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STUDIES TO IMPROVE THE LOW TEMPERATURE PERFORMANCE OF PALM OIL PRODUCTS

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ABSTRACT

The objectives of this research were to find some additives suitable for reducing the pour points and cloud points of palm oil products and hence, improve their low temperature performance. All the additives used showed satisfactory results, with greater reduction in the pour points and cloud points in POME, PKOME, POMEPOo, POMESOo and PKOMESOo. The biggest depression in pour point was about 7.5ºC (addition of 1.0% DHFA to POMEPOo) and the biggest reduction in cloud point about 10.5ºC (addition of 1.0% DHFA and 1.0% PP to POME).

Keywords: pour point depressant, cloud point, palm oil, palm oil methyl esters, cold stability.

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INTRODUCTION

Palm oil is one of the most important revenue earners for Malaysia. Malaysia currently accounts for 47.9% or 11.9 million tonnes, of the world palm oil production, making it the world's largest producer. Of the 11.9 million tonnes of palm oil produced in 2002, some 91.4% of it was exported (MPOB, 2003).

The People's Republic of China was the leading export market for Malaysian palm oil in 2002, taking in 1 838 710 t (16.9% of total palm oil exports), followed by India with 1 676 580 t (15.4%), the European Union 1 497 466 t (13.8%), Pakistan 1 084 718 t (10.0%), Egypt 526 949 t (4.8%), Japan 427 208 t (3.9%) and Hong Kong 348 253 t (3.2%). Cumulatively, these countries accounted for 68.0% of total Malaysian palm oil exports in 2002 (MPOB, 2003).

The crystallization of palm oil results in formation of a cloud, sometimes observed as a white sediment at the bottom of the bottle. The presence of crystals is often seen as a defect by the consumers although there is actually no deterioration in the oil quality, it is just that the consumer wants a clear oil (Nor Aini *et al.*, 1993a , b; Siew and Ng, 1996; Siew, 1998; Teah and Ahmad, 1991).

According to Asadauskas and Erhan (1999), cloudiness, precipitation, poor flowability, poor pumpability and solidification are some of the common problems suffered by vegetable oils at low temperatures. Palm oil, which is more saturated than other vegetable oils, is the most affected. The poor cold stability of palm oil has limited its applications in among other things, cooking oil, salad oil, lubricant and biodiesel.

Some of the common methods used to enhance the use of palm oil and palm oil products at low temperatures are the adding of additives (known as pour point depressant, wax crystal inhibitor and cold flow improver) and blending with other more unsaturated oils (Siew, 1999). Of the two, additives is usually the preferred method as it is more economical.

MATERIALS AND METHODS

Materials

Eight palm oil samples were studied - palm olein (POo), super olein (SOo), palm oil methyl esters (POME), palm kernel oil methyl esters (PKOME), a mixture of POME and POo at 2:1 ratio (POMEPOo), a mixture of POME and SOo at 2:1 ratio (POMESOo), a mixture of PKOME and POo at 2:1 ratio

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(PKOMEPOo) and a mixture of PKOME and SOo at 2:1 ratio (PKOMESOo).

The additives used were Tween 80 (T80), dihydroxy fatty acid (DHFA), acrylated polyester pre-polymer (APP), palm-based oligomer (PP), a mixture of DHFA and PP at 1:1 ratio (DHFAPP), castor oil ricinoleate (COR) and an additive synthesized using DHFA and 2-ethylhexanol (DHFAEH).

Initially, the samples were characterized for their pour point, cloud point, viscosity, fatty acid composition, free fatty acid content and iodine value. The pour point, cloud point and viscosity tests were re-run after each addition of the additives to determine the effectiveness of the additives used.

Analyses

Pour point test. The method and apparatus for pour point measurements was based on the ASTM D97 test method.

Cloud point test. The cloud point test was performed using the AOCS Cc 6-25 (97) test method.

Viscosity test. The viscosities of the samples were analysed using a Brookfield Programmable Digital Rheometer Model DV-III. Only a small volume (0.5 ml) was needed to run the test. The spindle used was CP40. The temperature and speed were set at 40.0ºC and 150 rpm.

Other tests. The fatty acid compositions of the samples were determined using gas-liquid chromatography, with reference to the AOCS Ce 1-62 (97) standard method. The acid value of the samples was analysed using the AOCS Cd 3d-63(97) test method and the iodine value using the AOCS Cd 1d-92 (Reapproved 1997) standard method.

RESULTS AND DISCUSSION

Characteristic Studies

Table 1 shows the characteristics and properties of the samples before the addition of additives while *Table 2* shows their fatty acid compositions.

Most of the samples had high pour points and cloud points, except PKOME, PKOMEPOo and PKOMESOo. In order to have good low temperature properties, a sample should have a low pour point and cloud point, preferably below 0ºC.

The viscosities of all the samples were relatively low, except for POo and SOo. Viscous samples usually have poor low temperature properties. To enhance their use at low temperatures, a cold flow improver is usually added.

TABLE 1. CHARACTERISTICS AND PROPERTIES OF THE SAMPLES

Sample	Pour point/ºC (ASTM D97)	Cloud point/ºC [AOCS Cc 6-25 (97)]	Viscosity/ cP (40 ºC)	Acid value [AOCS Te 1a-64 (89)]	Iodine value [AOCS Cd 1d-92 (97)]
POo	9.0	11.5	29.5	0.5	53.8
SOo	6.0	5.0	20.1	0.7	61.8
POME	12.0	13.5	3.5	0.4	50.7
PKOME	-3.0	-1.5	2.7	0.8	17.1
POMEPOo	12.0	9.0	7.3	0.6	64.6
POMESOo	9.0	7.0	6.2	0.8	65.7
PKOMEPOo	-3.0	2.0	6.1	0.9	30.4
PKOMESOo	-3.0	3.0	6.1	1.1	32.5

Notes:
POo = palm olein.
SOo = super olein.
POME = palm oil methyl ester.
PKOME = palm kernel oil methyl ester.
POMEPOo = mixture of POME and POo at 2:1 ratio.
POMESOo = mixture of POME and SOo at 2:1 ratio.
PKOMEPOo = mixture of PKOME and POo at 2:1 ratio.
PKOMESOo = mixture of PKOME and SOo at 2:1 ratio.

TABLE 2. FATTY ACID COMPOSITIONS OF THE SAMPLES

Sample	Fatty acid composition (%)									
	C8	C10	C12	C14	C16	C18:0	C18:1	C18:2	C18:3	Others
POo	-	-	0.3	1.0	39.8	4.2	43.8	10.4	-	0.6
SOo	-	-	0.3	1.1	34.6	3.7	47.6	11.7	0.2	0.8
POME	-	-	0.2	1.0	43.9	4.5	39.9	9.6	0.3	0.6
PKOME	-	0.2	48.6	18.1	10.6	2.6	17.5	2.1	0.1	0.2
POMEPOo	-	-	0.3	0.9	32.7	3.9	47.9	13.1	0.3	0.9
POMESOo	-	-	0.3	0.9	30.7	3.8	49.4	13.5	0.4	10.2
PKOMEPOo	-	0.1	31.9	12.2	20.6	3.2	26.5	5.2	0.1	0.4
PKOMESOo	-	0.1	32.4	12.4	19.0	3.0	27.7	5.4	-	-

The determination of fatty acid composition is important in studying the crystallization behaviour of palm oil products. According to Siew (1999), the palmitic acid content should be below 35.0%, preferably below 31.0%, for palm olein to remain stable and clear.

Of the samples, only PKOME, PKOMEPOo and PKOMESOo had a palmitic acid content below 31.0%. The three, as expected, had better cold stability than the others with their lower pour points and cloud points.

Addition of 1% PP and 1% DHFA with 1% PP greatly lowered the pour point of POME, POMEPOo and POMESOo. For example, 1% PP and 1% DHFA with 1% PP depressed the pour point of POME from 12.0ºC to only 3.0ºC while the other additives had no effect at all.

POMEPOo and POMESOo recorded lower pour points with all the additives used. The pour point of POMEPOo was reduced from 12.0ºC to 3ºC.

Pour Point Analysis

Most of the additives produced satisfactory results. *Table 3* shows the effects of the additives on the pour points of the samples.

Addition of 2% T80, 1% DHFA, 1%APP, 1% DHFAEH and 1% COR did not have much effect on the pour points of most of the samples, except for POMEPOo and POMESOo. Almost all the samples only recorded a slight reduction of about 3.0ºC or no reduction at all in their pour points while the pour points of POMEPOo and POMESOo were successfully depressed by 6.0ºC to 9.0ºC. POMEPOo and POMESOo recorded reductions in their pour points by all the additives used. The pour point of POMESOo was reduced from 12.0ºC to 3.0ºC by all the additives except 1% PP while, all the additives greatly depressed the pour point of POMEPOo from 9.0ºC to 3.0ºC.

TABLE 3. EFFECTS OF THE ADDITIVES ON THE POUR POINTS OF THE SAMPLES

Sample	Pour point/°C							
	Without additive	+2% T80	+ 1% DHFA	+ 1% APP	+1% PP	+ 1% DHFA + 1% PP	+ 1% DHFAEH	+ 1% COR
POo	9.0	9.0	9.0	9.0	6.0	6.0	9.0	9.0
SOo	6.0	3.0	3.0	3.0	6.0	6.0	6.0	6.0
POME	12.0	12.0	12.0	12.0	3.0	3.0	12.0	12.0
PKOME	-3.0	-3.0	-3.0	-3.0	-3.0	-3.0	-3.0	-3.0
POMEPOo	12.0	3.0	3.0	3.0	6.0	3.0	3.0	3.0
POMESOo	9.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
PKOMEPOo	-3.0	-3.0	-3.0	-3.0	0	0	-3.0	-3.0
PKOMESOo	-3.0	-3.0	-3.0	-3.0	-3.0	0	-3.0	-3.0

TABLE 4. EFFECTS OF THE ADDITIVES ON THE CLOUD POINTS OF THE SAMPLES

Sample	Cloud point/°C							
	Without additive	**+2% T80**	**+ 1% DHFA**	**+ 1% APP**	**+1% PP**	**+ 1% DHFA + 1% PP**	**+ 1% DHFAEH**	**+ 1% COR**
POo	11.5	11.0	11.5	7.5	7.0	7.5	8.0	7.0
SOo	5.0	4.5	4.0	3.0	3.0	4.0	4.0	3.5
POME	13.5	10.0	6.5	6.5	6.5	3.0	8.5	8.0
PKOME	-1.5	-5.0	-5.0	-6.5	-6.5	-5.0	-5.0	-5.0
POMEPOo	9.0	5.0	3.5	3.0	3.0	2.0	2.5	2.0
POMESOo	7.0	2.0	1.5	0.5	0.5	1.5	2.0	1.5
PKOMEPOo	2.0	1.0	0	1.0	0	-2.0	0	-1.0
PKOMESOo	3.0	-3.0	-3.0	-5.0	-4.5	-3.0	-3.0	-3.5

Cloud Point Analysis

Almost all the additives studied showed positive results for the cloud point. *Table 4* shows the effects of the various additives on the samples.

Addition of 2% T80 and 1% DHFA reduced the cloud points of POME, PKOME, POMEPOo, POMESOo and PKOMESOo. However, 1% APP, 1% PP, 1% DHFA with 1% PP, 1% DHFAEH and 1% COR performed better, with greater reductions in the cloud points of POo, POME, PKOME, POMEPOo, POMESOo and PKOMESOo.

T80 was less effective in lowering the cloud points of the samples than the other additives. For example, addition of 2% T80 to POME only lowered the cloud point of POME by a slight 3.5ºC while the other additives recorded depressions of 5.0ºC to 10.5ºC.

APP and PP, however, were the most effective in reducing the cloud points of the samples. The performances of both APP and PP were similar while the performance of DHFA was similar to that of DHFAEH.

Addition of 1% APP and 1% PP to POMESOo lowered the cloud point from 7.0ºC to 0.5ºC. Addition of 1% APP and 1% PP to PKOMESOo greatly lowered the cloud point by 8.0ºC and 7.5ºC, respectively.

The additives used were less effective in lowering the cloud points of POo and SOo possibly due to the molecular structures of POo and SOo. The molecules of POo and SOo, which are much bigger than those of POME and PKOME, could have hindered the additives from penetrating through to inhibit the crystallization. However, this has to be elucidated.

Viscosity Analysis

The analysis showed great increases in viscosity of POo and SOo with the additives. Some of the raised values were twice the initial values. For instance, the addition of 1% COR to SOo increased the viscosity from 20.1 to 44.2 cP, while addition of 1% DHFA with 1% PP to POo increased the viscosity from 29.5 cP to 42.2 cP.

Other samples, however, only recorded slight changes in their viscosities with the additives. *Table 5* shows the effects of the additives on the viscosities of the samples.

TABLE 5. EFFECTS OF THE ADDITIVES ON THE VISCOSITIES OF THE SAMPLES

Sample	Viscosity/cP							
	Without additive	+2% T80	+ 1% DHFA	+ 1% APP	+1% PP	+ 1% DHFA + 1% PP	+ 1% DHFAEH	+ 1% COR
POo	29.5	40.1	39.7	38.3	39.6	42.2	39.4	41.6
SOo	20.1	38.2	40.1	36.1	40.6	40.7	42.6	44.2
POME	3.5	4.1	4.3	3.8	4.0	5.2	4.9	9.1
PKOME	2.7	3.1	2.8	3.0	3.0	3.4	3.0	7.9
POMEPOo	7.3	7.9	8.5	9.2	9.1	8.9	8.4	13.3
POMESOo	6.2	7.6	8.6	8.7	8.2	9.1	8.6	13.3
PKOMEPOo	6.1	6.8	6.3	7.9	7.9	7.3	6.8	11.5
PKOMESOo	6.1	6.4	7.2	6.5	7.0	7.5	6.9	11.5

CONCLUSION

This research has shown that additives, particularly DHFA and PP, can be used to improve the cold stability of palm oil products.

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