Synthesis and elaboration of modified comb type (maleic anhydride-α-tetradecene) copolymers for cold flow improvers of biodiesel

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Abstract:

The maleic anhydride-α-tetradecene copolymer (OMAC) with an approximate relative maleic anhydride to α-tetradecene composition ratio of 1:1.2 was synthesized by free radical copolymerization. The copolymers were modified by the esterification reaction between the anhydride groups and the OH- group of hexadecanol. Comb-type (-maleic acid cetyl ester-co-α-tetradecene-) copolymers (MCEC) with various ratios of alkyl group/carboxyl group (*r*) were investigated. Upon cooling, the MCEC changed the crystallization state of the wax crystals, and reduced the pour point of the biodiesel, which was observed by pour point and dynamic viscosity testing. The MCEC efficiency that improved the cold flow properties of the biodiesel was found to be correlated to *r*. MCEC with *r*=2.76 was found to be the most effective in improving the flow ability of the palm oil biodiesel. Our study demonstrates the ability of MCEC3 at 1000 ppm concentration to reduce the pour point of palm oil biodiesel to 10.5°C and the dynamic viscosity up to 1.04 mPa.s. A correlation was found between the number and the length of the pendant alkyl groups of additives and the compositions of the fatty acid methyl ester of the biodiesel.

Keywords: biodiesel, cold flow property, comb type copolymer, flow-ability, wax crystals.

Classification number: 2.2

Introduction

Today, humans face an impending energy crisis as fossil fuel resources are being depleted and the environment is becoming seriously polluted. People are seeking solutions to overcome these problems by using new energy sources such as wind power, solar energy, biomass, etc. Biodiesel is a fuel produced from animal fats or vegetable oils. It can not only replace fossil energy but also contribute to the treatment of environmental pollution. It is well known that most of biodiesel fuel properties are equivalent to those of diesel, except for the ability to flow at low temperatures. So far, improving the flow ability of biodiesel remains a major challenge for use in diesel engines. To avoid a negative impact on edible oils in the food sector, countries around the world, including Vietnam, have developed a strategy to use non-edible oils, including waste oil and fats, as raw materials for producing biodiesel. Depending on the choice of vegetable oil as a starting material, the pour point (PP) of biodiesel ranges between 15-40°C, which is much higher than that of petro-diesel. In the cold season, viscosity of biodiesel increases and crystals appear due to the presence of saturated fatty acid chains. These solid crystals clog fuel lines and filters, which then obstructs the engine's operation. Indeed, there have been many approaches to overcome this significant problem, for example, the use of additives [1-7], blends of biodiesel with petro-diesel [8-11], anti-frost compounds [12-14], and esters with side chains [15-17]. Among those approaches, the use of additives that have economic advantages and convenience are the most appropriate [18]. These additives are known as cold flow improver (CFI), which include PP depressants (PPDs), surfactants [19, 20], and diluents [21, 22]. The CFIs are added to biodiesel in order to change the crystallization state of the wax to prevent the network structure from forming and therefore lower the pour point and viscosity of the biodiesel fuels. As a result, the working temperature range of biodiesel is extended. Although some additives are reported to be available for biodiesel, employing them to improve the flowability of biodiesel at low temperatures remains a challenge and more research is needed.

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A number of studies have reported that many commercial petro-diesel cold flow improver additives also greatly reduced PP and the cold filter plugging point of biodiesel. The majority of diesel CFIs are poly (vinyl acetate) copolymers, poly (olefin) copolymers, alkyl methacrylate copolymers, and poly (maleic anhydrite) copolymers [2-5]. These CFIs have a common chemical structure that consists of a hydrocarbon chain capable of co-crystallizing with the hydrocarbon chains of fatty acids of biodiesel and thus affects the nucleation and growth of wax crystals [23, 24]. Cold flow properties of biodiesel generally depend on the fatty acid compositions. So, it becomes essential to design copolymeric CFIs with a special structure that would be suitable for a specific biodiesel [25]. It is known that copolymers with the comb shape structure exhibit a good flow improver for fuels in general. However, the synthesis of copolymers with a comb shape structure that consists of long and short branch chains in a regular arrangement is still a challenge for researchers [2, 3, 15, 23, 26]. It is well known in polymer chemistry that the generation of copolymers with a regular alternative structure requires the use of the pairs of monomers containing a small copolymerization constants (~0). Maleic anhydride (MA) is a unique and interesting monomer, which has almost no affinity to homopolymerization but easily forms copolymers [2, 23]. Thus, MA and an olefin as copolymers are a reasonable choice to form the desired alternative structure. In our previous reports, comb-shaped poly(maleic anhydride-co-α-olefin) (OMAC) [27, 28] and poly(maleic acid alkyl ester-co-vinylacetate) esters (MAVA) [29] were used to improve the cold flowing ability of palm oil biodiesel. The results proved that copolymers having comb-shape structures, with long and short side alkyl chains arranged alternatively to one another, determined the activity of the additives [27]. So, to design the comb-shape copolymer additives, the number and length of their branch alkyl chains for a specific biodiesel should be adjusted. In our present work, comb-type copolymers poly (maleic anhydride-co-α-tetradecene) esterified by the long alkyl chain alcohol with various ratios of alkyl group/carboxyl group were synthesized. This study assessed the effect of different proportions of alkyl/carboxyl group ratio and alkyl side chain length on cold flow improvement on wax crystallization and biodiesel flow ability by pour point testing and dynamic viscosity measurements. Moreover, the palm oil biodiesel (PB), the waste oil biodiesel (WB), and the animal fat biodiesel (AFB) were used to test the pour point reducing ability of the synthesized CFIs.

Experimental

Materials

Benzoyl peroxide and p-toluene sulfonic acid were purchased from Merck, Co., Ltd and 1-tetradecene was purchased from Kasei Kogyo. Maleic anhydride and 1-Hexadecanol were purchased from Wako, Japan. Palm oil biodiesel was produced from the palm oil in Viet Nam. Waste cooking oil biodiesel and animal fat biodiesels were produced in Japan. Other chemicals like ethanol, toluene, and methanol were supplied from Merck Co., Ltd and used without further purification. Table 1 presents the results of composition and distribution of the fatty acid methyl esters (FAMEs) of different biodiesels analysed by gas chromatography-mass spectroscopy (GC-MS) on an Agilent 6890N.

Table 1. GC-MS analysis of biodiesel from PB, AFB, and WB.

Name of FAME, corresponding acid	Mass percent (%)		
	PB	AFB	WB
Methyl hexadecanoate, C16:0	44.23	26.68	5,7
Methyl octadecanoate, C18:0	3.63	23.42	2,7
Methyl oleate, C18:1	41.06	33.94	53.8
Methyl linoleate, C18:2	8.36	6.33	23.5
Methyl linolenoate, C18:3	0.12	1.72	11.8
Other	2.64		

Preparation methods

Synthesis of MCAC copolymer:

MCEC copolymers were synthesized by radical polymerization in two steps (Scheme 1). In the first step, maleic anhydride and α-tetradecene were copolymerized in toluene at 110°C for 8 h with benzoyl peroxide as an initiator under nitrogen gas atmosphere, to get the OMAC.

MCEC copolymers were synthesized by a two-step polymerization reaction (Scheme 1). In the first step, maleic anhydride reacted with α-tetradecene in toluene at 110°C for 8 hours, in a nitrogen atmosphere. Benzoyl peroxide served as an initiator. The product in the first step was OMAC.

In the second step, 1-hexadecanol was fed into the reactor with the copolymer OMAC at 120°C for 8 h. The crude product of MCEC was isolated from the reaction mixture by precipitating with methanol, was then washed thoroughly with warm water, and finally dried in a vacuum

oven at 60°C to reach a constant weight. By changing the feeding ratios of maleic anhydride/cetyl alcohol (1:1.0, 1:1.5, 1:2.0, 1:2.5 and 1:3.0), several MCECs were obtained and named MCEC1, MCEC2, MCEC3, MCEC4 and MCEC5, respectively.

Step-1:
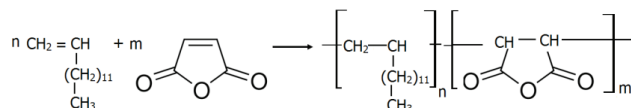
Step-2:
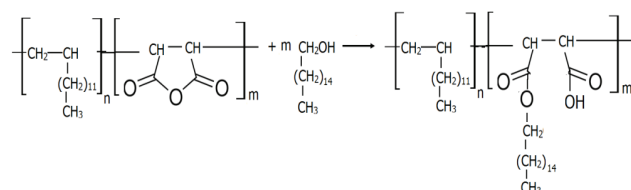
Scheme 1. Synthesis routine for the preparation of MCEC.

Methods of analysis:

- Fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer GX spectrophotometer using samples prepared as pressed KBr discs. All spectra were scanned 4 times at a resolution of 2 cm^{-1} from 400 to 4000 cm^{-1}.

- ^{1}H-NMR spectra were recorded on a JNM-ECX400 (Japan) spectrometer operating at 400 MHz and a Bruker Advance III spectrometer operating at 500 MHz (Faculty of Chemistry, HUS, Vietnam) at ambient temperature using CDCl$_3$ as the solvent.

- Gas chromatography mass spectroscopy (GC-MS) was used to determine the FAME content. The gas chromatograph (Agilent 6890 N) was equipped with a direct capillary column DB-5ms (film thickness of 30 m×0.25 mm×0.25 µm). The column temperature was initially kept at 60°C and then increased with speed of 4°C/min to 200°C, then held at this temperature for 2 min, followed by an increase to 280°C, and a hold at this temperature for 2 min. The temperature of the injector was set to 300°C. Helium was used as the carrier gas at a constant flow rate of 1 ml/min. Electron ionization (EI) mass spectra were recorded at 70 eV ionization voltage in the range of m/z 40-550 in full scan mode. The ion source and the transfer line temperatures were set to 200°C and 250°C, respectively. Measurements of the pour points of biodiesel were conducted in accordance with ASTM D97 [30].

- The viscosimetric molecular weight was determined by the measurement of the viscosity of the polymer solutions at 25°C in toluene and using the Mark - Houwink - Sakurada equation:

$$Log[\eta]=logK+\alpha.log\ M \qquad (1)$$

where [η] is the intrinsic viscosity, M is the molecular weight, and K and α are constants that depend on polymer, solvent, and temperature (in our case K=1.52.10^{-4} and α=0.71 [6]).

- The dynamic viscosity of the control and PPD-treated biodiesels were measured on a viscometer of the falling ball type (Gilmont, Thermo Scientific) using an isothermal bath at 40°C. The dynamic viscosity determinations were performed in accordance with ASTM D445-97 [25].

Results and discussion

Synthesis and characterization of MCEC

The chemical structures of the OMAC and MCEC4 copolymers were confirmed by the FTIR spectra shown in Fig. 1.
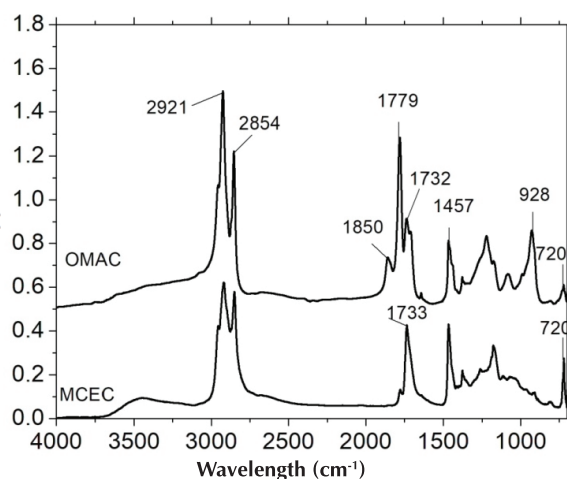
Fig. 1. FTIR spectra of synthesized OMAC and MCEC4.

It is clearly seen that the stretching vibration of C-H (in CH$_3$ and CH$_2$) absorbs strongly at 2921 cm^{-1} and 2854 cm^{-1} and the stretching vibration of C-H appears at 1457 cm^{-1}. The strong absorption band of the scissoring vibration of the (CH$_2$)$_n$ alkyl chains of α-tetradecene appears at 720 cm^{-1}. The carbonyl group C=O of the anhydride was demonstrated by strong bands at 1779 cm^{-1} and 1732 cm^{-1}, and a weak band at 1850 cm^{-1} characteristic for the MA ring. In addition, the absorption peak of the characteristic C=C group at 1630-

1642 cm^{-1} [8] of the monomers disappeared completely, which indicates the polymerization reaction was thoroughly completed.

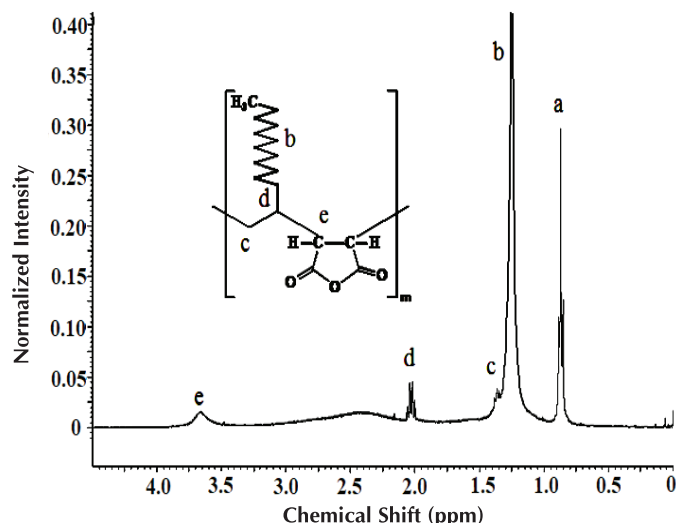The chemical structure of the OMAC was also confirmed by the ^{1}H-NMR spectrum shown in Fig. 2.

Fig. 2. ^{1}H-NMR spectra of synthesized OMAC.

It can be seen from Fig. 2 that the -CH$_3$ exhibited the chemical shift at 0.88 ppm (peak a), and the -(CH$_2$)$_n$- displayed a chemical shift at 1.25 ppm (peak b), while the hydrogen peak of the methylene groups of the MA showed the chemical shift at 3.6 ppm (peak e) [15]. Thus, the presence of all the structural groups in the OMAC and MCEC copolymers was confirmed by FTIR and ^{1}H-NMR spectra. The FTIR in combination with ^{1}H-NMR are commonly used to confirm the structure of the polymer compounds [15, 18].

Based on the peak intensity of -CH in maleic anhydride and of -CH$_2$- in the α-tetradecene, it is possible to determine the percentage of MA residue in a polymer unit. Using this method, the obtained polymer had an MA to α-tetradecene composition relative ratio of 1:1.2.

The obtained OMAC was esterified by cetyl alcohol with varying feeding ratios of MA:alcohol (1:1.0, 1:1.5, 1:2.0, 1:2.5, 1:3.0) and the resulting copolymers were named MCEC1, MCEC2, MCEC3, MCEC4, and MCEC5, respectively. The structures of all modified copolymers were confirmed by the FTIR spectra. The FTIR spectrum of MCEC4 is shown in Fig. 3. By analysing the significant signals in the FTIR spectra we can see the intensities of the CH$_3$ and CH$_2$ bands increase with the increase of the number of cetyl alkyl that are attracted to the main chain of the copolymer. It can be clearly seen that the intensities of the characteristic C=O stretching peaks of the MA at 1857 cm^{-1} and 1778 cm^{-1} decrease and that of the characteristic C=O adsorption peaks of alkyl ester at 1733 cm^{-1} increase. The decreasing C=O bands of MA (1857 cm^{-1} and 1778 cm^{-1}) in the OMAC confirmed the formation of the MCEC.
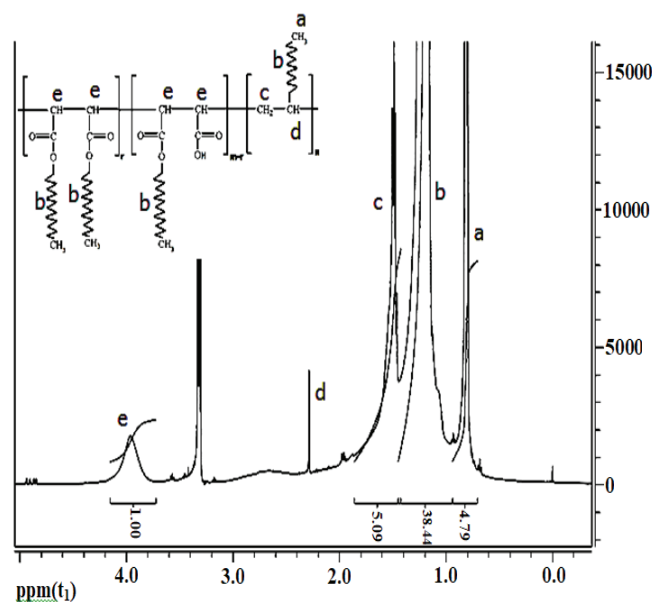

Fig. 3. ^{1}H-NMR spectra of MCEC4.

The esterification ratio (f) is defined as the molar amount of the alkyl-alcohols for one mole of the maleic anhydride group in a polymer (0<f< 2), which is estimated from the integrated area of the H$_a$ and H$_e$ peaks (H$_a$, H$_e$ are protons at positions a and e, respectively, in Fig. 3).

From the relation $\dfrac{A_{He}}{A_{Ha}} = \dfrac{2}{3x1.2 + 3xf}$, the esterification ratio (f) can be given as follows:

$$f = \frac{2A_{Ha}}{3A_{He}} - 1.2 \tag{2}$$

In this equation, A_{Ha} and A_{He} are the integrated area of protons H$_a$ and H$_e$, respectively and r is defined as the ratio of total alkyl groups (C-16 and C-14) to carbonyl group (-COOH) and is calculated by using the following equation:

$$r = \frac{f + 1.2}{2 - f} \tag{3}$$

The viscosimetric method was used to determine the molecular weight of the MCEC copolymers. The values of f, r, and molecular weight (M$_w$) of all samples are presented in Table 2.

Table 2. Values of f, r and M$_w$ of OMAC samples.

Sample	Molar ratio of MA-Cetyl	f	r	M$_w$
OMAC		-	-	11700
MCEC1	1:1.0	0.92	1.98	19900
MCEC2	1:1.5	0.97	2.12	20500
MCEC3	1:2.0	1.04	2.34	21050
MCEC4	1:2.5	1.15	2.76	21900
MCEC5	1:3.0	1.46	3.35	24400

From Table 2, it can be seen that the values of *f*, *r*, and M$_w$ increase with the increase of molar ratio of MA-Cetyl. These results prove that when the MA-Cetyl ratio rises, the number of alkyl pendant chains attached to the OMAC copolymer increases.

***Effect of MCECs on the improvement of palm oil biodiesel cold flow***

The efficiency of the cold flow improvement of MCECs on palm oil biodiesel was investigated by PP and dynamic viscosity measurements. The results are presented in Table 3. From this table, all the MCECs exhibit a positive effect on the reduction of the PP of palm oil biodiesel. The PP of the biodiesel decreases with increase in *r* and at *r*=2.76 the most effective improvement of the biodiesel flow ability is reached. However, we also can see that PP increases as *r* further increases to 3.35. This indicates that the MCEC5 had a value of *r* that was too high and not reducing the pour point. This feature can be explained as follows: it is known that the most beneficial profile structure of additives for reducing PP are alkyl groups C14 and C16 alternatively grafted to the polymer backbone. Too many alkyl groups will disrupt their alternative attachment and cause their reducing ability to trap the biodiesel's long alkyl chains that create favourable conditions for self-crystallization.

Table 3. PP and dynamic viscosity (μ) values of PB and MCECs treated PB at 1000 ppm.

Sample	PP, °C	μ, 40°C, mPa.s	
		Average	*Std.dev*
PB	15.0	4.10	0.04
PB+ MCEC1	7.0	3.39	0.04
PB+ MCEC2	6.5	3.30	0.06
PB+ MCEC3	5.8	3.19	0.04
PB+ MCEC4	4.5	3.06	0.03
PB+ MCEC5	5.5	3.15	0.04

The dynamic viscosity values in Table 3 show that the trend in viscosity variation looks similar to that of PP. A high reduction in viscosity was observed upon increase in *r* from 1.98 to 2.76 while insignificant decrease was observed when *r* was further raised to 3.35. Thus, there is a correlation between the influence of additives on the PP and viscosity of biodiesel. The additives that promote the reduction of PP also produce the highest viscosity reduction. This is clearly related to the additive's ability to provide the formation of small waxy crystals dispersed in the fuel environment [9]. The assembly between the carboxyl and alkyl groups of MCECs with the methyl ester group appears to stabilize the biodiesel under the steric effects of the number of alkyl groups of MCEC polymers, thereby improving the flow-ability of the biodiesel gels formed upon cooling [18]. So, the balance between the alky groups of the additive and the methyl ester groups of the biodiesel is an important factor.

One of the goals of this study was to clarify the effect of additive loading on the ability to reduce PP of biodiesel. Here, different concentrations of MCEC4 (500, 1000, 2000 and 3000 ppm) were taken. The results are presented in Fig. 4.
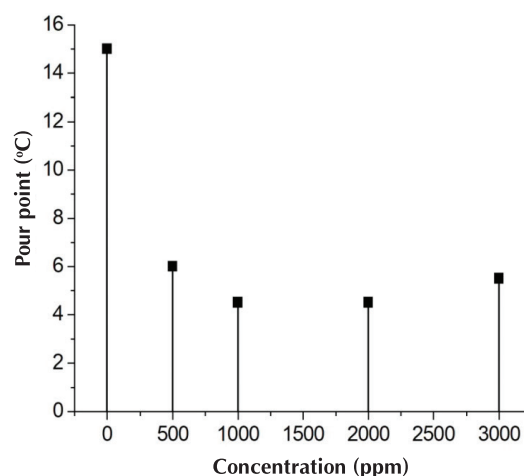
Fig. 4. The change in activity of the MCEC4 additive with different concentrations.

It can be seen that ΔT increases with increasing additive concentration whereas an optimum additive concentration of 1000 ppm was found. If the concentration is lower than the optimum value, it may be difficult for the additive to completely co-crystallize with the FAMEs and the cold flow performance of the biodiesel does not further improve. On the other hand, if the copolymer additive concentration is higher than the optimum value, the additive molecules could form small wax crystals to prevent them from co-crystallization with the FAMEs and then the higher concentrations would not be economical. Therefore, at the 1000 ppm concentration, the additive shows a better ability to lower PP of the palm oil biodiesel.

At present, there are different commercial additives available for biodiesel and blends with diesel, but for the additives to be effective a much higher concentration is needed than the one used in this work [7, 15, 19, 26, 31]. Moreover, the performance of the additives compared to the biodiesel control was often negligible. When using poly (dodecyl acrylate-co-tetradecyl methacrylate) as an improver for the palm oil biodiesel, Oliveira [18] reported that PP dropped from 14.7°C to 13°C at 1000 ppm concentration. Here, better PP reductions were found in the control palm biodiesel.

Effect of additive' side chain length on the cold flow-ability of biodiesel

Although biodiesel has a potential for environmental emission reduction, it also has a high PP and a high viscosity compared to conventional diesel fuel [7]. The correlation between the FAMEs composition and the number of alkyl pendant chains of MCECs on the activity of the additive was investigated at 1000 ppm concentration. The results of these tests are shown in Table 4.

Table 4. Results of the test on activity of MCEC for different biodiesels and some methyl ester of fatty acids.

Sample	PP, °C (1000 ppm)	
	No additives	*MCEC-C16*
PB*	15.0	**4.5**
AFB**	22.0	18.0
WB**	-10.0	-15.0
Methyl hexadecanoate** (C16:0)	30.0	**25.0**
Methyl octadecanoate** (C18:0)	40.0	36.0
Methyl oleate** (C18:1)	-3.0	-12.0

(*) Biodiesel was supplied from Vietnam.
(**) Biodiesels and methyl ester of fatty acids were supplied from Japan.

The data in Tables 1 and 4 show that biodiesel with a lot of methyl esters of saturated fatty acids has a high PP value. On the other hand, it is seen that at the same additive concentration, the effectiveness of the MCEC on the PB was better than that of AFB and WB. As seen above in Table 4, PP has the dominate amount of C16 alkyl chains compared to WB and AFB. This means there is a greater similarity between alkyl chain length in PB and the additive.

The effect of the additive side chain length on the cold flow ability of biodiesel was also investigated by viscosity measurements. The dynamic viscosities of all samples are presented in Fig. 5.
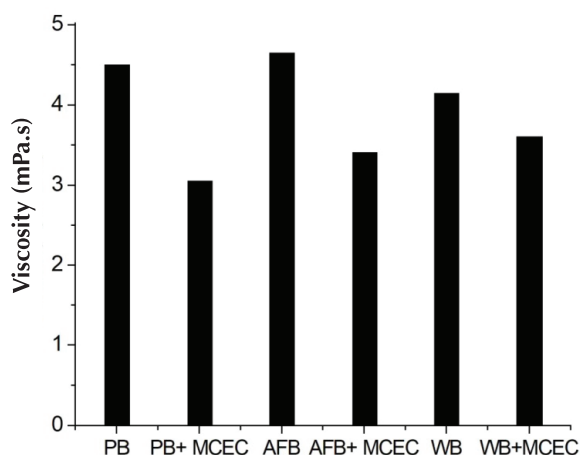
Fig. 5. The viscosity of neat and MCEC treated biodiesels.

This figure shows that biodiesel with higher percentages of saturated fatty esters has a higher dynamic viscosity, which is in agreement with results of other authors [11,17, 32]. Some researchers have pointed out the effect of unsaturated levels on cold flow properties. They showed that the higher the unsaturated level, the better the cold flow performance [9]. It was observed that the effectiveness of the MCEC in the dynamic viscosity of the PB was also significantly better than that of AFB and WB. This, in turn, explains the higher efficiency of the MCEC as a flow improver for the PB as the one most suitable between the alkyl saturated chain length of the FAMEs and the alkyl side chain length of the additive. The trend in viscosity variation looks similar to that of PP.

Conclusions

Comb-type MCEC copolymers with various ratios of alkyl group:carboxyl group (*r*) were synthesized by the esterification of OMAC with alkyl alcohols. The structure and molecular weight of the obtained copolymers were characterized by FTIR, ^{1}H-NMR, and the viscosimetric method. The results showed that with *r*=2.76, the additive MCEC appears to be the most effective in improving the flow ability of the palm oil biodiesel. In addition, by using MCEC4 of 1000 ppm concentration, the PP of the palm oil biodiesel could be reduced up to 10.5°C and the viscosity up to 1.04 mPa.s. The results also indicated that similarity between the alkyl length in both additives and biodiesel is important for improving the flow ability of biodiesel upon cooling.

COMPETING INTERESTS

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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