

Synthesis and modification of maleic anhydride-vinyl acetate copolymer by a long alkyl chain alcohol for cold flow improvers of biodiesel

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Abstract:

This research illustrates the results of a study on the synthesis of maleic anhydride-vinyl acetate copolymers (MAVA) with the monomer molar ratio of 1:1 by the radical polymerisation method in which benzoyl peroxide was used as a catalyst. The structure and composition of MAVA were characterised by FTIR, ¹H-NMR and ¹³C-NMR spectra. The molecular weight of the copolymers was determined by the viscosity method. The copolymers were then modified by the esterification reaction with hexadecanol - a long alkyl chain alcohol. The modified copolymer products (MAVAC) were used as additives to improve the cold flow properties of palm oil-based biodiesel through pour point temperature measurement according to standard ASTM-D97 and dynamic viscosity according to ASTM D445-97. The results showed that the MAVAC additives with the comb-shape structure at the concentration of 1000 ppm could decrease the pour point temperature of palm oil-based biodiesel by 5.5°C and dynamic viscosity by 0.17 cPs.

Keywords: additive, cold flow property, maleic anhydride-vinyl acetate copolymer, palm oil-based biodiesel.

Classification number: 2.2

Introduction

The study of producing biodiesel from non-edible oils, such as palm oil, rubber seed oil, waste cooking oil, animal fats, is a strategy of development in most countries in the world, including Vietnam. This biodiesel has the disadvantage of having poor flow properties at low temperatures. When the temperature drops, the monomethyl esters of fatty acids are separated in the form of either crystals or wax thus preventing the flow of oil which causes clogging of the fuel nozzle. This ultimately leads to a stop in the working of the engine [1, 2]. Numerous methods have been assessed for improving the cold flow property of biodiesel [3], including winterisation [4, 5], ozonisation [6], addition of cold flow improvers (CFIs) [7] and modification of the fatty ester composition [8]. Among these, the use of polymeric CFIs provides an effective and feasible approach that has been investigated in many studies [9-11]. Recent studies reported that copolymeric CFIs can remarkably improve the low temperature performance of biodiesel. These CFIs have chemical structures consisting of a hydrocarbon chain that is able to co-crystallise with the hydrocarbon chain of the fatty acids in biodiesel fuels and thereby affect the growth and nucleation of the wax crystals [12-14]. Using polymer additives to reduce the pour point temperature of biodiesel is the useful solution to this problem. In particular, copolymers with comb-shape structures prove most active [3, 9-11]. Copolymerisation is of great interest while synthesising polymers to obtain the desired physical and chemical properties by controlling monomer ratios, their concentrations and the polymerisation procedure [1]. However, the synthesis of copolymers with comb-shape structures, that consist of long and short branch chains which are arranged regular alternatively, is still a challenge for scientists [11, 15-17]. It is very important to be able to generate copolymers with regular alternative structures by choosing the pairs of monomers that contain

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a small copolymerisation constant (~ 0) [18]. Maleic anhydride (MA) is a unique comonomer because it does not readily undergo homopolymerisation, but forms copolymers without difficulty [14]. So, maleic anhydride (MA) and vinyl acetate (VA) have been selected [1, 14]. They have the copolymerisation constant $r_1 = 0.072$ and $r_2 = 0.01$, respectively ($r_1, r_2 = 0.00072 \sim 0$) [16, 18, 19], and so are able to generate copolymers with alternative structures, as desired.

Cold flow properties of biodiesel generally depend on fatty acid composition. The relative concentration proportion of saturated and unsaturated fatty acid methyl ester species in biodiesel may have a significant effect on the thermodynamics of nucleation and crystallisation under cold weather. Biodiesel derived from palm oil has a relatively high saturated fatty acid residue content, most of which is palmitic acid (C16), leading to pour point value in the range of 13-17°C [2, 14, 20]. So, it is essential to design suitable copolymeric CFIs that would be most effective in improving the cold flow for specific biodiesel.

In this research, combshape poly-(maleic anhydride-co-vinyl acetate) copolymers esterified with hexadecanol were synthesised. The effect of various of alkyl group/carboxyl group as well as the side chain length of CFIs on the wax crystallisation and the flowability of biodiesel was studied by measuring the pour point temperature and dynamic viscosity. Solubility of the synthesised copolymers in different solvents was investigated to identify whether there is an increase in their efficiency on palm oil biodiesel.

Experiment

Chemicals

The main chemicals used in this study include: Maleic Anhydride-MA (Merck), Vinyl Acetate-VA, Benzoyl Peroxide-BPO, p-Sulfonic Acid-PTSA (Wako, Japan), Cetyl Alcohol (Sigma Aldrich). The solvents include Methanol, Ethanol, Acetone, Toluene, Dimethyl Formamide-DMF (Merck). Monomethyl Ethyl Ketone-MEK (Prolabo), Palm oil Biodiesel from Palm oil of Vietnam [21].

Preparation methods

Synthesis of MAVA copolymer: MA and VA with molar ratio 1:1 [16, 18, 22] and MEK solvent (ratio of monomeric mass to volume of solvent is 30%, g/ml) were poured into a four-neck round-bottom flask, equipped with a reverse condenser, a thermometer and a N₂ gas pipe. N₂ gas was supplied for thirty minutes. Then, a solution of BPO (0.6% mass of monomers) in MEK (0.02 mmol) was prepared separately and added to the

above mixture. The mixture was heated with vigorous stirring. The reaction temperature remained at 80°C for six hours. When the reaction ended, the copolymer was precipitated three times with an excess volume of cold diethyl ether, then dried at a temperature of 50°C under vacuum pressure for six hours. The end product was solid with light pink-white colour.

The molecular weight of copolymers was determined by viscometry [18]. The reaction yield (H), molecular weight (M, g/mol), % mol of MA in copolymer unit and vibration wavenumbers of the copolymer are given in Table 1.

Table 1. Parameters and vibration wavenumbers of copolymer samples.

Sample	Mol ratio MA:VA	H (%)	M (g/mol)	% mol MA	Vibration wavenumbers (cm ⁻¹)
MAVA	1:1	75	22410	55	ν_{C-H} 2924-2853, $\nu_{C=O}$ 1730, ν_{C-O} 1244, ν_{C-O-C} 1033, ν_{C-H} 954
MA			98		ν_{C-H} 3125, $\nu_{C=O}$ 1853, $\nu_{C=O}$ 1777, ν_{C-C} 1627, ν_{C-O-C} 1059
VA			86		γ_{C-H} (-CH ₃) 1375, ν_{C-H} (-CH ₂) 1442, ν_{C-H} 2924-2854, $\nu_{C=C}$ 1646, $\nu_{C=O}$ 1772, ν_{C-O} 1222, ν_{C-H} 720

Esterification of MAVA copolymer: MAVA copolymer was esterified by hexadecanol with the mol ratio 1:1 based on molar portion of anhydride in copolymers [21]. Hexadecanol was dissolved in toluene to keep dry from water by azeotropic method. Solution of MAVA copolymers was added to the reaction flask. Finally, PTSA catalyst (1% mass of reactants) was introduced. The reaction was performed in 6h. The water formed during the reaction was separated by using the Dean-Stark trap. The reaction product was gained by precipitation with an excess volume of cold methanol. Next, the precipitate was dissolved two times with excess cold methanol. The pure modified MAVAC product was dried overnight at 50°C under vacuum pressure. The final product is a pale-yellow powder.

The yield, some physico-chemical parameters, the average molecular weight and the spectral data of the modified copolymers are given in Table 2.

The reaction yield (H), molecular weight (M, g/mol), % mol of MA in copolymer unit, and vibration wavenumbers of modified copolymer are given in Table 2.

Table 2. Parameters and vibration wavenumbers of modified copolymer samples.

Sample	H (%)	M	FTIR (cm ⁻¹)
MAVAC	83	39830	v _{C-H} 2922-2851, v _{C=O} 1857, v _{C=O} 1780-1734, v _{C=O} 1074, v _{C-H} 929, v _{C-H} 720

Determination of solidifying temperature for biodiesels: the pour point temperature with and without copolymer additives was measured according to standard ASTM D97 [23]. The modified copolymer was dissolved in a mixture of toluene and acetone with volume ratio 1:1. This additive solution was then added to the biodiesel at a certain mass fraction before it was poured into a test tube. The temperature of the test tube was slowly decreased by using a mixture of salt and ice. When the temperature of the sample was 9°C above pour point, we started to monitor it every 3°C. The determinant of pour point ends when laying the test tube horizontally in 5s but there is no emotions of biodiesel. The pour point is that temperature plus 3°C. The pour point of biodiesel without additives is got similarly to determining activity of the additive.

Determination of dynamic viscosity (μ) by using Gilmont viscometer: the dynamic viscosity (μ) of biodiesel with and without copolymer CFIs was measured by using Gilmont viscometer of Thermo Scientific Company (Faculty of Chemistry, HUS). It was measured at 40°C according to standard ASTM D445-97.

Research methods

Infrared spectroscopy (FTIR): FTIR spectra were recorded on FT/IR-6300 type spectrometer (Faculty of Chemistry, HUS). The spectra were scanned 32 times, with a resolution of 4 cm⁻¹, in the wave range of 600-4000 cm⁻¹.

Proton Nuclear Magnetic Spectroscopy (¹H-NMR): ¹H-NMR spectra were recorded on Bruker Avance 400MHz FT-NMR spectrometer (Faculty of Chemistry, HUS). The solvents used were CDCl₃ and DMSO-d₆. TMS was used as the internal standard.

Viscosity measurement method: the average molecular weight (M) of copolymers was determined by viscometry according to the Mark and Houwink-Sakurada equation [17]:

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

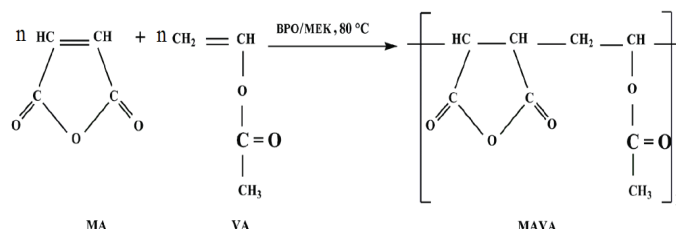
Where $[\eta]$ (dl.g⁻¹) is the intrinsic viscosity; M is the average molecular weight of polymers; K and α are characteristic constants for the used polymer-solvent systems. $K = 9,32 \cdot 10^{-6}$ dl/g và $\alpha = 0,94$ [22].

Intrinsic viscosity measurements were carried out using an Ubbelohde capillary viscometer having an internal diameter of 0.5 mm and a length of 10 cm. The flow times were recorded using a stopwatch.

Results and discussion

Synthesis of MAVA copolymer

The copolymerisation reaction scheme is described as follows:



Schem 1. Synthesis routine for the preparation of MAVA copolymer.

The structure of synthesised copolymers was confirmed by FTIR, ¹H-NMR and ¹³C-NMR spectra.

FTIR Spectra: FTIR spectrum of MAVA copolymer is given in Fig. 1, the spectral data are presented in Table 1.

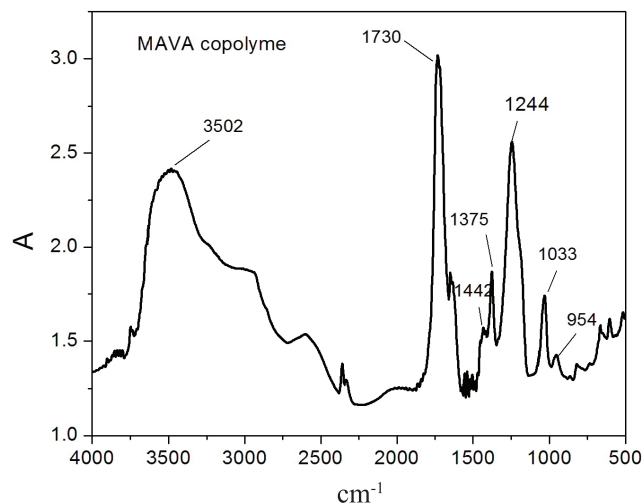


Fig. 1. FITR spectrum of MAVA copolymer.

As shown in Fig. 1, the deformation vibration in the plane of the C-H (in CH₃) of VA appears at 1375 cm⁻¹ [16], while the deformation vibration of C-H (in CH₂) appears at 1442 cm⁻¹. Carbonyl groups of both MA and VA have absorption peaks close to each other, thus forming a large and strong overlap peak at 1730 cm⁻¹. However, there was a shift of C=O peak to the lower frequency (compared to the C=O peak in the acid and esters). This could be due to the C=O of acetate group attracting electrons. This makes the H atoms

in the methyl groups more electron deficient and thus have the ability to create hydrogen bonds with oxygen atoms of the adjacent MA. The formation of hydrogen bonds did shift the peak to the lower frequency [24]. Besides, the presence of VA is also characterised by the appearance of vibrations of C-H at 954 cm⁻¹; the peak at 1244 cm⁻¹ is attributed to the vibrations of the C-O linkage [16]. The peak at 1033 cm⁻¹ corresponds to the vibrations of the C-O-C linkage in MA [16].

At the same time, it can be seen that the absence of characteristic spectral bands for scissing vibrations of linkage C=C of the monomers at 1646 cm⁻¹ (VA) and 1627 cm⁻¹ (MA) [16, 18, 19, 25] showed that the copolymerisation had taken place completely. It also showed that the copolymer product had high purity and contained no traces of residual monomers. So, the FTIR spectra confirmed the formation of MAVA copolymers.

¹H-NMR Spectra: the structure of MAVA copolymer was also confirmed by proton nuclear magnetic resonance spectroscopy. The ¹H-NMR spectrum of MAVA copolymer is indicated in Fig. 2.

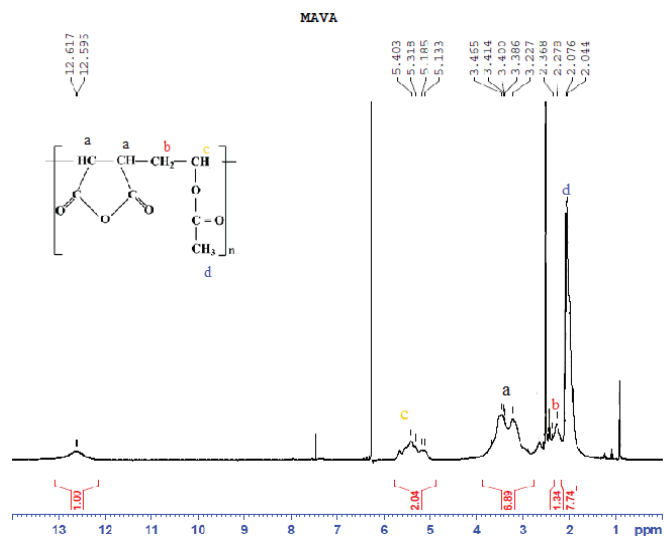


Fig. 2. ¹H-NMR spectrum of MAVA copolymer.

It can be seen that the peak at 5.1-5.4 ppm corresponds to the proton in CH, the peak at 2.04-2.07 ppm - to the protons of the CH₃, the peak at 2.27-2.36 ppm - to the protons of the CH₂ in VA, and the peak at 3.2-3.5 ppm - to the protons of the MA. So, as in the case of infrared spectroscopy, the ¹H-NMR spectra could also explain in full the chemical structure of MAVA copolymers. The MA monomer content in the MAVA copolymer was determined based on the ¹H-NMR spectral data according to the following equation [18]:

$$\%MA = \frac{\frac{S_a}{2}}{\frac{S_a}{2} + \frac{S_d}{3}} \cdot 100\% \approx 57\% \quad (1)$$

Where S_a, S_d are peak areas at 3.4 ppm and 2.07 ppm corresponding to the protons in -CH of MA and -CH₃ of VA, respectively.

It can be seen that by using the technique of slow drip of catalyst solution into the reaction mixture for 30 minutes, one can acquire MAVA copolymers with constituent monomer molar ratio that almost equals 1.

¹³C-NMR Spectra: ¹³C-NMR spectroscopy has been used to assert the alternative structure of the obtained copolymers (Fig. 3).

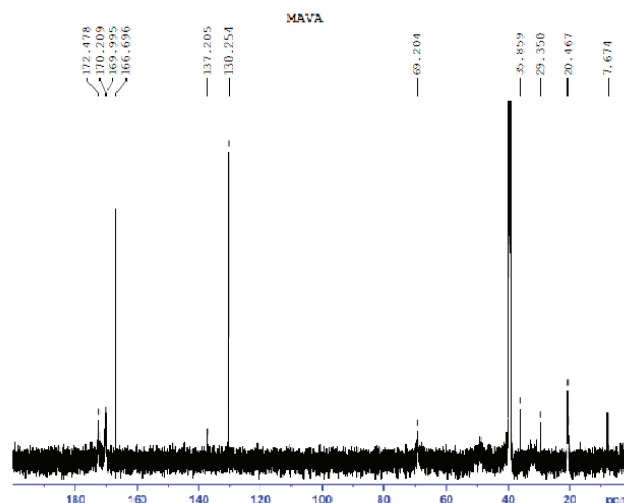


Fig. 3. ¹³C-NMR spectrum of MAVA copolymer.

From Fig. 3, the appearance of a peak at 172 ppm that belongs to carbon in the group C=O of VA and the dual peak at 170 ppm and 166 ppm for the two C=O groups of MA has asserted that the obtained MAVA copolymers had a regular alternative structure. Similar results were also announced in the work of Gabrielle, et al. [22]. The molecular weight of the MAVA copolymers determined by viscosity methods are presented in Table 1.

Study on the solubility of MAVA copolymer: the solubility of the synthesised MAVA copolymers influence the scope of the polymer's application, especially the ability to purify the product. Hence, the study on solubility of the reaction products is essential. A survey on the solubility of MAVA copolymers in different solvents has been conducted. Results are presented in Table 3.

Table 3. Solubility of MAVA copolymers in solvents.

Solvent		Soluble	Insoluble
Aprotic	Acetone	✓	
	DMF	✓	
	MEK	✓	
Protic	Methanol	✓	
	Ethanol	✓	
	Water	✓	
Non-polar	Toluene		✓

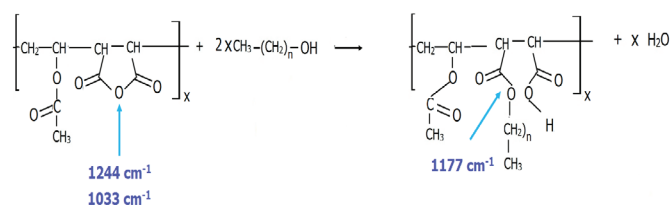
From Table 3, it is understood that the MAVA copolymers have the ability to dissolve in polar solvents. This is understandable, because the C=O in MA has a free electron pair, and due to the difference in electronegativity C=O can be polarising. Moreover, in the MAVA copolymers, CH₃COO-acetate groups also have polar C=O. Therefore, MAVA copolymer can dissolve in polar solvents and are insoluble in non-polar solvents such as toluene.

Based on the above results, acetone was chosen as a solvent to dissolve the MAVA copolymers in subsequent experiments.

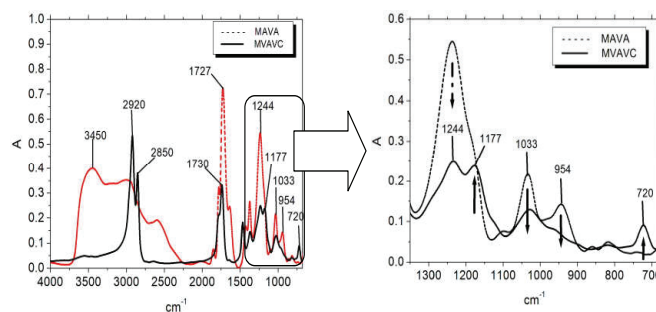
Modification of MAVA copolymers with hexadecanol

The structure and molecular weight of polymer additives have a great influence on the ability to improve cold flow properties of biodiesel. Additives having the comb-shape structure [1, 14, 18, 20], with long alkyl side chains and short chains alternative to each other embedded in the polymer main chains, demonstrated the ability to reduce the solidifying temperature of biodiesel.

The long alkyl side chains interact with long alkyl chains of methyl esters of fatty acids (FAME) in biodiesel, inhibits or slows the crystallisation process, thus prevents the formation of wax plates in biodiesel at low temperatures. According to this approach, the ring-opening reaction of MA in the MAVA copolymers has been conducted using hexadecanol, as shown in Scheme 2:


Scheme 2. Synthesis routine for the preparation of MAVAC.

The opening of the anhydride ring was confirmed by the decrease in IR peak intensity of the absorption bands at 1244 cm⁻¹ and 1033 cm⁻¹, characterising the vibration of the C-O-C linkage in the anhydride ring and the increase in intensity of peak at 1177 cm⁻¹ of the formed C-O- ester linkage (Fig. 4).


Fig. 4. FTIR spectra of MAVA and MAVAC.

Moreover, the presence of long alkyl chains (C16) of hexadecanol in the product was confirmed by the appearance of a new peak at 720 cm⁻¹ characterizing the vibration of the C-H in (CH₂)_n when n ≥ 4. The yield of esterification is relatively high about 83. The molecular weights of MAVAC copolymers determined by viscosity method are presented in Table 2.

Study on solubility of MAVAC copolymer: in order to find a suitable solvent that disperses additives into the biodiesel efficiently, the solubility of additives in different solvents was investigated. The results obtained are presented in Table 4.

Table 4. Solubility of MAVAC in solvents.

Solvent	Soluble	Insoluble
Toluene		✓
Acetone		✓
Toluene + acetone	✓	
Methanol		✓

From Table 4, it is understood that the MAVAC copolymer can be dissolved in a mixture of toluene and acetone (ratio of volume is 1:1), so this solvent mixture will be chosen to dissolve the polymer additives for biodiesel.

Test on flow property improvement of biodiesel: a test was conducted on the ability of the polymer additives to improve cold flow properties of palm oil biodiesel via the determination of pour point temperature and dynamic viscosity. The results are given in Table 5.

Table 5. Solidifying temperature (T) and dynamic viscosity (μ) of palm oil biodiesel with and without polymer additives at a concentration of 1000 ppm.

Samples	T(°C)	μ (cPs)
Palm oil biodiesel (BDF)	13.5	4.16
BDF + MAVA	14.0	4.20
BDF + MAVAC	8.0	3.99

The MAVAC copolymers can help to improve the cold flow property of palm oil biodiesel. For instance, the solidifying temperature of BDF containing MAVAC reduced by 5.5°C and dynamic viscosity by 0.17 cPs in comparison with the original BDF (see Table 5). At the same time, it showed that the MAVA copolymers did not have this ability; their presence barely increased both pour point temperatures and dynamic viscosity. As such, the results have proved that copolymers that have comb-shape structures, with long and short side alkyl chains arranged alternatively to one another, mainly determined the activity of the additives.

From this opens a prospect that one can design copolymer additives having regularly alternative structures from MA and VA. One can also adjust the number and the length of the branch chains for a specific biodiesel in order to achieve the best cold flow property improvement.

Conclusions

- The polymerisation of vinyl acetate with maleic anhydride was conducted with a monomer molar ratio of 1:1. The structure and compositions of the synthesised MAVA copolymers were characterised by FTIR, ¹H-NMR and ¹³C-NMR spectra. The molecular weight was determined by the viscosity method.

- The esterification of MAVA copolymers with hexadecanol was conducted. The modified MAVAC product was used as an additive for cold flow property improvement of palm oil biodiesel. It was able to reduce the pour point temperature of the obtained biodiesel by 5.5°C, and the dynamic viscosity by 0.17 cPs at 1000 ppm concentration.

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