

Synthesis and characterization of alkyl-methacrylate-maleic anhydride copolymer for use as a biodiesel flow improver

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Abstract:

Due to its many advantages such as renewable raw materials and small negative impact on the environment, biodiesel has the most potential as an alternative to petro-diesel. However, one weakness of biodiesel is due to its origin of vegetable oil or animal fat. This is because during the cold season, when the ambient temperature is lower than 15°C, the viscosity of biodiesel increases and produces precipitation that causes difficulties for engine operation. Methacrylic acid was esterified with four alcohols: 1-decanol, 1-dodecanol, 1-tetradecanol, and 1-cetanol. Afterwards, the obtained monomers were copolymerized with maleic anhydride. The synthesized monomers and copolymers were characterized by ¹H-NMR (Nuclear magnetic resonance) and Fourier transform infrared (FTIR) spectroscopy. The ability of the obtained copolymers to reduce the pour point of waste cooking oil-based biodiesel was investigated. The results showed that the polymer additive with the alkyl chain C₁₄H₂₉ demonstrated the best flow improvement performance. At a concentration of 1000 ppm, this polymer additive reduced the pour point of waste cooking oil-based biodiesel from 12 to 5°C. In this study, the effect of alkyl chain length, molecular weight, as well as the concentration of the additives on the pour point of biodiesel was also discussed.

Keywords: cold flow improver, cooking oil-based biodiesel, copolymer, maleic anhydride, pour point, waste.

Classification number: 2.2

1. Introduction

Due to its many advantages such as renewable raw materials and small negative impact on the environment, biodiesel has the most potential as an alternative to petro-diesel. However, one weakness of biodiesel is due to its origin of vegetable oil or animal fat. This is because during the cold season, when the ambient temperature is lower than 15°C, the viscosity of biodiesel increases and produces precipitation that causes difficulties for engine operation [1]. To overcome this weakness, one of the best solutions is the application of a flow - improving biodiesel additive called a cold flow improver. A small amount of cold flow improver added to biodiesel has been shown to greatly improve its fluidity. Among the polymers used as flow improvers for biodiesel, vinyl compound-co-maleic anhydride copolymers are commonly used [2].

It is well known that the properties of a copolymer depend strongly on its composition [3, 4]. The creation of a copolymer is successful when its composition and molecular mass are well controlled. The composition of a copolymer depends on the reactivity of its monomers. In fact, the monomer molar ratio of an obtained copolymer

is often different from that of its initial monomers due to a difference in monomer reactivity [5]. Two of the most commonly used methods to determine the composition content ratio of a polymer are FTIR [6] and NMR spectroscopy [5].

While there have been numerous studies on the manufacture and use of a cold flow improver for petro-diesel [7], studies related to cold flow improvers for biodiesel are hardly available. Therefore, the purpose of this study was to synthesize a cold flow improver suitable for biodiesel derived from waste cooking oil. More specifically, four monomers were synthesized. They were esters of methacrylic acid and the alcohols 1-decanol, 1-dodecanol, 1-tetradecanol, and 1-cetanol. These four monomers were then copolymerized in turn with maleic anhydride. The synthesized monomers and copolymers were characterized by ¹H-NMR and FTIR spectroscopy. The ability of the four obtained copolymers to reduce the pour points of biodiesel was investigated. The effect of alkyl chain length, molecular weight, as well as the concentration of copolymer additives on their ability to improve the flow of biodiesel was discussed.

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2. Experiment

2.1. Chemicals

The chemicals used in this study are listed in the Table 1. Before use, all alcohols were properly vacuum dried at 50°C for 6h. The others were used without purification.

Table 1. Chemicals.

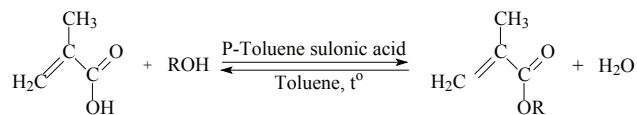
Chemicals	Company	Country	Appearance
1-decanol (C ₁₀ H ₂₁ OH)	Wako	Japan	Liquid
1-dodecanol (C ₁₂ H ₂₅ OH)	Wako	Japan	Liquid
1-tetradecanol (C ₁₄ H ₂₉ OH)	Wako	Japan	Solid
1-cetanol (C ₁₆ H ₃₃ OH)	Wako	Japan	Solid
Benzoyl peroxide	Wako	Japan	Solid
Maleic anhydride	Wako	Japan	Solid
Methyl-methacrylic acid	Merck	Germany	Liquid
p-toluene sulfonic acid	Wako	Japan	Solid
Hydroquinone	Wako	Japan	Solid

The biodiesel was received from the Key Laboratory of Bioenergy development, VNU, University of Science, Hanoi. It was made from waste cooking oil with a conversion of 98%, moisture content of 400 ppm, and solidifying temperature (pour point) of 12°C [8].

2.2. Preparation methods

Synthesis of alkyl methacrylate monomer:

Alkyl methacrylate is synthesized by the reaction as described in Scheme 1:



Scheme 1. Preparation of alkyl methacrylate monomer.

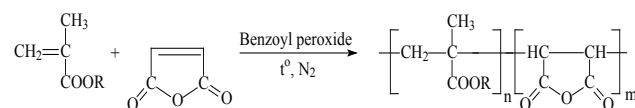
Where R is alkyl chains in alcohol (R=C₁₀H₂₁-, C₁₂H₂₃-, C₁₄H₂₉- and C₁₆H₃₃-).

To obtain a methacrylate monomer, alcohol reacts with methacrylic acid. The reaction was carried out in a three-necked and round-bottomed flask. A Dean - Stark trap was used to remove water. Toluene was used as a solvent and hydroquinone as an inhibitor. P-toluene sulfonic acid served as a catalyst. The molar ratio of alcohol to methacrylic acid was 1.0/1.1. The reaction proceeded for 6 h. After the reaction was completed, toluene was distilled off. Then, the reaction mixture was neutralized with a saturated sodium bicarbonate solution to a pH=6.5-7.0. The excess acids and catalysts were removed by washing the mixture with distilled water three times. The upper

organic layer was separated and collected. The obtained ester was dried by sodium sulfate and next by vacuum drying for 6 h. The prepared monomers had a colour from light-yellow to brown-yellow. The yield of the reaction ranged from 75 to 80%.

Copolymerization of alkyl-methacrylate with maleic anhydride:

The copolymerization reaction is described in Scheme 2:



Scheme 2. Synthesis of AMA copolymers.

Maleic anhydride and alkyl methacrylate were completely dissolved in toluene. After that, benzoyl peroxide (1 wt. %) was added to the reaction mixture. The reaction mixture was bubbled with nitrogen for 10 min, stirred vigorously, and heated to 90°C. The reaction proceeded for 4 h. The resulting copolymer was purified by the precipitation of its toluene solution with excess methanol. After filtration, the product was dried in a vacuum oven at 40°C for 6 h. The yield of the reaction ranged from 75-90%.

2.3. Research methods

Infrared spectroscopy (FTIR): Infrared spectroscopy was used to detect the presence of functional groups in the research compound, thereby contributing to its structural confirmation. An FT/IR-6300 spectrometer was used to record the FTIR spectra in the wave range of 600-4000 cm⁻¹ and with a resolution of 4 cm⁻¹.

Proton Nuclear Magnetic Spectroscopy (¹H-NMR): Proton NMR spectroscopy is an effective tool to confirm the structure of research compounds. A Bruker Avance 400 MHz FT-NMR spectrometer was used to record the NMR spectra. CDCl₃ and DMSO-d₆ were used as solvents. TMS was used as an internal standard.

3. Results and discussion

3.1. FTIR spectrum of alkyl methacrylate and maleic anhydride copolymer

The structure of all alkyl methacrylate - maleic anhydride copolymers were proven by the FTIR spectra. The FTIR spectra of the four studied copolymers (denoted AMA-10, AMA-12, AMA-14, and AMA-16) look similar to one another. Fig. 1 shows the IR spectrum of AMA-10. It can be seen that the bands at 1845.8 and 1780.3 cm⁻¹ are due to >C=O of the anhydride groups. The strong

peak at 1722.43 cm^{-1} is due to $>\text{C}=\text{O}$ of the ester groups. The vibration of the C-O bond in the ester group absorbs at 1165 cm^{-1} . The stretching vibration of C-H (in CH_3 and CH_2) corresponds to the bands at 2852.72 , 2920.23 , and 2954.95 cm^{-1} . A summary of important signals of the groups in the expected copolymers is given in Table 2. We see that all typical groups in the alkyl-methacrylate-maleic anhydride copolymers are fully characterized by FTIR spectra.

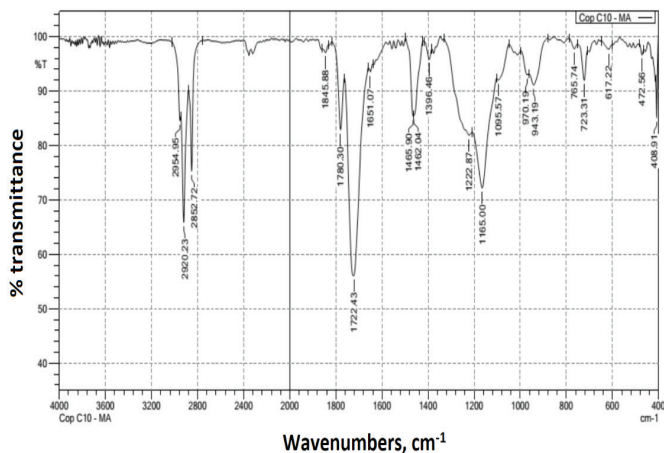


Fig. 1. IR spectrum of copolymer AMA-10.

Table 2. Typical peaks of copolymers of in FTIR spectra.

Group	AMA-10 (cm^{-1})	AMA-12 (cm^{-1})	AMA-14 (cm^{-1})	AMA-16 (cm^{-1})
C=O of ester	1722.43	1722.43	1732.08	1731.09
Stretching vibration of C-O bond in ester	1165	1149.57	1165	1150.55
C=O of MA	1780.30 1845.88	1780.30 1847.81	1772.58	1775.07 1846.36
Stretching vibration of C-H (in CH_3 and CH_2)	2852.72 2920.23 2954.95	2852.72 2921.16 2954.02	2852.72 2920.23 2953.02	2852.72 2921.18 2953.05

3.2. $^1\text{H-NMR}$ spectra of alkyl methacrylate - maleic anhydride copolymers

The structure of alkyl methacrylate - maleic anhydride copolymers is also confirmed by $^1\text{H-NMR}$ spectroscopy. For example, the $^1\text{H-NMR}$ patterns of the AMA-10 copolymer is given in Fig. 2 and all resonance signals are listed in Table 3. From Fig. 2, the methine protons ($-\text{CH}-$) of the maleic anhydride moiety appears at 2.689 ppm while the methylene protons ($-\text{CH}_2-$) of the alkyl chains appear at 1.291 ppm . The $-\text{CH}_3$ protons of the alkyl chains are seen at 0.906 ppm . The chemical shift

of 4.106 ppm belongs to the proton H of the methylene groups adjacent to the oxygen atom of alkyl alcohol. The proton adjacent to the methylene and connected with the oxygen atom of alkyl alcohol ($-\text{CH}_2-\text{CH}_2-\text{O}-$) shows a chemical shift of 1.639 ppm . Thus, the structure of the AMA copolymers is also confirmed by $^1\text{H-NMR}$ spectra.

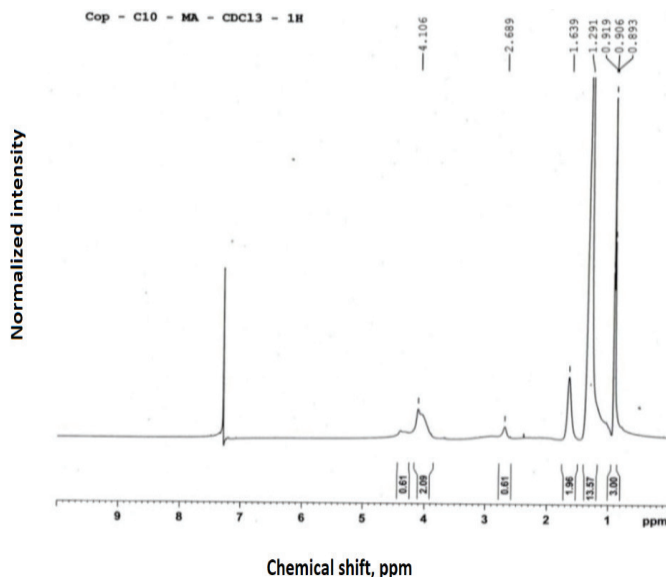


Fig. 2. $^1\text{H-NMR}$ spectrum of copolymer AMA-10.

Table 3. Typical peaks of AMA copolymers in $^1\text{H-NMR}$ spectra.

Groups	Denote	Peak (ppm)			
		AMA-10	AMA-12	AMA-14	AMA-16
$-\text{CH}_3$ (of alkyl chain)		0.906	0.813	0.655	0.803
$-\text{CH}_2-$ (in alkyl chain)		1.291	1.195	1.033-1.073	1.223
$-\text{CH}_2-\text{CH}_2-\text{O}-$ (acrylate)		1.639	1.552	1.384	1.549
$-\text{CH}_2-\text{O}-$ (acrylate)	δ_1	4.106	3.943	3.886	3.925
$-\text{CH}-$ (maleic anhydride)	δ_2	2.689	2.439	2.742	2.788

3.3. Determination of mol fraction of monomer units in copolymers

By controlling the molar ratio of the starting materials under the same conditions mentioned above, the AMA copolymers can be prepared. However, the real molar ratio of maleic anhydride (MA) in the copolymer product may not match that of the initial raw materials. Thus, determining the actual molar ratio of MA in the AMA copolymers is very important because that molar ratio can directly affect the copolymer structure and consequently affect their performance to improve flowability of liquid fuels. In this research, the FTIR technique was used to

determine the real compositions of the copolymers. To determine the MA and alkyl-methacrylate (AA) units in the AMA copolymer, FTIR spectroscopy method was used. The absorption bands for the characteristic groups are 1780 cm^{-1} (asymmetric C=O group of MA) and 1722 cm^{-1} (C=O group of methacrylate). By using the FTIR spectra, the mole fractions (mol.%) of the comonomer units (m_1 and m_2) in the AMA copolymers were calculated. For the calculation, the following equation was used [9]. The obtained results are shown in Table 3.

$$m_1 = \frac{A_{1780}/M_{MA}}{A_{1780}/M_{MA} + A_{1722}/M_{AA}}$$

$$m_2 = \frac{A_{1722}/M_{AA}}{A_{1780}/M_{MA} + A_{1722}/M_{AA}}$$

And $A = \log (I/T)$

where A =absorbance, T =% transmittance, and M_{MA} and M_{AA} are the molecular weights of MA and AA monomer units, respectively.

The real molar ratio of MA and AA in the copolymers was also calculated based on the $^1\text{H-NMR}$ signals using the following equation [10]:

$$\%MA = [S_2/(S_2+S_1)] \times 100$$

where S_1 and S_2 are the peak areas of the resonance at δ_1 ($-\text{CH}_2\text{-O-}$, alkyl methacrylate) and δ_2 (2H in $-\text{CH-CH-}$ of maleic anhydride), respectively. The results are shown in Table 4.

Table 4. Monomer mol fraction obtained by FTIR and $^1\text{H-NMR}$ analysis.

Copolymer	Monomer feed (mol.%)		FTIR results		NMR results	
	[MA]	[AA]	[MA]	[AA]	[MA]	[AA]
AMA-10	50.00	50.00	39.23	60.77	44.10	55.90
AMA-12	50.00	50.00	34.74	65.26	40.34	59.66
AMA-14	50.00	50.00	25.46	74.54	33.82	66.18
AMA-16	50.00	50.00	23.45	76.55	30.82	69.18

It can be seen from the Table 4 that, although the feed molar amount of the both MA and AA is equal, the molar fraction of MA in the copolymer is always less than that of AA. This is due to a difference in the reactivity ratios of MA and AA. As is well known, when the reactivity ratios of two monomers are different ($r_1 > 1$, $r_2 < 1$), the more active monomer will be more present in the resulting copolymer [11]. For the copolymer AMA, a reactivity ratio of AA is 3.10 meanwhile that of MA is 0.01 [12]. Thus, in the copolymer AMA, MA is present with less than its amount in the reaction mixture. The values in Table 4 also show that it is more difficult for maleic anhydride to react with the methacrylate molecules that have longer alkyl chains. This can be understood as follows: the methacrylate molecules have a high tendency to react with each other ($r=3.10$) and the longer alkyl chains create the environment of higher viscosity making it more difficult for maleic anhydride radicals to combine with methacrylate radicals.

Looking at the Table 4, it shows that the figures received from the FTIR and $^1\text{H-NMR}$ methods are different. This is understandable, because the nature of these two analysis methods is different. The question may be which method would be more accurate? In our case with copolymer AMA, it could be said that the $^1\text{H-NMR}$ method would be more accurate. The reason for this accuracy may come from the separation in peak of $^1\text{H-NMR}$ pattern in comparison with FTIR pattern. Two peaks of FTIR (1780 cm^{-1} and 1722 cm^{-1}) that were used for calculation are overlap each other (see Fig. 1). In contrast, two $^1\text{H-NMR}$ -signals for MA (2.689 ppm) and AA (4.106 ppm) distinguish to each other. Because of that, the results of $^1\text{H-NMR}$ method can be considered more accurate. However, the FTIR method is still useful if the chosen peaks for calculation are more separated. On a further note, the four copolymer additives obtained are copolymers with weak polarity. They are considered to be suitable for use as flow improvers for liquid fuel in general [13].

3.4. Molecular weight determination

The molecular weight of copolymers was determined by viscosity measurement. The solvent used was toluene. After the intrinsic viscosity $[\eta]$ was determined, the molecular weight of copolymers was calculated by Mark-Howink formula [14]:

$$[\eta] = K \cdot M^\alpha$$

where K and α are constants depending on the nature of the solvent and temperature.

In our case, $K=0.000078$ and $\alpha=0.697$ [14]. The results are presented in Table 5.

Table 5. Molecular weight of copolymers.

Copolymer	Molecular weight (g/mol)
AMA-C10	13190
AMA-C12	18549
AMA-C14	18896
AMA-C16	12084

In general, under the condition of the copolymer synthesis reaction as mentioned in the experimental section, the molecular weights of the copolymers are in the range of 12000 to 18000. Experiments show that the molecular weight of polymer additive is suitable for each specific oil in terms of flow improvement [15]. It is possible that the molecular weight range obtained above is suitable to improve the flow performance of biodiesel derived from waste cooking oil. It has been also shown that, both molecular weight and polydispersity index of polymer additives that significantly affect their ability to reduce the solidifying temperature of biodiesel [16] This

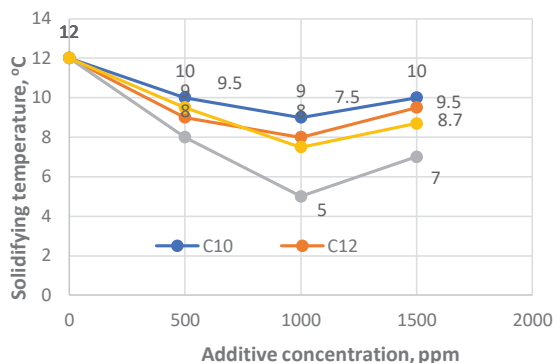
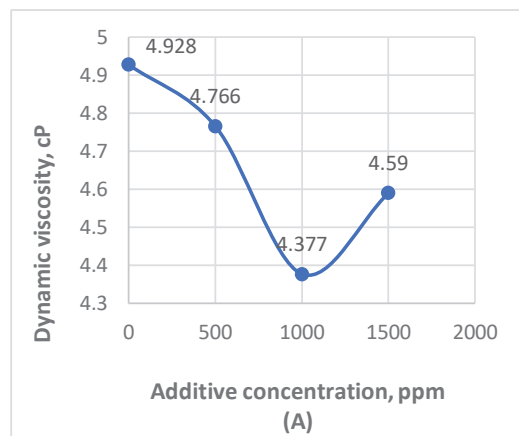


Fig. 3. Solidifying temperature of copolymers.



issue is very interesting and will be further investigated.

3.5. Determination of solidifying temperature of biodiesel

The determination of the solidifying temperatures (pour point) of oils complied with the procedure in ASTM D97-09 [17]. The pour point of the biodiesel was 12°C. As shown in Fig. 3, when adding the additives AMA-C10, AMA-C12, AMA-C14, and AMA-C16 at different concentrations, AMA-C14 had the best solid point depression (SPD=7°C, reduction from 12 to 5°C). According to [14], it is possible that the $n\text{-C}_{14}\text{H}_{29}$ - alkyl chain is an optimal fit to the composition of the wax in the biodiesel selected for this study. In the studies made by some authors on improvers for petro-diesel, similar results have been noted [18]. Fig. 3 also shows that the ability of additives to reduce the pour point of biodiesel strongly depends on their concentration. Thus, the four types of research additives tend to reduce the pour points as their content increases. Specifically, at an additive concentration of 1000 ppm, their pour points are the lowest, however, if their content continues to increase, the pour points tend to increase as well. This trend is understandable because increasing the contents of additives means reducing their solubility in biodiesel.

3.6. Determination of dynamic viscosity of biodiesel

Dynamic viscosity was determined according to the ASTM D445-11 standard using a Giltmol viscometer [19]. The results are shown in Fig. 4A. It can be seen that the viscosity decreases with increasing additive concentration until it reaches a minimal value of 4.377 cP at an additive concentration of 1000 ppm. As the additive concentration continues to increase, the viscosity decreases.

The increase of the additive concentration after reaching the threshold of 1000 ppm reduces their

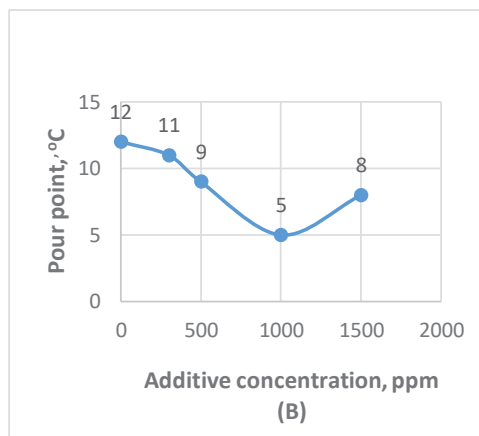


Fig. 4. The change in dynamic viscosity (A) and pour point (B) along with the change in additive concentration.

solubility in biodiesel, which results in the reduction of flow performance of biodiesel. This finding is supported by the variation trend of the biodiesel's pour point along with the change of additive concentration, as shown in Fig. 4B. Indeed, the variation of viscosity and pour point of biodiesel upon the change of additive concentration is completely similar.

4. Conclusions

Four copolymers based on maleic anhydride and alcohols containing the alkyl chains $C_{10}H_{21}$ -, $C_{12}H_{25}$ -, $C_{14}H_{29}$ -, and $C_{16}H_{31}$ - were developed. Their structure was confirmed by FTIR and 1H -NMR spectroscopy methods.

For the first time, these copolymers were studied for use as cold flow improvers for waste cooking oil-based biodiesel.

It has been found that the polymer additive with the alkyl chain $C_{14}H_{29}$ - showed the best flow improvement performance. This additive could reduce the pour point of a waste cooking oil-based biodiesel from $12^\circ C$ to $5^\circ C$ at a concentration of 1000 ppm.

The effect of the alkyl chain length, molecular weights, as well as the concentration of additives on the pour point of biodiesel was investigated.

CRedit author statement

Ngoc Lan Pham, Van Boi Luu: Data analysis and interpretation, Writing and manuscript revising; Thi Tuyet Mai Phan, Thi Son Nguyen: Method, Data analysis and Writing.

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COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

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