while the peak at 1064cm^{-1} assigned to the C-O bond in the maleic anhydride, two peaks appeared at 2935 cm^{-1} and 2870 cm^{-1} assigned for the methyl and methylene groups respectively. Figure (2) shows the esterification of maleic anhydride groups with 1- tetradecanol the peak at 1724 cm^{-1} representing the ester group, with the disappearance of the C=O peak which characterized for maleic anhydride. the appearance of ester peak at 1165 cm^{-1} . Figure (3) shows the FTIR spectra esterification of maleic anhydride with 1-hexadecanol, the Peak appearance 1728 cm^{-1} was attributed for the ester group and the peak at 1165 cm^{-1} for C-O ester bond with the disappearance of the C=O peak maleic anhydride. Figure (4) represent the FTIR spectra of poly(methyl methacrylate-CO-maleic anhydride) from the figure two peak appear at 1782 cm^{-1} and 1855 cm^{-1} for the C=O group of maleic anhydride, with peak at 1065 cm^{-1} representing the C-O bond. the two peaks at 1728cm^{-1} and 1149 cm^{-1} was attributed to the C=O and C-O of the acrylate, while the peak at 2955 cm^{-1} was asserted for the methyl group. the esterification of poly(methyl methacrylate -CO-maleic anhydride) by 1- tetradecanol was Shows. Figure (5) appears two peaks at 2924 cm^{-1} and 2854 cm^{-1} which assigned to the methyl and methylene groups respectively. also a peak at 1165 cm^{-1} assigned to C-O bond of the ester[10]. with the peaks disappearance of the maleic anhydride

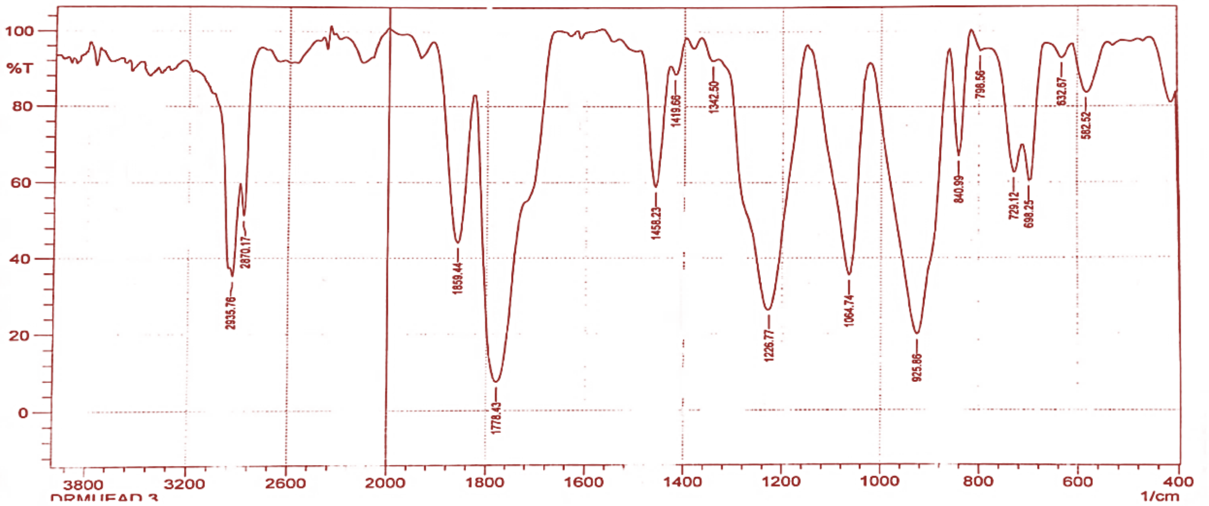

Figure (1) FTIR for poly (1-hexene-CO-maleic anhydride)

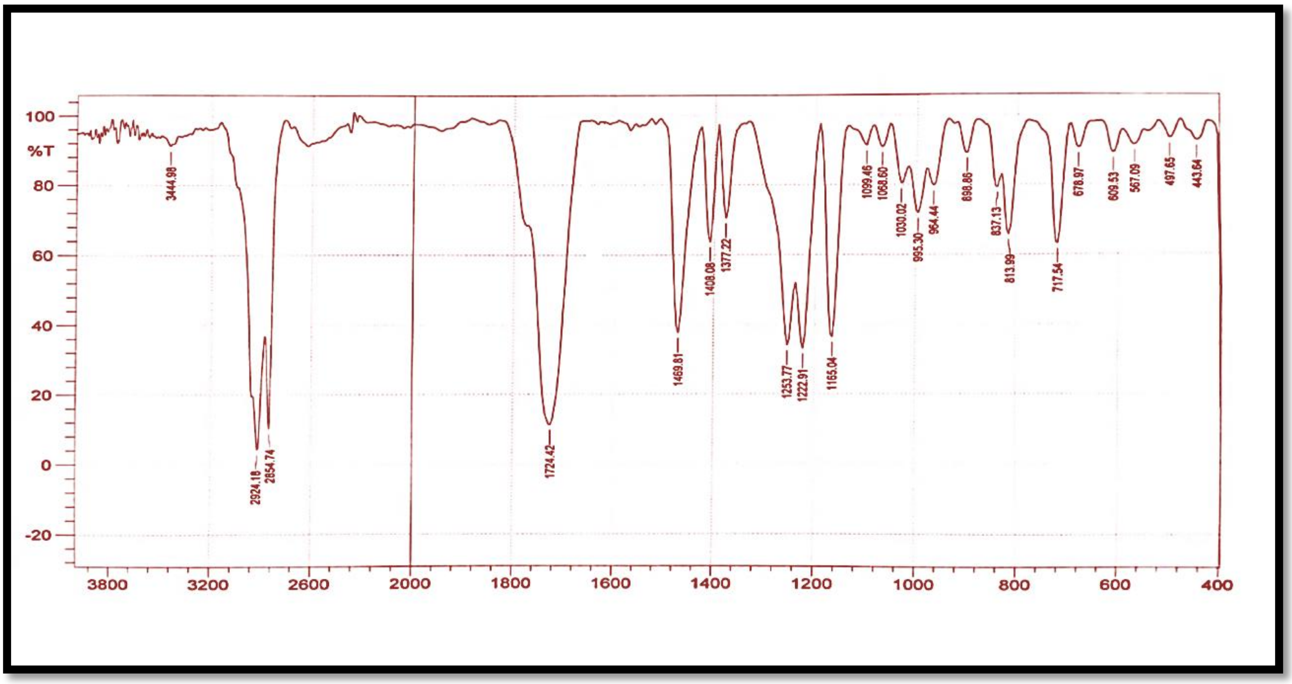

Figure (2) FTIR for poly (1-hexene-CO-ditetradecyl maleate)

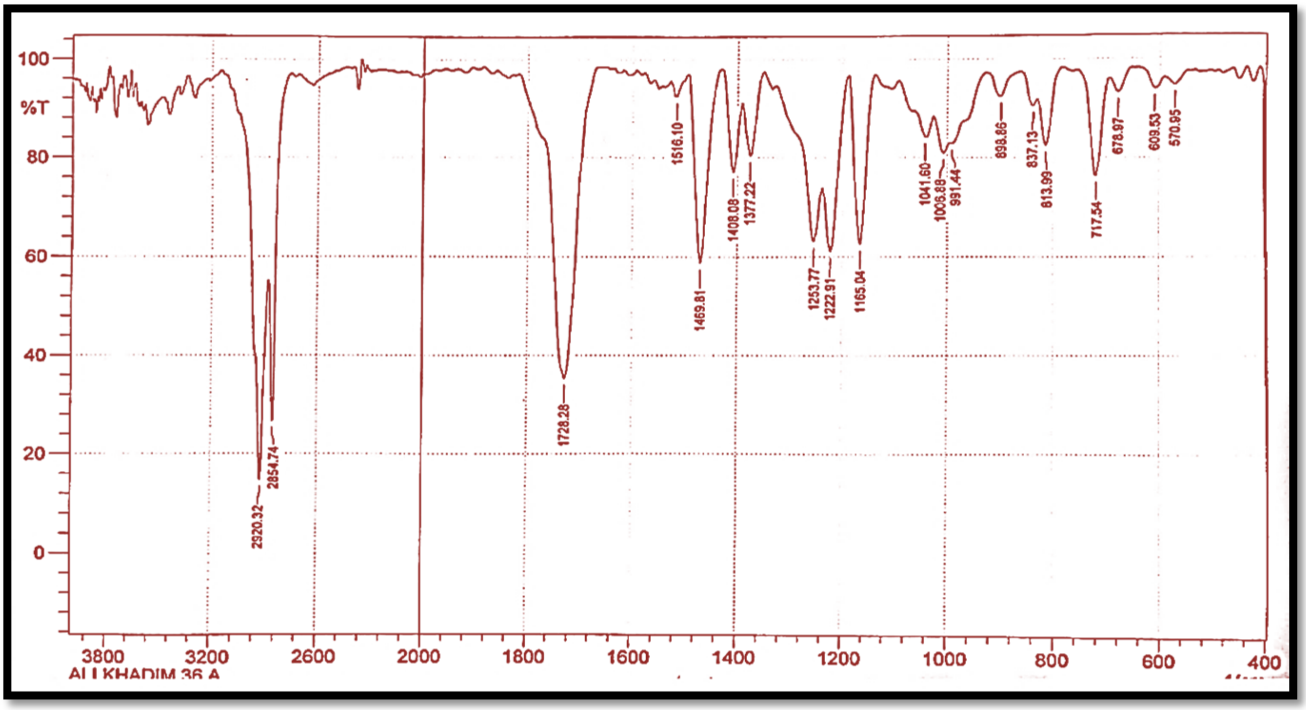

Figure (3) FTIR for poly (1-hexene-CO-dihexadecyl maleate)

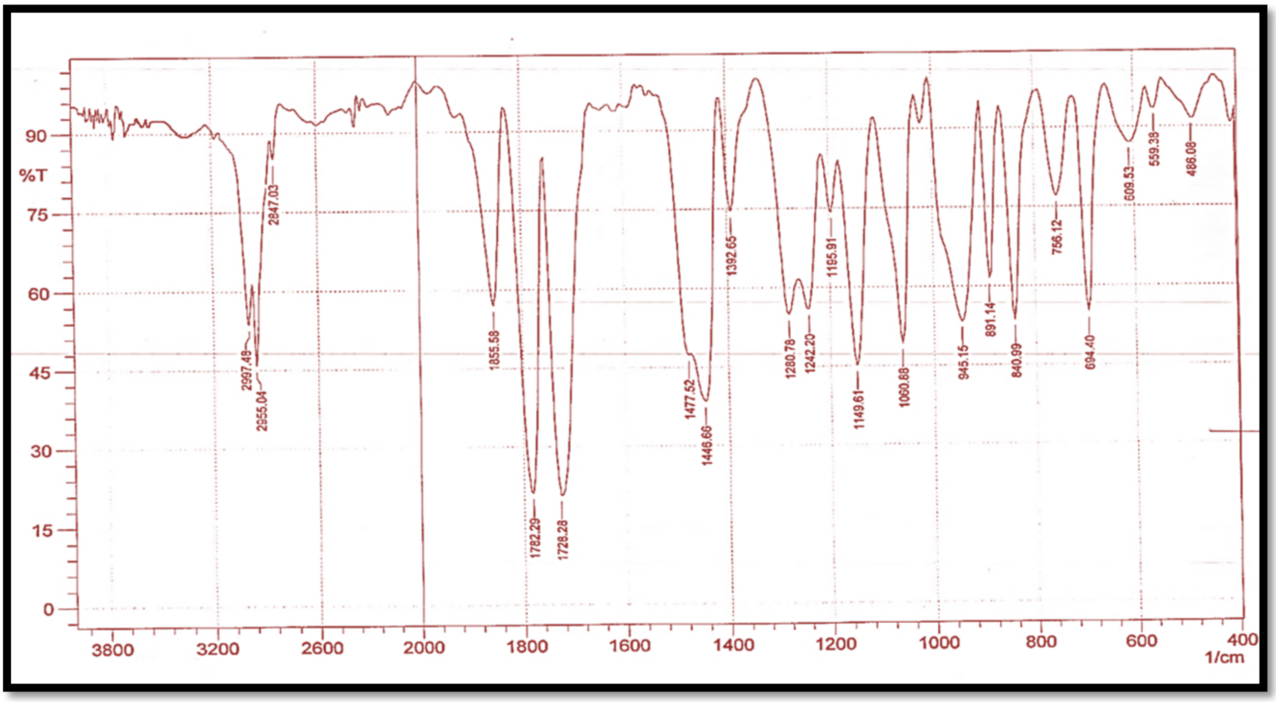

Figure (4) FTIR for poly (methyl methacrylate-CO-maleic anhydride)

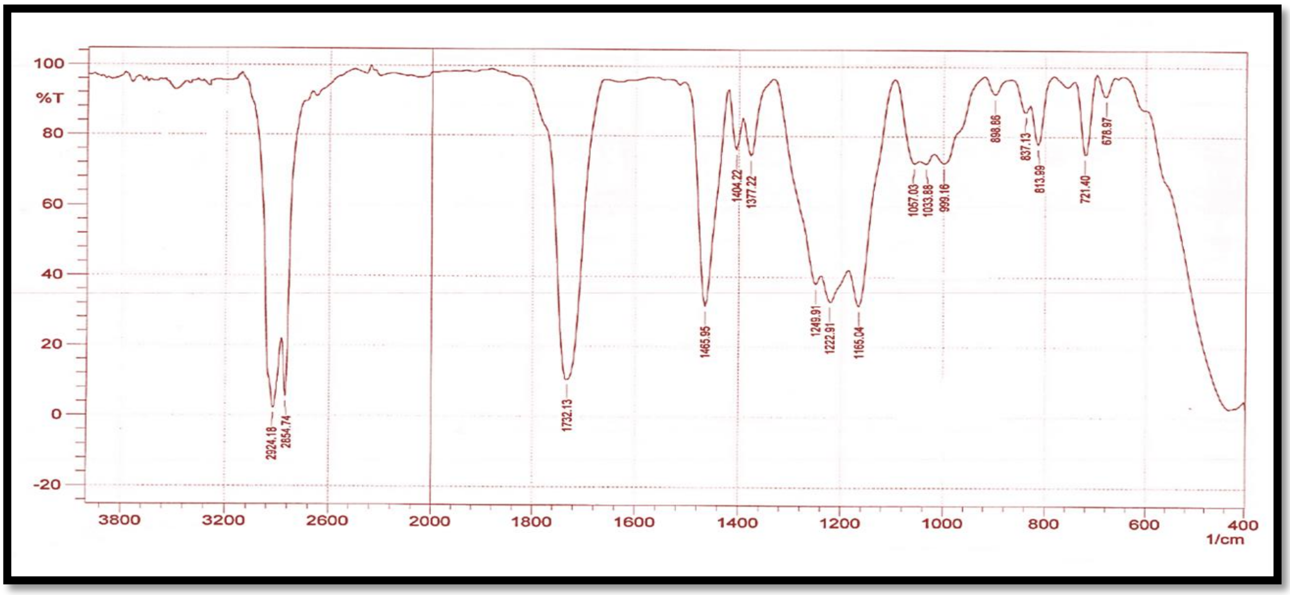

Figure (5) FTIR for poly (methyl methacrylate-CO-ditetradecyl maleate)

^{1}HNMR

The ^{1}HNMR spectra of Poly (1-hexene-CO-maleic anhydride) was shown in figure (6). from the figure a signal at 0.9 ppm was indicated to Protons (a) of methyl side group in the polymer and the Protons (b) signal appear of 1.4 ppm, which attributed to the protons of methylene side group. the signal at 1.8 ppm was assigned to the (c) Protons of the copolymer backbone, the (d) protons signal appear at 2.1 ppm while the (e) Protons of the methylene group directly attached to the carbonyl of the maleic anhydride appears at signal 3.2 ppm. Figures (7 and 8) shown the ^{1}HNMR spectra of the esterified copolymer (A and B), the ^{1}HNMR spectra of the esters have the same pattern and shown signal 0.8 ppm of Protons (a) represent to the methyl group. The protons (b) signal appear at 1.25 ppm, which resulting from ring opening during esterification reaction .the signal appears at 1.6 ppm for protons (c) of the methylene group and Proton (d) appear at 2 ppm. the (e) Proton near the carbonyl appears at signal 2.8 ppm, while the protons (g) and (f)appears at signal 3.7 ppm and 4.1 ppm respectively. Figure (9) shown the ^{1}HNMR spectra of the Poly(methyl methacrylate-co-maleic anhydride) from the figure signal appears 0.9 ppm represent Protons of the methyl group (a) and the signal appears at 1.5ppm represent protons of the methylene group (b). while the signal appears. at 2.9 ppm represent the Proton (c) near the carbonyl group . the signal appear at 3.6ppm was signed for the Protons of methyl group (d) [11]. Figure (10) shown the ^{1}HNMR spectra for the esterification of poly(methyl methacrylate-co-maleic anhydride). the same signals appears for the poly(methyl methacrylate-co-maleic anhydride), only two new signals appears at 3.8 ppm and 4.2 ppm for protons (g) and (f) respectively resulting from ring opening of the maleic anhydride. The appearance of weak signal in the region 7.3 ppm to 7.7 ppm represents the protons of the decomposition of the initiator (benzoyl peroxide)[12].

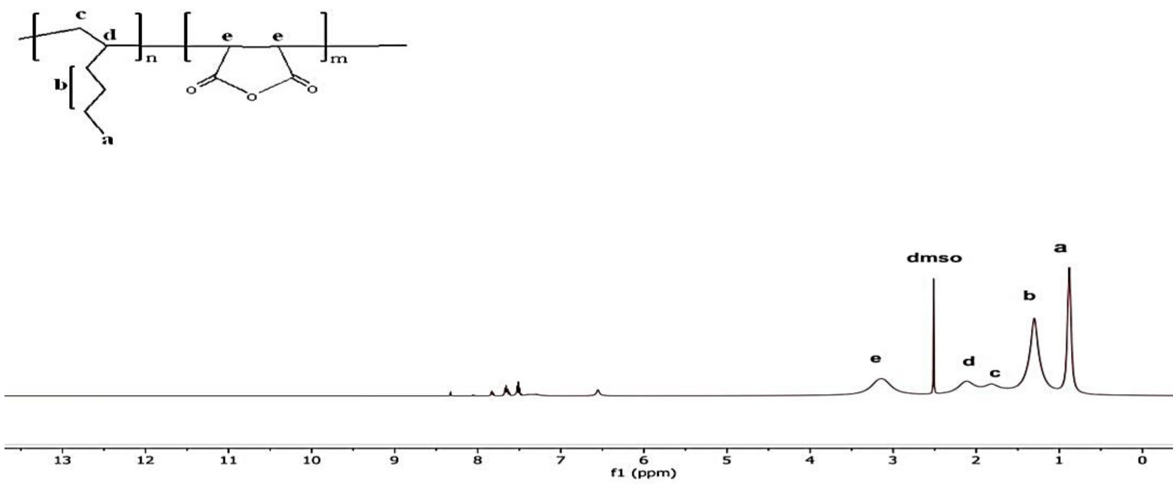

Figure (6) poly (1-hexene-co-maleic anhydride)

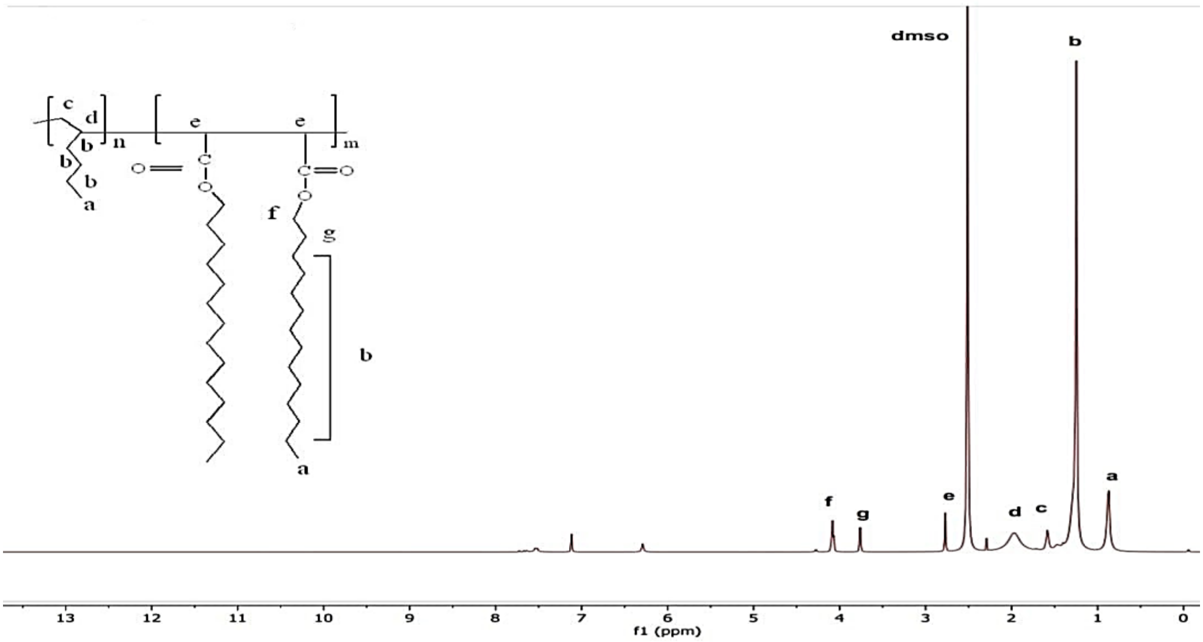

Figure (7) poly (1-hexene-co-ditetradecyl maleate)

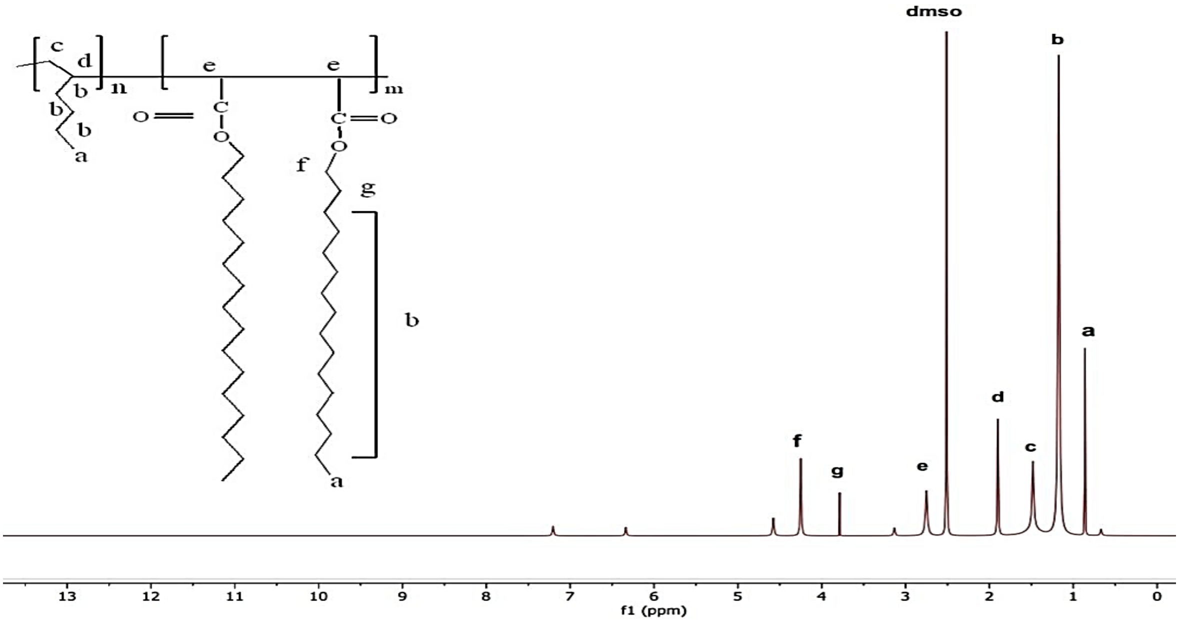

Figure (8) poly(1-hexene-co-dihexadecyl maleate)

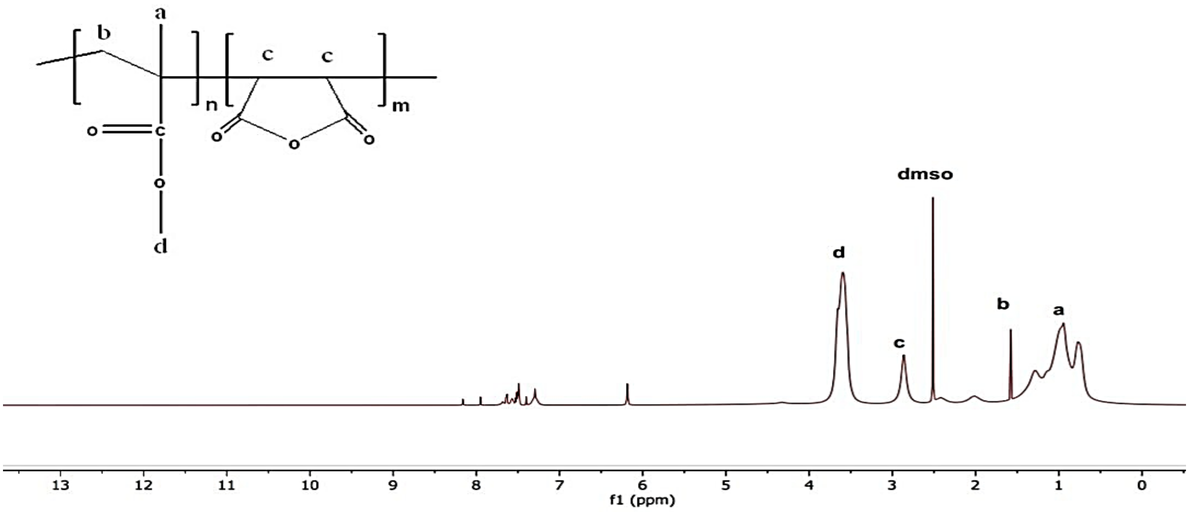

Figure (9) Poly (methyl methacrylate-co-maleic anhydride)

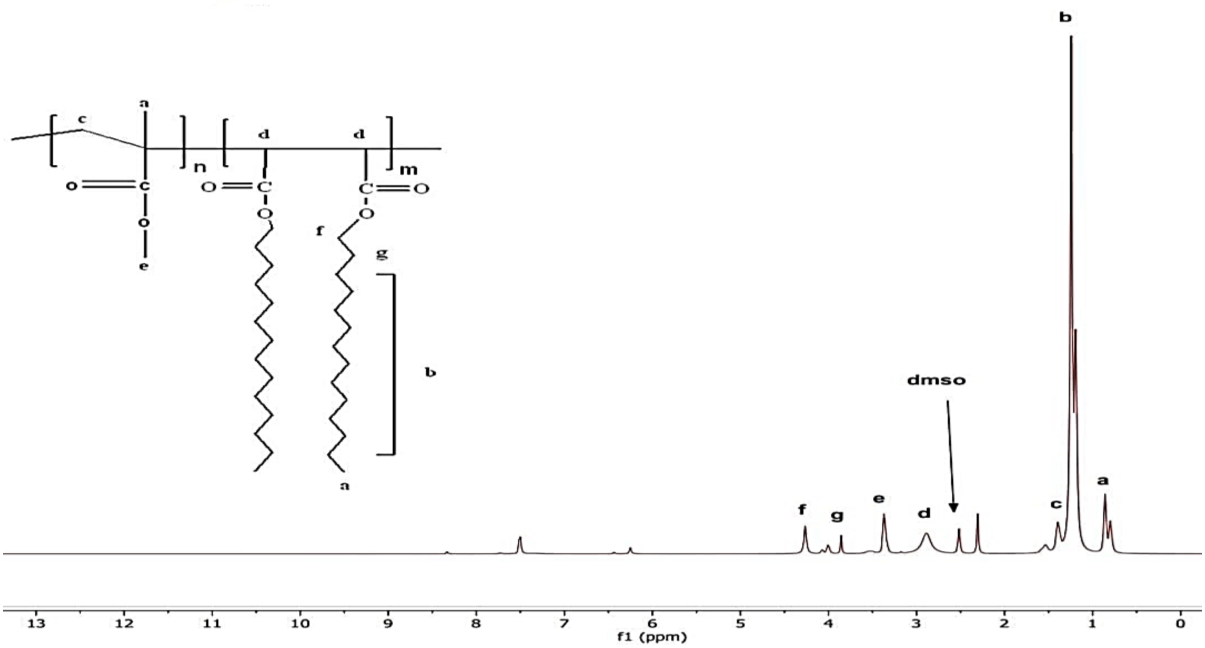

Figure (10) poly (methyl methacrylate-co-di tetradecyl maleate)

Thermo gravimetric analysis (TGA)

The figures (11-13) shows the thermo gravimetric of the three esterified Polymers. from the figures it show that the three polymers (A, B, and C) are thermally Stable and start decomposition at temperature near 200C^0. the 20% weight loss of the three Polymers (A, B,

C) was at (260, 280, and 300) C^0. respectively, which the three polymers are highly to the temperature of application.

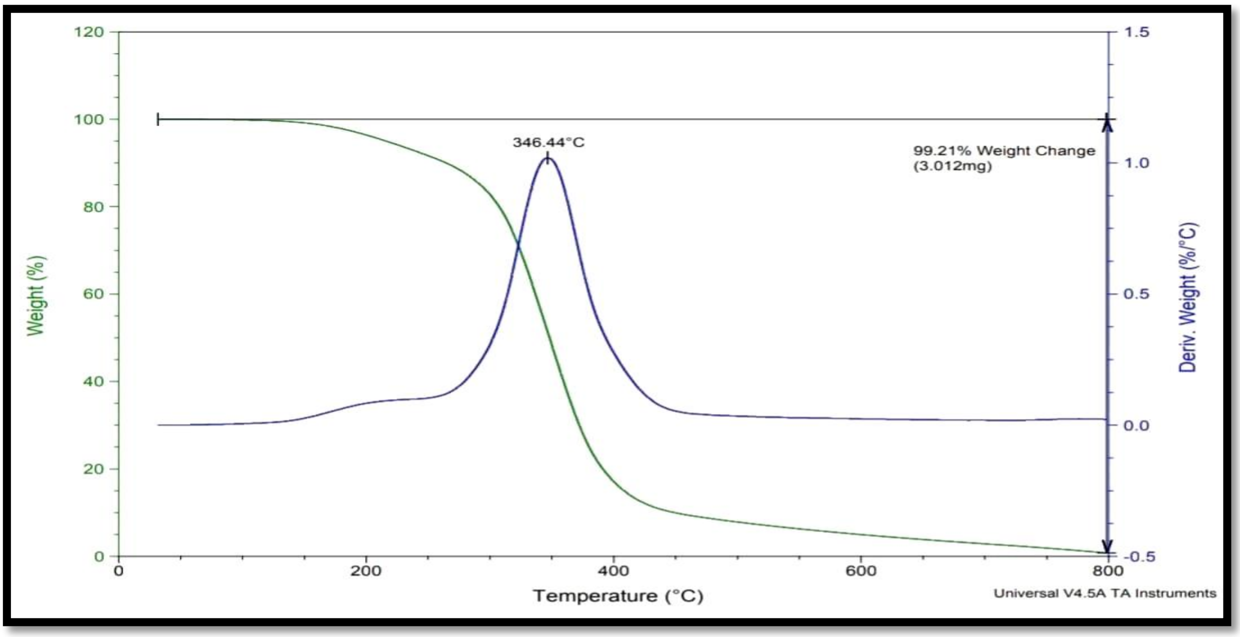

Figure (11) polymer (methyl methacrylate-co-di tetradecyl maleate)

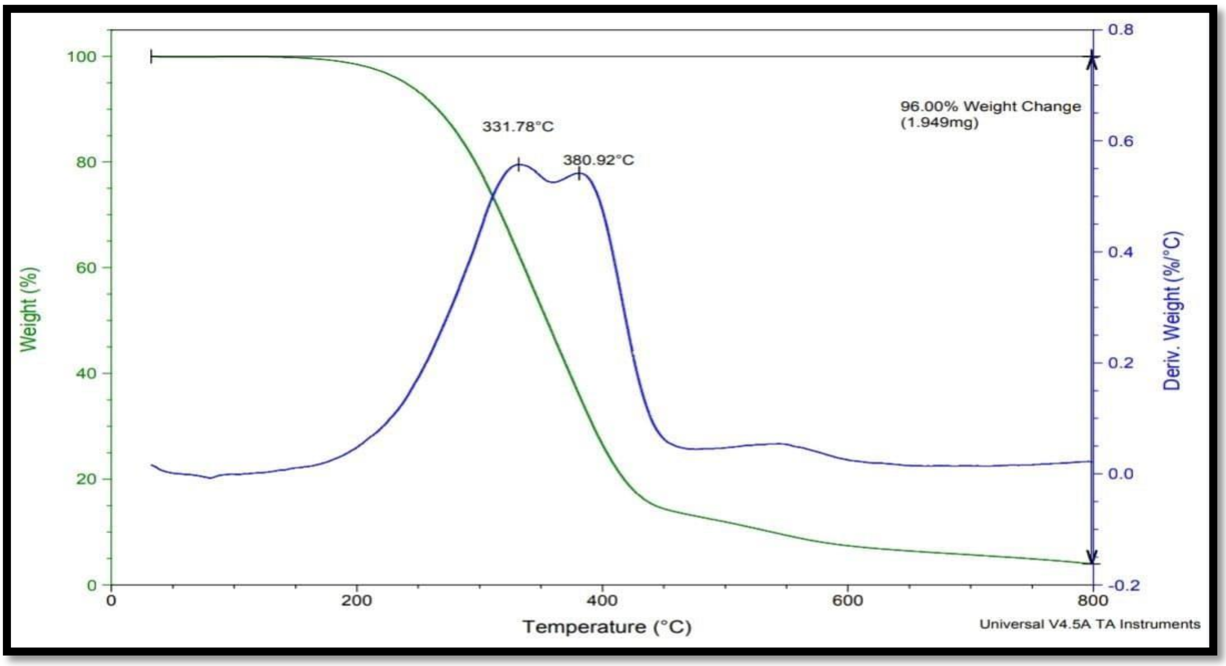

Figure (12) polymer poly(1-hexene-co-dihexadecyl maleate)

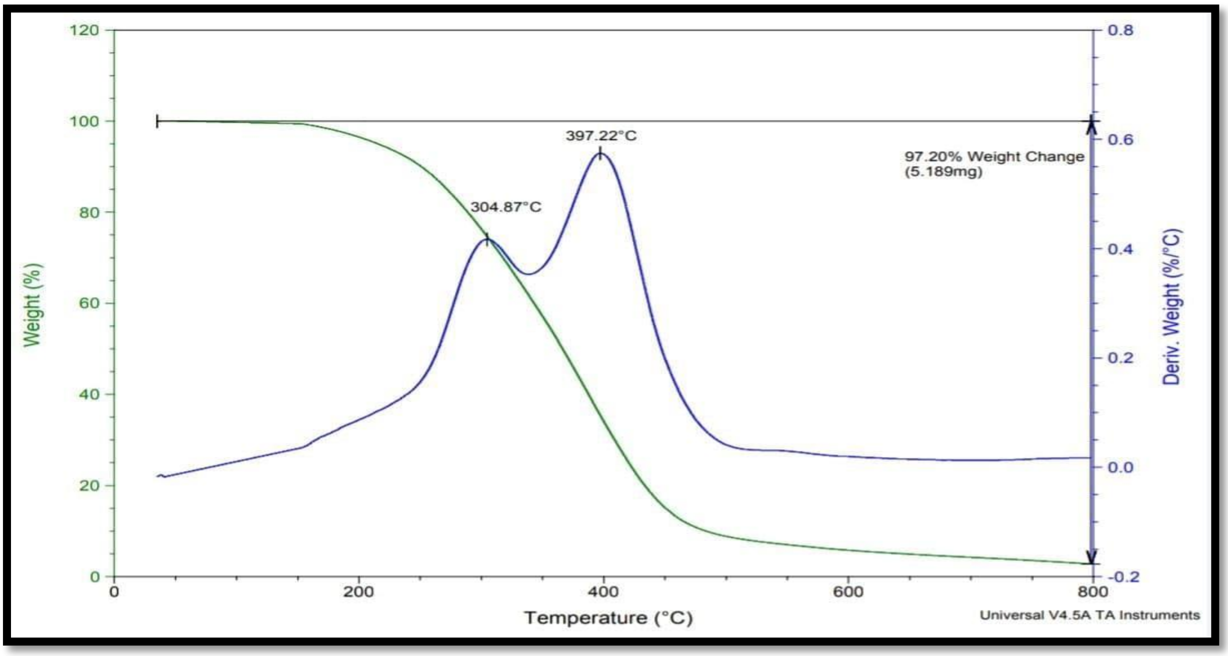

Figure (13) polymer poly (1-hexene-co-ditetradecyl maleate)

Molecular weight determination

Molecular weight is an important characteristic of the prepared Polymers to determine the efficiency in the field of their use as polymeric additives. Table(2)showing experimental Values of number average molecular mass (Mn) weight average molecular mass (Mw) and Polydispersity index date (PDI) of the prepared polymers (A,B,C), Using gel permeation chromatography (PGC) technology by dissolving additives in tetra hydro furan (THF) ..

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Polymer code	Mw	Mn	PDI
A	12030	5437	2.212729
B	44194	31409	1.407055
C	16068	7000	2.295301

Table (3) the mean molecular weight of prepared polymer

Performance of the prepared polymers as pour point

different concentrations (1000-5000) ppm of the prepared polymers were added to the three types of base oils. the experimental results was shown in table (3) that the pour point was decreased for all three types of base oil until the (5000) ppm of the concentration of the prepared copolymer and decreased with increasing the concentration of the polymer to 4000 ppm. this was attributed to the solubility of the base oil the prepared polymer because the solubility ability of the materials decreased with decreasing the temperature[13]. polymer (A) with molecular weight (12030 g /mol) was more effective than polymer (C) with molecular weight (16068 g/mol), and polymer (B) with molecular weight (44194 g/mol) was the less effective in decreasing the pour Point.

		Pour point C^0		
		Base oil 40	**Base oil 60**	**Base oil 150**
	Blank	-8	-5	0
	1000	-10	-8	-3
Polymer A	**2000**	-13	-11	-6
	3000	-17	-15	-10
	4000	-18	-15	-11
	5000	-17	-11	-10
	Blank	-8	-5	0
	1000	-10	-7	-3
Polymer B	**2000**	-13	-9	-5
	3000	-15	-12	-8
	4000	-15	-12	-9
	5000	-13	-11	-9
	Blank	-8	-5	0
	1000	-10	-7	-3
Polymer C	**2000**	-12	-10	-6
	3000	-14	-13	-8
	4000	-16	-14	-10
	5000	-14	-14	-10

Table 4 Pour Point for base oil after adding different concentrations of polymers

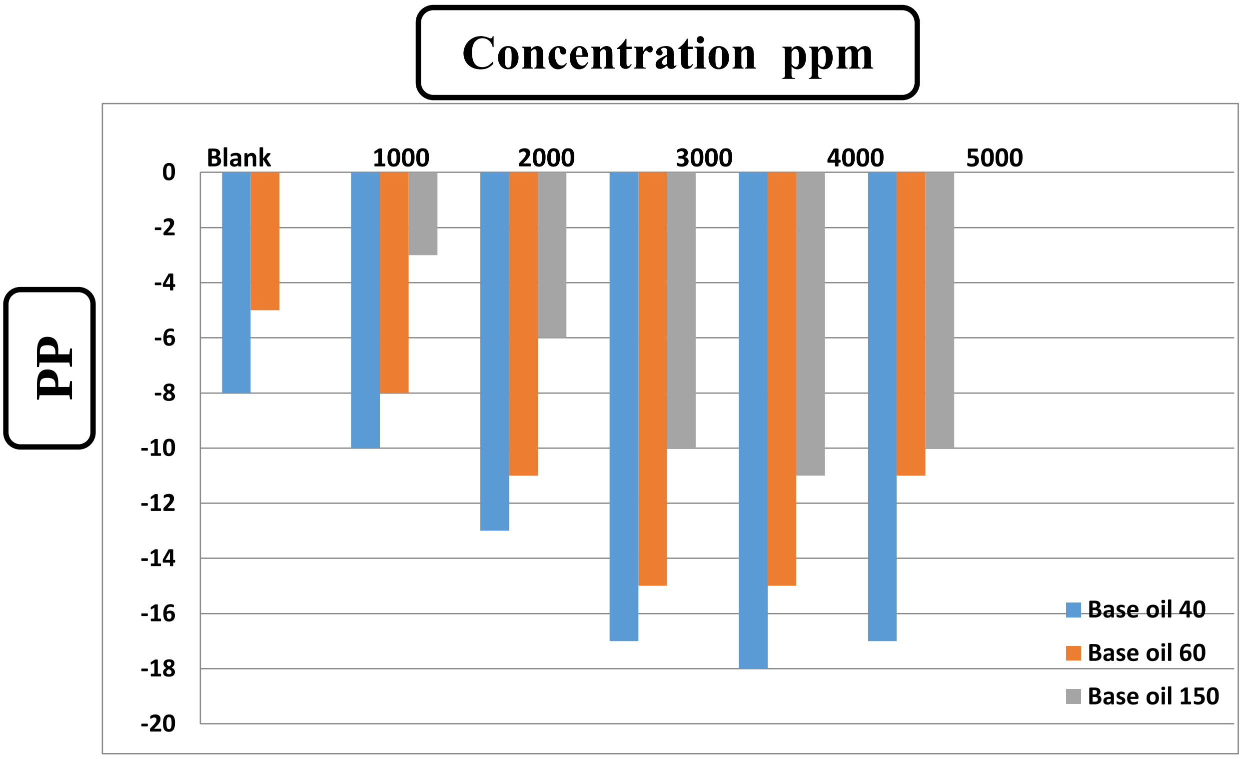

Fig.14 Variation of pour point of the three base oils where adding different Concentrations of polymer A

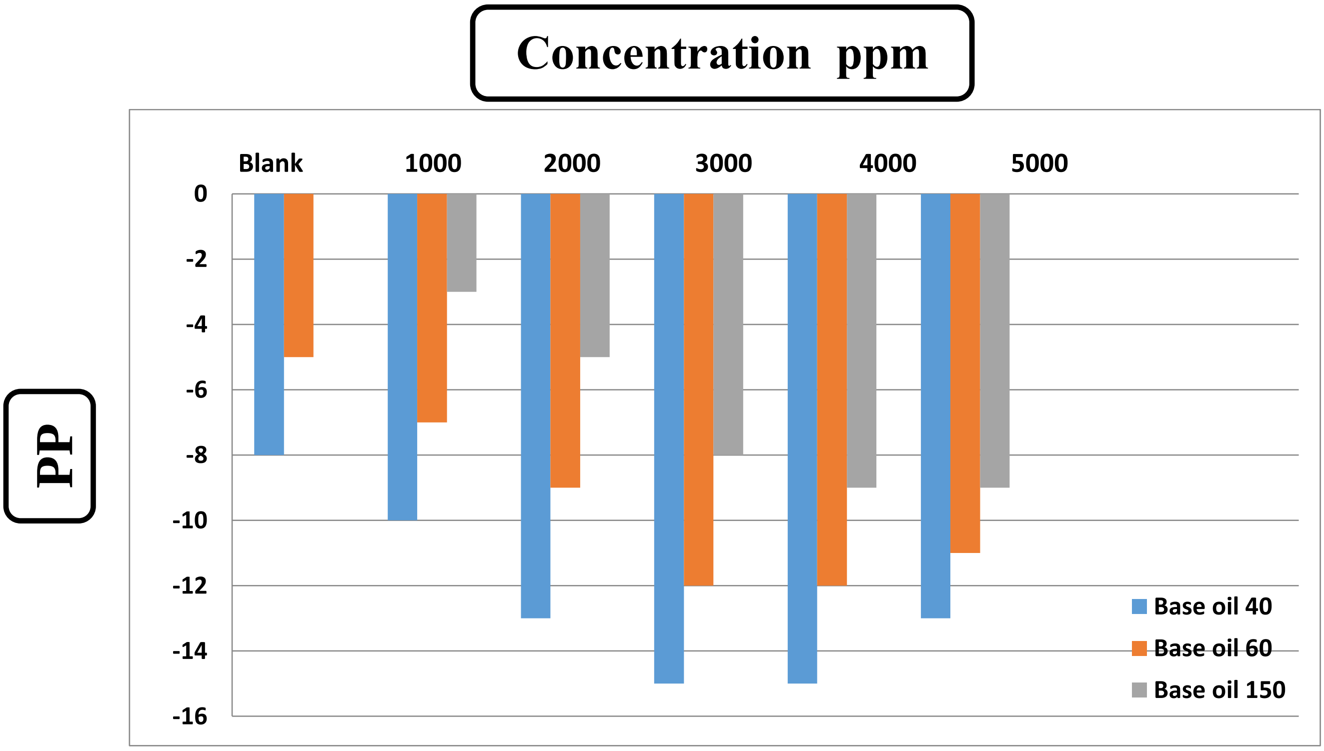

Fig.15 Variation of pour point of the three base oils where adding different Concentrations of polymer B

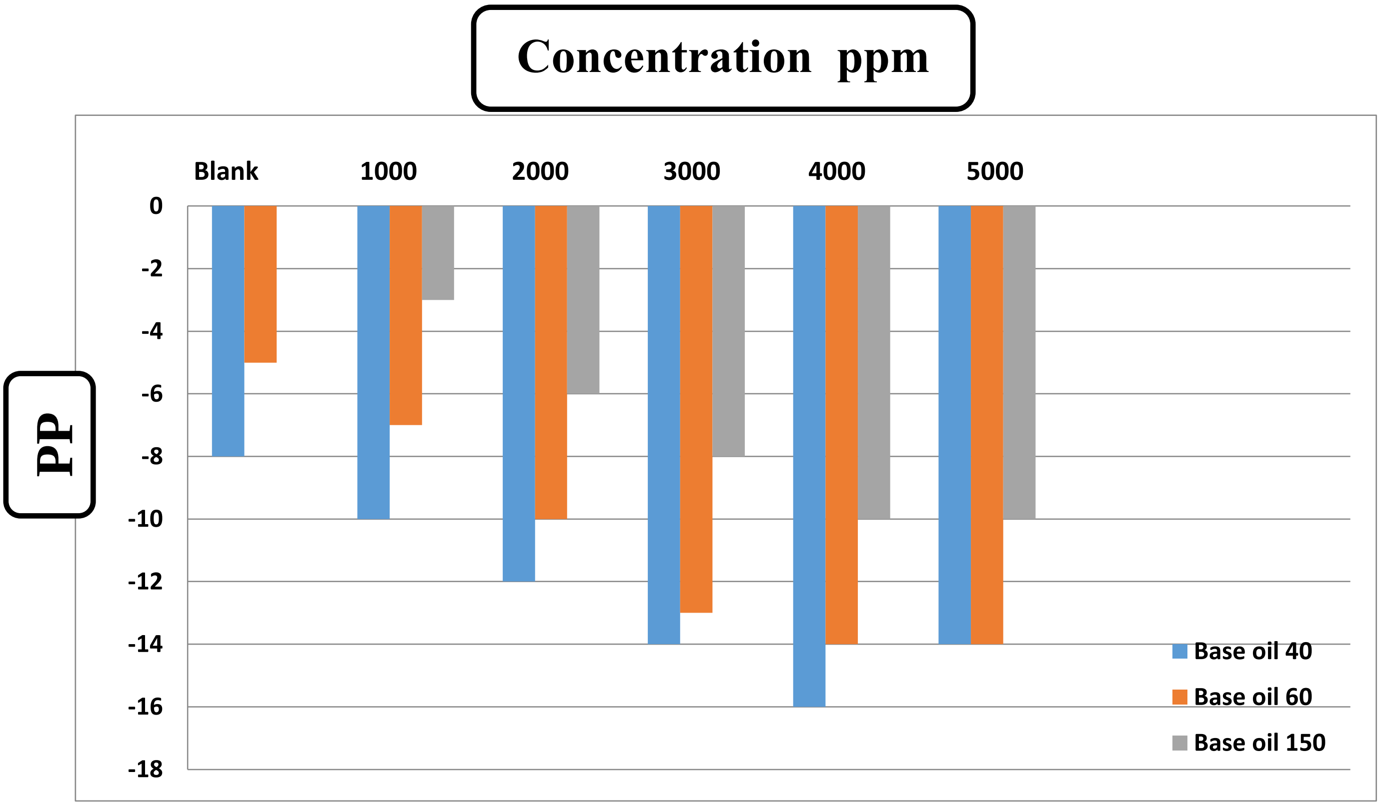

Fig.16 Variation of pour point of the three base oils where adding different Concentrations of polymer C.

Performance of the prepared polymers as viscosity index improvers

Tables (4,5,6) shows that all the prepared copolymers are effective as viscosity index improvers, but copolymer (B) is more effective than copolymers (A,C), and this can be explained by the increase in the molecular weight of the copolymers, (molecular weight 44194 g/mol). Most of the viscosity index improvers are Long-chain copolymers with high molecular weight, whose effect is weak at low temperatures because they are in the form of coiled micelles, and at higher temperatures the strength of the solvent increases, which facilitates the expansion of coiled micelles and compensates for the low viscosity of the oil[14]. the viscosity index of the three base oils increases with increasing the concentration of the Polymers because the long chains of the copolymer in the form of coils in the oil and when the temperature rise, these chains become more relaxed and tend to expand completely. So the interaction between the polymer chains and the oil increases, so increases in the volume and as result increase the viscosity of the base oil at higher temperature[15]. as shown in figure 17.

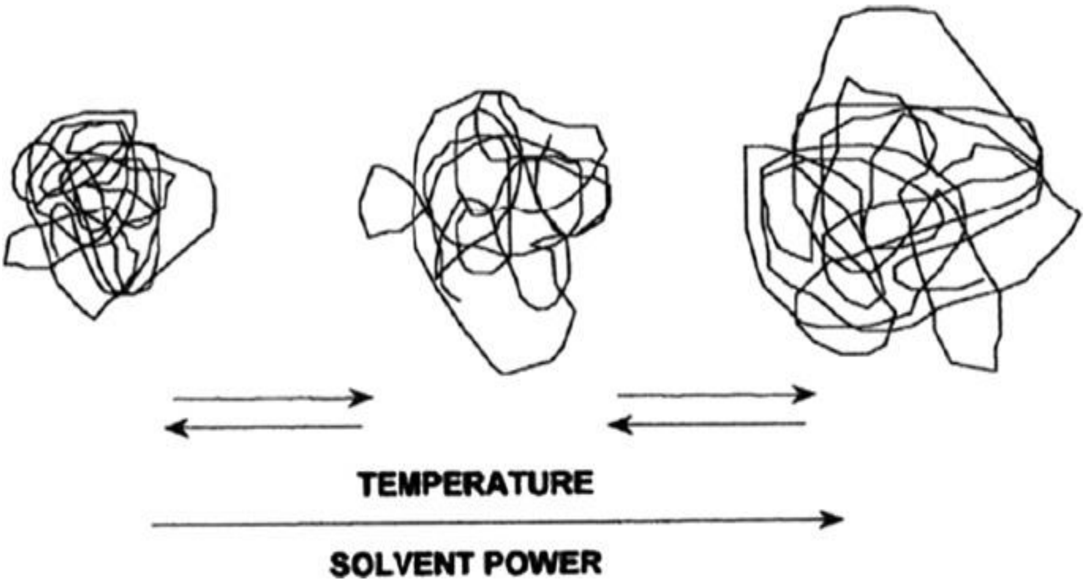

Fig.17 Expansion and contraction of the polymeric coils[16].

Oil type	Concentration	Vis at 40 C^0	Vis at 100 C^0	VI
Base Oil 40	**Blank**	**14.26**	**3.35**	**105.848**
	1000	14.29	3.40	112.018
	2000	14.35	3.48	121.664
	3000	14.42	3.58	134.017
	4000	14.52	3.69	147.011
	5000	14.71	3.83	161.809
Base Oil 60	**Blank**	**61.74**	**8.30**	**103.232**
	1000	61.80	8.53	109.424
	2000	61.88	8.75	115.246
	3000	62.06	9.04	122.485
	4000	62.18	9.29	128.610
	5000	62.65	9.60	135.140
Base Oil 150	**Blank**	**396.99**	**29.20**	**101.991**
	1000	397.32	30.30	107.229
	2000	398.61	31.66	113.449
	3000	399.56	32.83	118.683
	4000	400.94	34.11	124.214
	5000	402.85	35.64	130.520

Table 5 Viscosity index (VI) date for different concentration of polymer (A) in three types of base oils

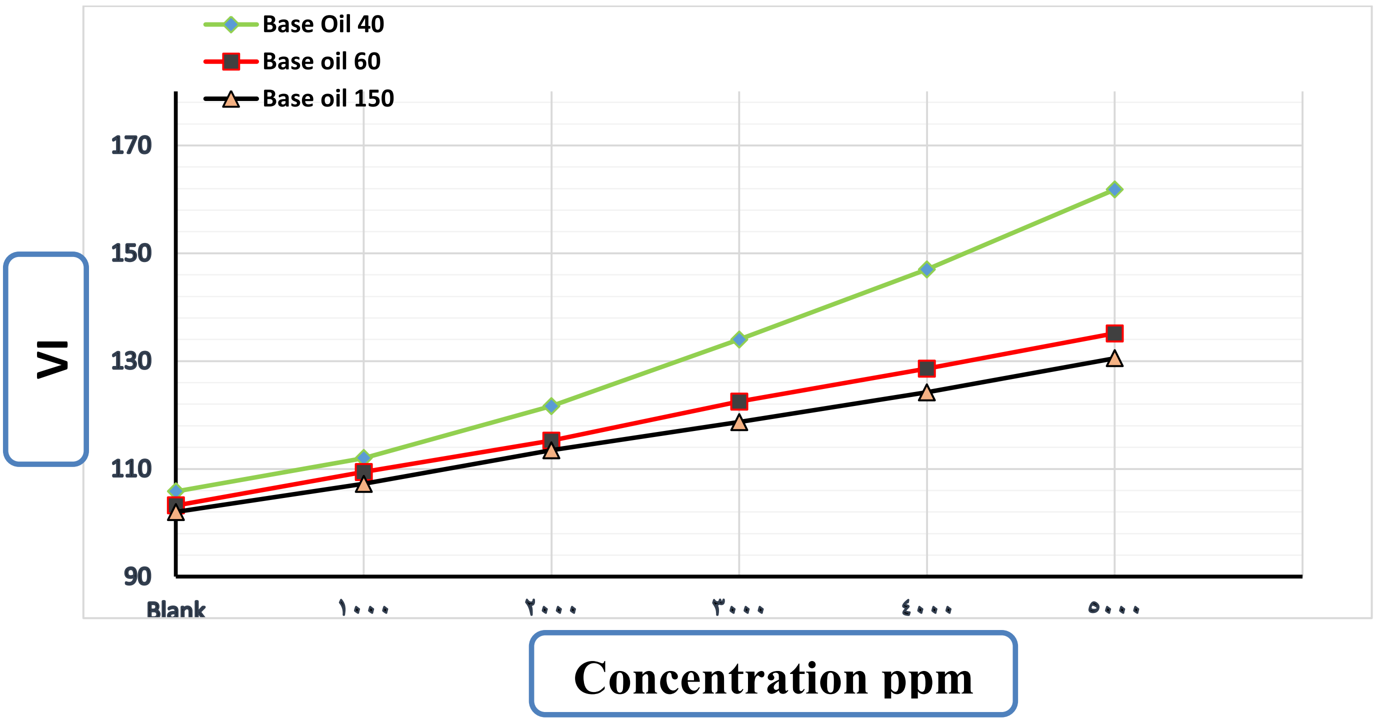

Fig.18 Variation of Viscosity index (VI) of the three oils when adding different concentration of polymer (A)

Oil type	Concentration	Vis at 40 C^0	Vis at 100 C^0	VI
Base Oil 40	**Blank**	**14.26**	**3.35**	**105.848**
	1000	14.30	3.44	117.273
	2000	14.37	3.52	126.742
	3000	14.48	3.64	141.022
	4000	14.62	3.76	154.338
	5000	14.82	3.91	170.063
Base Oil 60	**Blank**	**61.74**	**8.30**	**103.232**
	1000	61.85	8.58	110.680
	2000	61.97	8.81	116.615
	3000	62.14	9.12	124.369
	4000	62.28	9.42	131.639
	5000	62.95	9.74	137.802
Base Oil 150	**Blank**	**396.99**	**29.2**	**101.991**
	1000	397.64	30.58	108.515
	2000	398.80	32.10	115.474
	3000	400.04	33.54	121.810
	4000	402.79	34.85	127.055
	5000	405.30	36.42	133.211

Table 6 Viscosity index (VI) date for different concentration of polymer (B) in three types of base Oils.

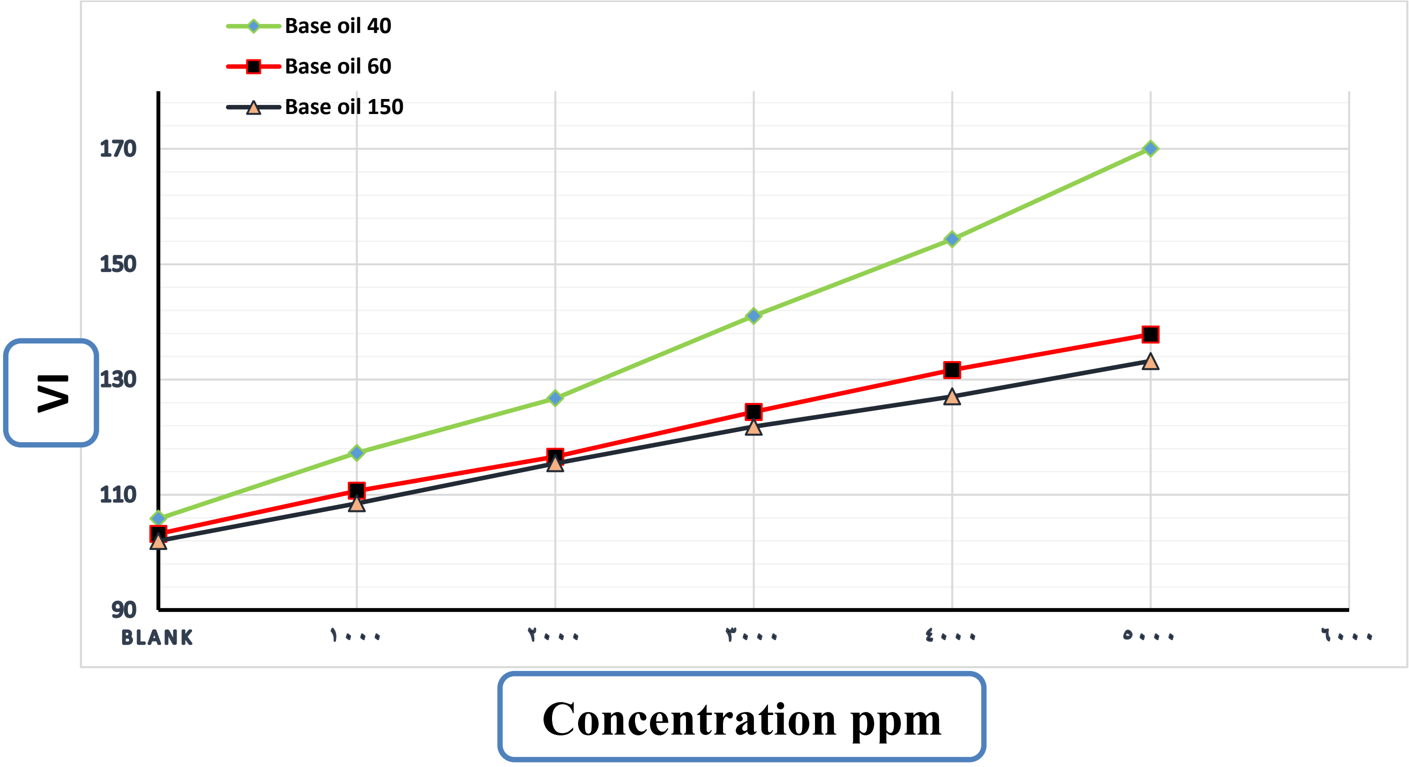

Fig.19 Variation of Viscosity index (VI) of the three oils when adding different concentration of polymer (B)

Oil type	Concentration	Vis at 40 C^0	Vis at 100 C^0	VI
Base Oil 40	**Blank**	**14.26**	**3.35**	**105.848**
	1000	14.29	3.42	114.750
	2000	14.36	3.51	125.553
	3000	14.44	3.60	136.341
	4000	14.57	3.72	150.005
	5000	14.79	3.88	166.747
Base Oil 60	**Blank**	**61.74**	**8.30**	**103.232**
	1000	61.83	8.56	110.179
	2000	61.92	8.77	115.677
	3000	62.10	9.07	123.170
	4000	62.26	9.35	129.914
	5000	62.81	9.69	136.953
Base Oil 150	**Blank**	**396.99**	**29.20**	**101.991**
	1000	397.50	30.41	107.721
	2000	398.64	31.86	114.386
	3000	399.72	33.29	120.754
	4000	401.82	34.58	126.114
	5000	404.35	36.14	132.281

Table 7 Viscosity index (Vl) date for different concentrations of polymer (C) in three types of base oils.

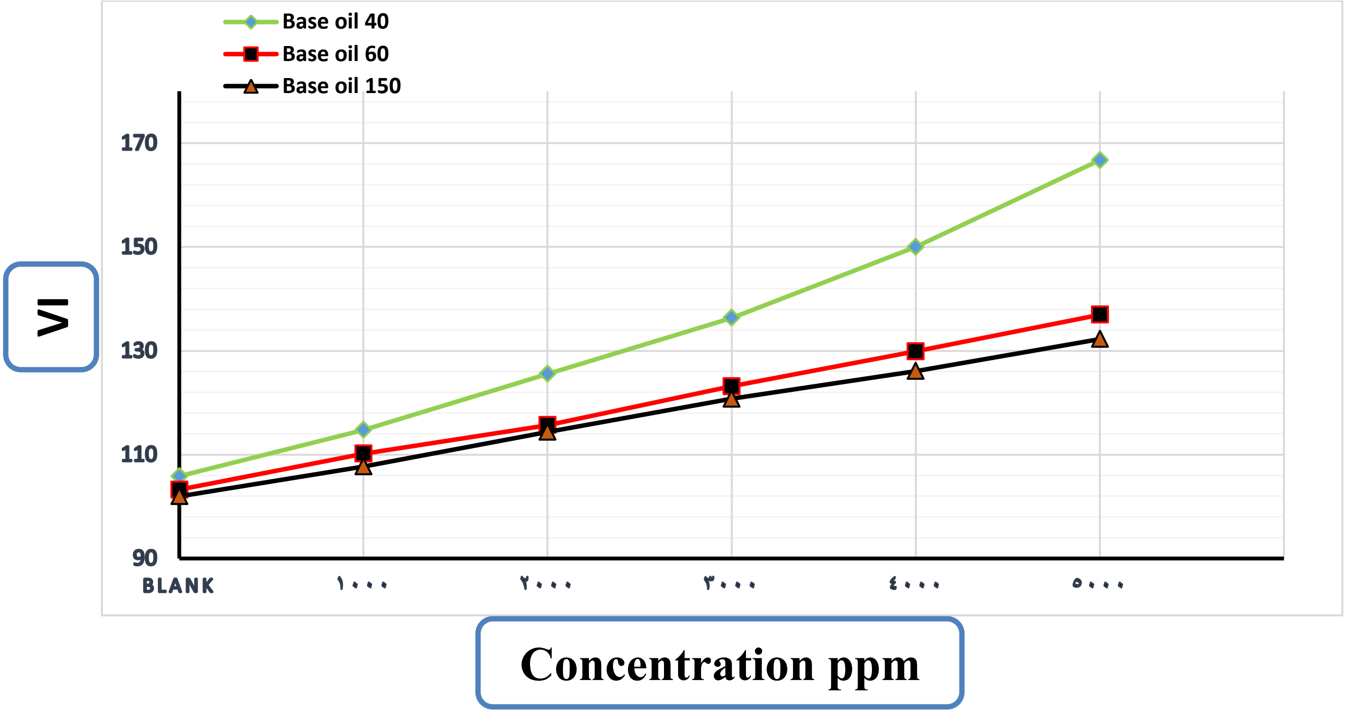

Fig. 20 Variation of Viscosity index (VI) of the three oils when adding different concentration of polymer (C)

Conclusions

From the results obtained in this research, the following conclusions can be written:

1. All prepared compounds dissolve in base oils.
2. All prepared compounds are effective as pour point depressants and viscosity index improvers.
3. With an increase in the concentration of additives, increase viscosity index (VI).
4. As the concentration of additives increases, the effectiveness of polymers as pour point depressants decreases.
5. The efficiency of the prepared compounds as pour point depressants increases with the increase in the alkyl chain length of the alcohol used.

References

[1] N. S. Ahmed, A. M. Nassar, R. M. Nasser, A. F. Khattab, and A.-A. Abdel-Azim, “Synthesis and evaluation of some polymeric compounds as pour point depressants and viscosity index improvers for lube oil,” Pet. Sci. Technol., vol. 26, no. 12, pp. 1390–1402, 2008.

[2] T. Du, S. Wang, H. Liu, C. Song, and Y. Nie, “The synthesis and characterization of

methacrylic acid ester-maleic anhydride copolymer as a lube oil pour point depressant," Pet. Sci. Technol., vol. 30, no. 2, pp. 212–221, 2012, doi: 10.1080/10916461003662984.

[3] P. Ghosh and D. Kumar Saha, "Acrylate Terpolymers as Potential Pour Point Depressant and Viscosity Modifiers for Lube Oil," Pet. Sci. Technol., vol. 33, no. 10, pp. 1126–1132, 2015, doi: 10.1080/10916466.2015.1040889.

[4] R. I. El-shazly, R. S. Kamal, A. M. Nassar, N. S. Ahmed, and G. H. Sayed, "The behavior of some terpolymers as lubricating oil additives," Appl. Petrochemical Res., vol. 10, no. 3, pp. 115–123, 2020.

[5] E. Faujdar, H. Negi, A. Kukrety, and R. K. Singh, "Study of alkyl acrylate-co-maleic anhydride-based novel amide copolymers as multifunctional lubricant additives," Polym. Bull., vol. 78, no. 4, pp. 2085–2102, 2021, doi: 10.1007/s00289-020-03204-5.

[6] N. S. Ahmed, A. M. Nassar, and R. M. Nasser, "Jojoba modified polymers as performance modifiers additives for engine oil," Ind. Lubr. Tribol., vol. 67, no. 5, pp. 425–433, 2015, doi: 10.1108/ILT-12-2013-0144.

[7] D. K. Saha and P. Ghosh, "Synthesis, characterization and performance evaluation of long chain methacrylate-octene copolymer for lubricant formulation," J. Macromol. Sci. Part A Pure Appl. Chem., vol. 56, no. 11, pp. 1050–1059, 2019, doi: 10.1080/10601325.2019.1651205.

[8] A. International, "ASTM D2270-93-Standard Practice for Calculating Viscosity Index From Kinematic Viscosity at 40 and 100° C." ASTM International West Conshohocken, 1998.

[9] A. International, "ASTM D97-17b (2017) Standard test method for pour point of petroleum products," 1998.

[10] M. A. Jalal, M. N. Khalaf, and M. A. Hussein, "Effect of variation in polymer structure on eddies suppression of basrah light crude oil turbulent flow," Egypt. J. Chem., vol. 64, no. 7, pp. 3365–3378, 2021, doi: 10.21608/ejchem.2021.61114.3317.

[11] H. H. Albahadly, N. H. Al-Haidery, and B. K. Al-Salami, "Synthesis, Biological Activity of Trimethoprim derivative and the Complexes," J. Phys. Conf. Ser., vol. 2063, no. 1, p. 012014, 2021, doi: 10.1088/1742-6596/2063/1/012014.

[12] M. A. Jalal, M. N. Khalaf, and M. A. Hussein, "Synthesis of Branched Copolymers of Poly (1-hexene- co -maleic anhydride)," Basrah J. Sci., vol. 39, pp. 135–148, 2021, doi: 10.29072/basjs.202119.

[13] A. M. Nassar and N. S. Ahmed, "Synthesis and evaluation of ethoxylated polyesters as viscosity index improvers and pour point depressants for lube oil," Int. J. Polym. Mater. Polym. Biomater., vol. 52, no. 9, pp. 821–832, 2003, doi: 10.1080/713743712.

[14] A. M. Salaheldin, Q. Zheng, X. Q. Lu, Y. Bin Guo, and J. Z. Zhu, "Numerical simulation of piston ring lubrication with Multi-Grade oil," Appl. Mech. Mater., vol. 595, pp. 83–90, 2014, doi: 10.4028/www.scientific.net/AMM.595.83.

[15] S. I. Shara, E. A. Eissa, and J. S. Basta, "Polymers additive for improving the flow properties of lubricating oil," Egypt. J. Pet., vol. 27, no. 4, pp. 795–799, 2018, doi: 10.1016/j.ejpe.2017.12.001.

[16] S. A. Mohamad, N. S. Ahmed, S. M. Hassanein, and A. M. Rashad, "Investigation of

polyacrylates copolymers as lube oil viscosity index improvers," J. Pet. Sci. Eng., vol. 100, pp. 173–177, 2012, doi: 10.1016/j.petrol.2012.06.015.