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EFFECT OF ESTER-ADDITIVES ON THE CRYSTALLIZATION TEMPERATURE OF METHYL HEXADECANOATE

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Solid methyl esters of saturated fatty acids can cause technological problems when modified vegetable oils are used at low temperatures. In this work the effect of adding tailored substances to lower the crystallization temperature (T_c) of methyl hexadecanoate (PalMe) was studied. These substances were esters of carboxylic acids with linear or branched alkyl chains of up to 16 carbon atoms with alcohols having cyclic or branched alkyl chains or an alkoxy group. Results of DSC measurements have shown that the crystallization temperature of PalMe could be decreased by 10°C depending on the molecular mass, molecular structure and concentration of the additive. The best results were obtained using hexadecanoic acid derivatives.

Keywords: *alkoxy-ester, branched-chain ester, cyclohexyl ester, methyl hexadecanoate, methyl palmitate, temperature of crystallization*

Introduction

Recently, extended research has been carried out on new biodegradable, renewable functional fluids to use them as lubricants, biodiesel and cosmetics. In general, lubricants and biodiesel based on fatty acid esters of vegetable oil exhibiting excellent lubricating and combustion properties, although they may present excessively high viscosities at low temperatures. It is well known that the high crystallization temperature of the saturated fatty acid esters can lead to difficulties in pumping in low temperature applications. Methyl esters of saturated fatty acids containing more than 14 carbon atoms are solid at room temperature, which can cause problems during low temperature operations when a liquid material is required. One of them is methyl hexadecanoate, a constituent of several modified vegetable oils, which have been tested as potential biodiesel oil source [1, 2]. The necessity of eliminating this component or lowering its crystallization temperature is in the focus of many research papers dealing with the development of alternative energy sources. Some of them include freezing the oils and separating the liquid phase [3] or adding esters to the methylated ester oils [1]. The addition of a second modified vegetable oil to the main oil phase, e.g., to methylated soya oil, has decreased the crystallization temperature of the main phase. However, adding an entirely modified oil instead of a certain amount of a specific ester does not allow to draw conclusions on the most effective additive structure.

It is known that branched chain hydrocarbons have lower boiling and melting points compared to their linear-chain isomers. The same is valid for alcohols, acid and esters homologues [4]. This can be attributed to the fact that branches decrease the cohesive forces leading to lower melting and boiling points. Similarly, cyclic alkyl hydrocarbon groups are also known to interfere with the crystallization process of esters due to their bulky geometry [5]. The introduction of ether groups into hydrocarbon chains produces molecules with more flexible chain and this could have a similar effect compared to the introduction of a bulky group, resulting in weaker hydrocarbon interactions. The addition of esters with such structural features to methyl hexadecanoate would certainly interfere with the crystallization of the last compound. One could expect an effect either on the nucleation kinetics or on the rate of crystal growth, or on both. Several papers dealing with the effect of solid additives on the crystallization of organic compounds can be found in the literature. They are mainly addressed to the study of pharmaceutical formulation, but no work was found correlating the molecular structure of additive and its effect on the crystallization temperature of the main organic compound. A general survey on crystallization is given by Mullin [6] who recognizes that crystallization studies have not yet been unified under a general approach.

The objective of the present work is to verify the capacity of different series of ester-additives, containing the mentioned functional groups to decrease the crystallization temperature of methyl hexadecanoate – which was chosen as a model substance. DSC measurements were useful to follow the effect of additives on the crystallization temperature of macro components [7, 8].

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However, the present authors did not aim to explain the effect of additives on the mechanism of the crystallization processes.

Experimental

Materials

The alcohols and acids used for the ester synthesis had 98% purity as indicated by their suppliers. Some of the alcohols were distilled before their use. The purity of all reagents was checked using infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy. The used acids and their respective suppliers were: dodecanoic (lauric) and hexadecanoic (palmitic) from VETEC S.A., Brazil, *n*-octanoic from Aldrich, USA and 2-ethylhexanoic acid from Quimibras S.A., Brazil. The used alcohols were: 2-ethoxyethanol and methanol from VETEC S.A., cyclohexanol and 2-butoxyethanol from Quimibras S.A., 2-methoxyethanol from Merck S.A., Germany; 2-propanol, 2-methyl-1-propanol and 3-methyl-butanol from Quimibras S.A..

Preparation of esters

For the preparation of esters, the acids and alcohols were mixed in 1:10 mole ratios followed by the addition of *p*-toluene sulfonic acid (2% in relation to the mass of acid) catalyst. The solution was refluxed for 36 h. The mixture was then washed with sodium carbonate solution to eliminate any unreacted acid and soluble alcohols. Water insoluble alcohols were eliminated by distillation. The esters were characterized by FTIR spectroscopy using a Nicolet FTIR module, by ^{1}H and ^{13}C NMR (Brucker, model Avance 200, frequency 200 and 50 MHz frequencies respectively), in $CDCl_3$ solutions, by DSC (Perkin Elmer – DSC-7) applying a 10 K min^{-1} heating rate and dynamic nitrogen atmosphere. The synthesized esters are listed in Tables 1–4.

DSC measurements

Methyl-hexadecanoate and additive solutions were prepared in 0.1, 0.25 or 0.5 mole ratios of additive per mole of methyl-hexadecanoate. The solutions were prepared at room temperature and warmed up in a water bath to 60°C to ensure thorough mixing. Some

Table 1 Esters synthesized from 2-ethylhexanoic acid with branched alkyl chain alcohol – $CH_3(CH_2)_3(C_2H_5)CHCOOR'$, their respective codes, boiling temperatures (*BT*) measured by DSC, and molecular masses (*MM*)

Ester code	*R*'	*BT*/°C	*MM*/g mol^{-1}
EHISP	$–CH(CH_3)_2$	213	186
EHISB	$–CH_2CH(CH_3)_2$	227	200
EHISA	$(CH_2)_2CH(CH_3)_2$	240	214
EHEH	$–CH_2CH(C_2H_5)CH_2)_3CH_3$	287	256

Table 2 Esters synthesized from linear alkyl chain acid with branched alkyl chain alcohol – RCOOR', with their respective codes, boiling (*BT*) or melting temperatures (*MT*) measured by DSC, and molecular masses (*MM*)

Ester code	*R*	*R*'	*BT*/°C	*MT*/°C	*MM*/g mol^{-1}
C8ISP	C_7H_{15}	$–CH(CH_3)_2$	242	–	186
C8EH		$–CH_2CH(CH_2CH_3)(CH_2)_3CH_3$	296	–	186
C12ISP	$C_{11}H_{23}$	$–CH(CH_3)_2$	253	–	232
C12EH		$–CH_2CH(CH_2CH_3)(CH_2)_3CH_3$	303	–	232
C16ISP	$C_{15}H_{31}$	$–CH(CH_3)_2$	–	11	298
C16ISA		$–(CH_2)_2CH(CH_3)_2$	260	–	330
C16EH		$–CH_2CH(CH_2CH_3)(CH_2)_3CH_3$	–	2	372

Table 3 Esters synthesized from linear alkyl chain acids with alcohols containing an ether group: $RCOOCH_2CH_2OR'$ with their respective codes, boiling (*BT*) or melting temperatures (*MT*) measured by DSC and molecular masses (*MM*)

Ester code	*R*	*R*'	*BT*/°C	*MT*/°C	*MM*/g mol^{-1}
C8Me	C_7H_{15}	CH_3	250	–	202
C8EE		CH_2CH_3	272	–	216
C8BE		$(CH_2)_3CH_3$	294	–	244
C12ME	$C_{11}H_{23}$	CH_3	>290	–	248
C16ME	$C_{15}H_{31}$	CH_3	–	20	318

Table 4 Esters derived from linear chain alkyl acid with cyclohexanol, $RCOOC_6H_{11}$, and their respective codes, boiling or melting temperatures (*BT* or *MT*) measured by DSC and molecular mass (*MM*)

Ester code	*R*	*BT*/°C	*MT*/°C	*MM*/g mol^{-1}
C8Cyclo	C_7H_{15}	290	–	226
C16Cyclo	$C_{15}H_{31}$	–	16	342

mixtures solidified after cooling down to room temperature, and therefore they were warmed up in a water bath before DSC measurements. The sample masses were between 1.2–2.5 mg for better reproducibility. After calibration of the instrument using organic compounds (benzophenone, *m.p.*=48°C and cyclohexane, *m.p.*=6.5°C), duplicate measurements were done on the samples. The crystallization temperatures (T_c) were determined under N_2 atmosphere, after a first run from 0 to 50°C at a heating rate of 10 K min^{-1}, followed by cooling at the same rate, from 50 down to 0°C. The deviations of the T_c measurements varied between 0.1 to 0.6°C.

Results and discussion

The IR and NMR measurements were important to characterize the esters and as well as their purity. The IR and NMR spectra of the synthesized esters did not show the presence of impurities. The melting (if they could be determined) and/or boiling temperatures of esters determined by DSC are summarized in Tables 1–4.

The crystallization curves obtained for pure methyl-hexadecanoate (PalMe) and for mixtures of the additive 2-ethylhexyl-hexadecanoate (C16EH) with PalMe in three different ratios are shown in Fig. 1.

The effect of the additives at different concentrations on the crystallization behaviour of methyl-hexadecanoate (PalMe) was examined according to the differences in their molecular structures.

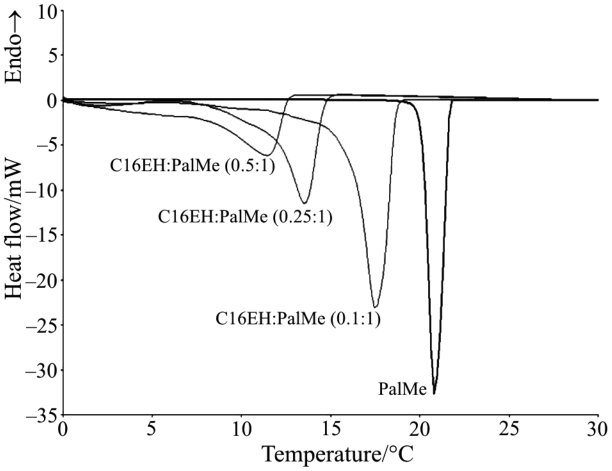

Fig. 1 DSC curves of pure PalMe, and mixtures of 2-ethylhexyl-hexadecanoate (C16EH) and PalMe with three different ratios

Effect of additive concentration

The crystallization temperature of the pure methyl-hexadecanoate (PalMe) is 22.5±0.5°C, under the applied experimental conditions. All additives decreased the crystallization temperature of PalMe. This effect was more pronounced as the concentration of the additives increased, as it can be observed in Figs 2, 3, 5, 6 and 7. However, when these effects were compared with each other at a given additive concentration, (Figs 5 and 7), it was observed that the alkyl ester-additives decreased the crystallization temperature of PalMe in a higher extent than the alkoxy ester-additives. This difference can be attributed to the differences in polarity between these two ester-additive groups. It can be expected that an ester with a hydrocarbonic molecular structure will interact better with the hydrocarbon chain of methyl-hexadecanoate than a substance that has a more polar group, as in the case of the alkoxy esters. Due to their more polar structures, the esters of alkoxy alcohols would adsorb themselves less effectively on the surface of the methyl hexadecanoate growing crystals, consequently, interfering less with the crystallization process.

Effect of additives of branched chain alcohols and branched chain acid

The different effects caused by the esters derived from branched chain alcohols and 2-ethyl-hexanoic acid (Table 1) on the crystallization temperature of PalMe were compared (Fig. 2). 2-propanol, 2-methyl-1-propanol, 3-methyl-1-butanol, which have the branched chain at the same position, compared to the position of the alcoholic hydroxyl group, and differ by one carbon atom, besides 2-ethylhexanol, were used. The T_c *vs*. additive concentration plots obtained for the additives derived from the first three mentioned alcohols indicate a clear trend of decreasing T_c of PalMe with increasing molecular mass of the additives. The 2-ethylhexanol ester (EHEH) gave the best results, leading to a larger decrease of the T_c of PalMe for all additive concentrations. Perhaps the larger effect of EHEH can be attributed to the position and the size of the branched chain. While in the other additives the branch is a methyl group at the end of the hydrocarbon chain of the alcohol segment, in the 2-ethylhexyl-ester the branch is an ethyl group near the C–O bond. The branch near the C–O bond possibly produces a bulkier molecular structure than the methyl group at the end of the chain and that is more detrimental to the molecular organization necessary for the formation of PalMe crystals.

Effect of the branched chain compared to the linear chain in acid segment

The above series of branched chain alcohols were also used to prepare the esters of octanoic acid. This ester series (Table 2) was compared to the one derived from these alcohols and 2-ethylhexanoic acid (Table 1) in order to study the influence of chain branching in the acid segment on the T_c of PalMe, keeping the same number of carbon atoms. Comparing the effect of these two ester series, no remarkable differences were registered with respect to the effect of branched chain (ethyl hexanoate – EH) compared to linear chain (octanoate – C8) in acid segment of esters. One can state that 2-ethylhexyl-ethylhexanoate presented the largest effect (Fig. 3).

This result suggests that increasing the molecular mass of the ester-additive or the size of the branch of the alcohol segment is more effective in decreasing the crystallization temperature of PalMe than the branching of the acid segment of the ester.

Effect of the length of hydrocarbon chain in the acid segment of the ester

When the acid segment chain was increased from 8 to 16 carbon atoms, the effect of the chain size on the crystallization temperature of PalMe was examined for different types of alcohol (Figs 4–6). The studied alcohols were branched chain alcohols, alkoxy-alcohols and cyclohexanol (Tables 1, 2 and 4).

In Fig. 4, the effect of additives derived from the branched chain alcohols on the T_c of PalMe is shown. A well observable decrease of T_c occurred when the acid chain was increased from 8 to 16 carbon atoms, regardless if 2-propanol or 2-ethylhexanol was used.

Comparing the DSC results of PalMe mixtures and the additives prepared using the same acids and cyclohexanol or 2-methoxy ethanol, it was observed that hexadecanoate esters had the largest effect on the decrease of the T_c of PalMe (Figs 5, 6). This effect can be a consequence of a greater similarity between the structures using the same acid, which favours the interaction of additives with PalMe molecules. The greater effect of cyclohexyl-hexadecanoate over the alkoxy ethyl-hexadecanoate can be a consequence of another factor, namely the volume of the cyclohexyl group.

Effect of the length of hydrocarbon chain present in the alkoxy alcohol segment

The effect of esters derived from octanoic acid with different alkoxy alcohols (Table 3) were compared. The lengths of the alkyl chains of the alkoxy group of these alcohols were different. Comparing the results obtained with the octanoates of 2-methoxy-ethanol, 2-ethoxy-ethanol or 2-butoxy-ethanol additives (Fig. 7), it was observed that the additives having methoxy and ethoxy groups had the same effect while butoxy group had a smaller ability to influence the crystallization of PalMe. It is interesting to note that, apparently, for esters with alkoxy structures, the volume of the additive molecule does not have much influence on the additive capacity in reducing the crystallization temperature of PalMe.

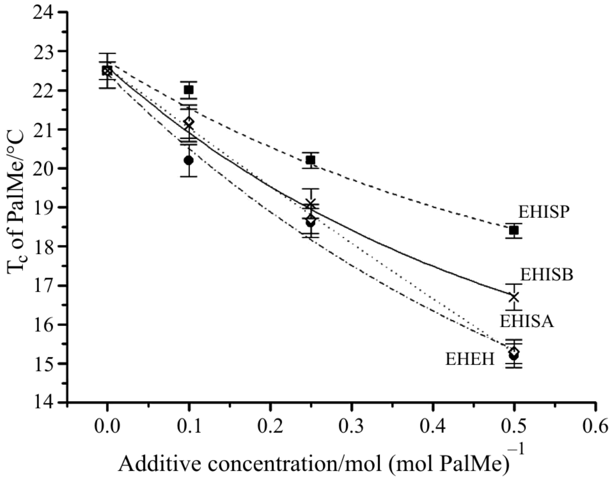

Fig. 2 Effect of esters synthesized from 2-ethyl-hexanoic acid (EH) and branched alcohols (Table 1) on the T_c of PalMe

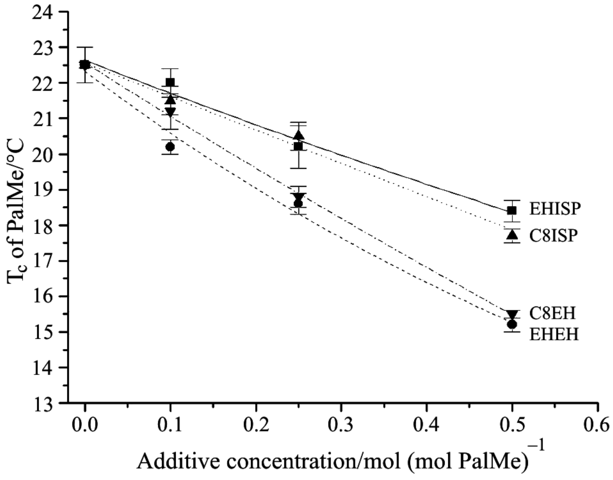

Fig. 3 The comparative effect between linear and branched acids having 8 carbon atoms (C8 and EH) with two different branched alcohols (Tables 1 and 2) on T_c of PalMe

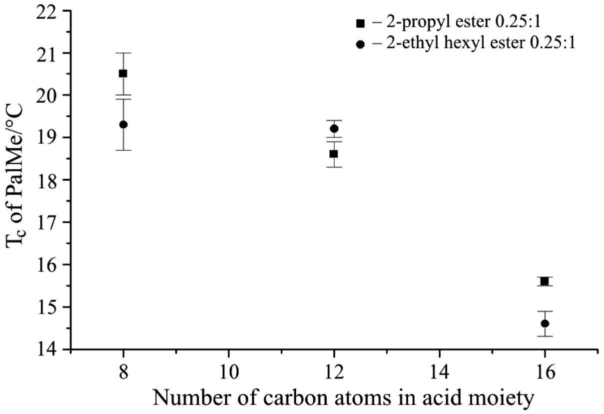

Fig. 4 Effect of the number of carbon atoms of the acid segment of 2-propyl and 2-ethylhexyl esters on the T_c of PalMe

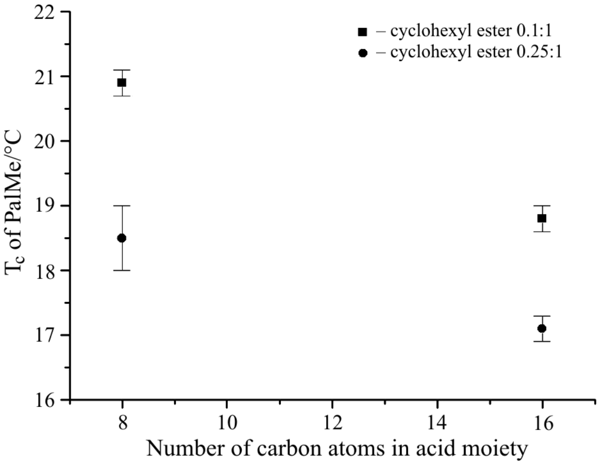

Fig. 5 Effect of the number of carbon atoms of the acid segment of cyclohexyl esters on the T_c of PalMe

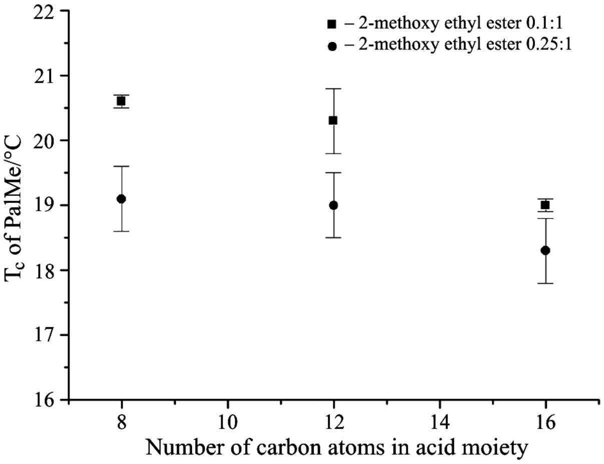

Fig. 6 Effect of the number of carbon atoms of the acid segment of 2-methoxy ethyl esters on the T_c of PalMe

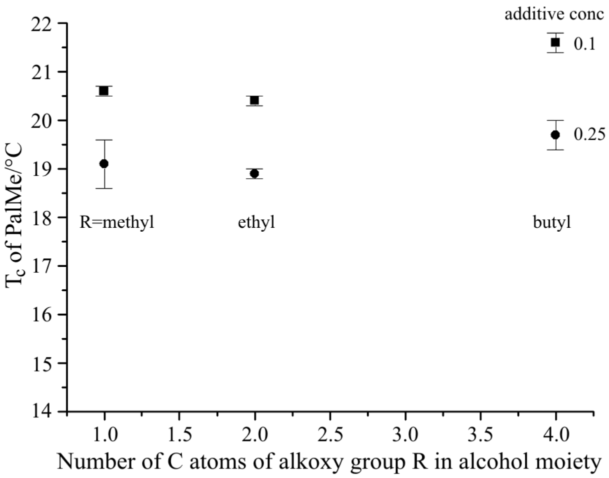

Fig. 7 Effect of the length of the alkoxy chain esters (R'COOCH$_2$CH$_2$OR) derived from octanoic acid on T_c of PalMe, at two different concentrations

The most effective additives

Considering the results obtained with additives at the lowest concentration (0.1:1), the most effective ester in depressing the T_c of PalMe among the branched alcohol derivatives (Fig. 2) was 2-ethylhexyl-2-ethylhexanoate (EHEH); the change of the branched-chain acid to *n*-octanoic acid (C8) did not cause significant variations of the T_c of PalMe. However, the combination of this alcohol (2-ethyl-hexanol) with a longer chain acid (C16) resulted the most significant shift in T_c towards lower temperatures.

Among the alkoxy-alcohol derivatives, there was no considerable difference in T_c of PalMe when the alkoxy segment was methoxy or ethoxy, but, combining with C16 acid, T_c decreased further. The same effect of the acid chain length was observed for cyclohexanol derivatives: the hexadecanoate gave the best result.

A plot of the molecular mass (*MM*) of the additives *vs*. T_c of PalMe (at 0.5:1 additive:PalMe molar ratio) is presented in Fig. 8. A good correlation was observed, showing that *MM* is indeed an important variable, but also indicating that each family of ester-additives follows a different curvature. This plot also highlights the difference in behaviour of the family of more polar additives – the esters derived from the alkoxy alcohols. One can conclude that among the investigated structures the presence of branched chains is one of the major influencing factor. A second one is the type of branching (the length of this alkyl chain and its position in the main chain). This plot also indicates that branching at the alcohol and acid segments of the ester (esters from Table 1) results in a higher decrease of T_c of PalMe than the simple branching at the alcohol segment (esters from Table 2).

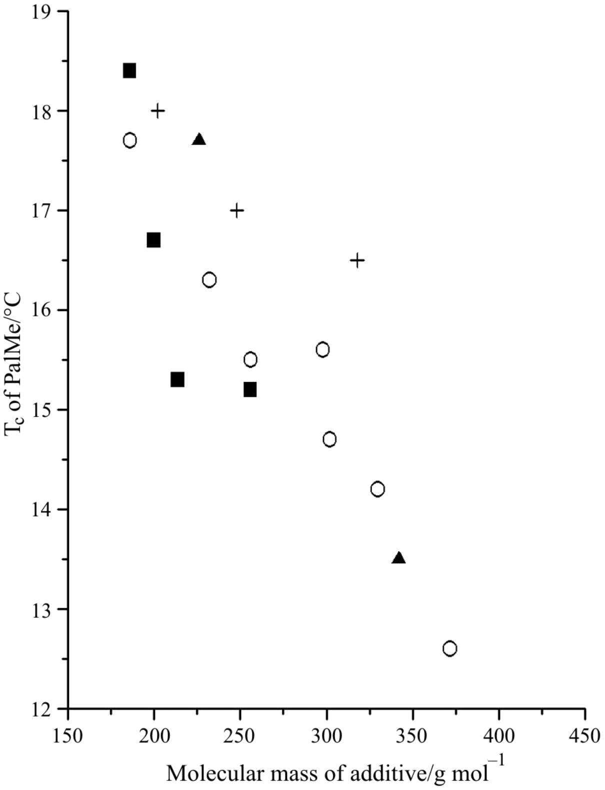

Fig. 8 Correlation between the molecular mass of the ester-additive and T_c of PalMe measured at 0.5:1 molar ratio of additive to PalMe: ○ – series of esters from linear acids and branched alcohols (Table 2); + – series of esters from linear acids and metoxyethanol (Table 3); ▲ – series of esters from linear acids and cyclohexanol (Table 4); ■ – series of esters from 2-ethyl-hexanoic acid and branched alcohols (Table 1)

Conclusions

As it has been expected, most synthesized ester-additives decreased the T_c of methyl hexadecanoate, general, from 1 up to 10°C, depending on the applied concentration. 2-ethylhexanol derivatives were the most effective among branched alcohol derivatives, but the few, originating from cyclohexanol were also effective. The length of the acid chain also affected the crystallization temperature of PalMe. The best combination was the hexadecanoic acid either with cyclohexanol or 2-ethylhexanol.

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