Plasticising and Stabilising Effect of Novel Epoxidised Mee Oil on PVC

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SUMMARY

The plasticising and stabilising effects of novel epoxidised Mee oil (EMO) and its derivatives on poly (vinyl chloride) were investigated. Peroxymethanoic acid was used to epoxidise Mee oil and the product was characterised by FTIR, iodine value, and oxirane content. Solubility parameter values were also determined. Plasticising effects of PVC incorporating EMO were evaluated using tensile and mechanical properties as well as FTIR. It was found that substantial levels of 100% epoxidised oil derivatives of Mee oil ($E_{100}M$) could be added to PVC; typically about 50 phr $E_{100}M$ with 30 phr of DOP. It was observed that increasing levels of $E_{100}M$ with DOP enhanced the plasticising efficiency; flexibility, percentage elongation, softness, and MFI. The stability provided by EMO in terms of changes in elastic modulus during high-temperature ageing was modelled kinetically, and it was found that the kinetic model obeyed a law of the form:

$\ln (\log E_a - \log E) = kt + C$

Activation energy values for the change in elastic modulus of PVC suggest some degree of synergism between EMO and Ca/Zn stearate system. Clearly $E_{100}M$ may be regarded as an effective secondary plasticiser as well as a stabiliser; perhaps more so than the other oil derivatives of Mee oil.

Keywords: Poly(vinyl chloride) (PVC), Degradation, Activation energy, Stabilization, Mee oil

1. INTRODUCTION

PVC is a versatile material with an extensive range of applications[1]. It is one of the three most abundantly produced polymers and one of the earliest that was developed[2]. A plasticiser is a substance incorporated into a polymer such as PVC to increase its flexibility, softness, distensibility or workability[3]. The plasticisers are high boiling organic liquids with negligible volatility, suitably compatible with PVC[4]. Stabilisers are added to PVC to protect against degradation under the influence of heat and mechanical shear in processing and also to impart longevity to PVC products in service[5].

The most commonly used plasticisers are phthalates, which are esters of ortho-phthalic acid, and other main group of plasticisers are adipate esters

and trimellitate esters[1]. The use and application of these petroleum-derived plasticisers are controlled by several significant factors. Firstly, they are processed from a non-renewable source, and increased consumption of fossil fuel has led to the reduction of underground–based carbon resources. As a result, they are often expensive. Secondly, there is a growing concern about the toxicity and the migration of small plasticiser molecules from the polymeric packaging material to foodstuffs[7-10] and these plasticisers are suspected to disrupt human endocrine activity[6].

The use of natural oils in PVC formulations will address the crisis of fossil fuel depletion and the toxic effects of conventional plasticisers and stabilisers that are currently in use. In view of this, there are considerable

pressures imposed on researchers to work on these possible alternatives, which are derived from renewable raw materials that are non-toxic, plentiful and under-utilised as polymer additives. Epoxidised soybean oil is one such example identified for its stabilising/plasticising actions in the PVC industry[1,2,11,12]. A variety of vegetable oils whose physico-chemical properties and fatty acid composition are similar to soybean oil, are found in nature. Mee oil is of such a type, and it is produced by pressing seeds. The tree belongs to the family sapotaceae, and there are two major species of the genus, *madhuca longifolia* and *madhuca indica*. It is widely distributed in tropical forests. The uses of products of the Mee tree are still limited to some ayurvedic medical applications. Moreover, the concept of exploiting Mee oil in polymers is a novel idea since there are no records of its use in the plastics industry.

In the present study the plasticising/stabilising effect engendered by *Mee*

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oil is reported and discussed. Mee oil was characterised for its fatty acid profile and epoxidised to two different degrees of epoxidation using peroxy methanoic acid. The plasticising efficiency of Mee oil incorporated in PVC was evaluated and compared to a standard composition comprising PVC and DOP in terms of mechanical properties and FTIR studies. The stabilising effect of Mee oil on PVC was kinetically modelled by following the changes in mechanical properties on thermal aging. The inhibitive effect of Mee oil derivatives on the degradation of PVC was interpreted on the basis of the activation energies of the degradation process.

2. EXPERIMENTAL

2.1 Materials

Mee oil was obtained from D. Peiris & Co. Ltd, Colombo, Sri Lanka. Hydrogen peroxide was acquired from East Anglia Chemicals (40% w/v) and from Fisher Chemicals (30% w/v) and was standardised before use. Analytical reagent grade formic acid from Fisher Scientific UK, was used after standardisation. Four epoxidised Mee oil derivatives shown in **Figure 1** were prepared as described in our previous publication[13]. The fatty acid profile of oil was determined according to standard procedures[14] using a Varian star 1 GC-MS instrument. Iodine values and Oxirane oxygen content of oil and its derivatives were determined using standard methods[14]. A standard procedure[15] was used to evaluate saponification values of the oils.

The suspension homopolymer of PVC (ICI- K value of 65, ISO viscosity 125) was acquired from European Vinyl Corporation, UK. The standard plasticiser, di(2-ethyl)hexylphthalate (technical grade) was obtained from CIBA-Geigy (UK) Limited. Technical grade calcium stearate and zinc stearate were supplied by Fisher Scientific Ltd. All other chemicals and solvents were classified as technical grades and were used as received without further purification.

2.2 Preparation of Test Specimens

2.2.1 Mee Oil Derivatives as Plasticisers

A basic formula[3] (F_1) was used to prepare plasticised PVC samples, with varying amounts of plasticisers. Quantities are given in parts per hundred grams of resin (phr) as follows:

Formula F_1

Suspension homopolymer of K- 65	100
Dibasic lead phthalate(DBLP)	5
Calcium stearate	0.5
Plasticiser	Varying amounts

Batches based on 300 g of PVC were prepared. Ingredients were weighed to the nearest gram and hand mixed. The mixture was processed on a conventional laboratory-sized two-roll mill operating at 140 ºC until a coherent melt was obtained; the duration of this procedure was about 10 minutes. The fused PVC mixture was removed from the mill as a continuous sheet or as chunks of PVC and subsequently compression-moulded using a temperature and pressure of 150 ºC and 9266.5 kPa respectively, to form sheets of nominal dimensions 152.4 x 152.4 x 1.14mm.

The flow chart in **Figure 1** shows the various PVC samples prepared

Figure 1. Prepared Mee oil derivatives and PVC samples with respective oil derivative (Values given in each box denotes the ratio of DOP:Oil derivative used in formulation)
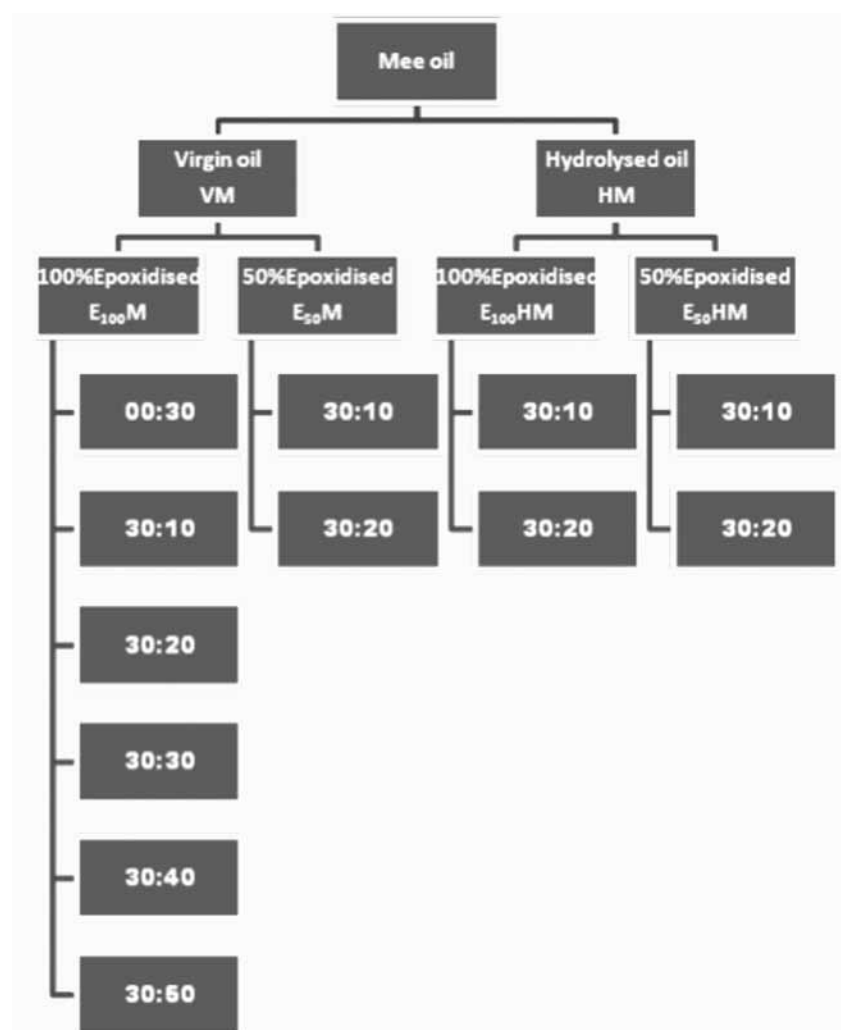
from each of the oil derivatives. The optimum level of oil derivatives that could be added in various PVC samples was based on trial and error using processing capability as the criterion. The ratio given in each box in the flow chart (see **Figure 1**) represents the ratio of DOP: oil derivative in phr. For convenience, each sample prepared was identified using an alphanumeric system as delineated in **Table 3.2**. Seven reference samples were also prepared under the same conditions with varying levels of DOP; for instance, 15, 30, 40, 50, 60, 75, and 90 phr.

2.2.2 Mee Oil Derivatives as Stabilisers

The formula (F_2) used for the preparation of test samples is given below. Values are given in parts per hundred grams of resin by weight.

Formula F_2

PVC Suspension homopolymer of
K-65   100
DOP   50
Stearic acid   1
Standard stabilisers Ca/Zn
       stearates (1:1)   2 **or / and**
Mee Oil derivative as a stabiliser   5
and 10

Batches based on 300 g of PVC were prepared as described in 2.2.1. **Table 1** gives the nomenclature used to identify the samples. The control sample was prepared using only Ca/Zn stearates as the stabiliser, and it was labelled as **zero.**

2.3 Tensile Properties

A *TINIUS OLSEN* tensometer coupled with an extentiometer and Q-Mat software was used for the determination of tensile properties. Standard dump-bell shaped test pieces (A standard cutter of ISO37, type 2) were punched using a single stroke of a hand press from the compression-moulded sheets (prepared as in 2.2). Six specimens were tested from each sample, rejecting any specimens which did not break within the central parallel portion.

The tensometer settings used for the determination of stress-strain properties were as follows:

Load range   =   250 N
Extension range   =   150 mm
Gauge length   =   25 mm
Speed   =   5 mm/min
(25 mm/min in some instances)

2.4 Softness Number

Two-roll milled samples prepared as in 2.2.1 were punched using a circular die to produce circular blanks and compression-moulded in a button mould for 10 minutes at 150 °C under a pressure of 9266.5 kPa. In this way moulded circular buttons with a thickness range between 9.0 and 9.5 mm were obtained. Softness numbers were measured using a Wallace softness tester. Five measurements were made on each sample and the mean was taken as representing the softness number.

2.5 Melt Flow Index (MFI)

Samples prepared as in 2.2.1 were utilised to measure MFI by employing an Extruder Plastograph at 190 °C using a dead load of 2.16 kg. Five measurements were taken from each sample and the average value was taken as representing the MFI.

2.6 FTIR Spectrometry

FTIR spectra of all samples were obtained from a BRUCKER VECTOR-22 FTIR spectrophotometer interfaced with Brucker OPUS NT software. 64 scans were made, using a resolution of 2 cm^{-1}.

2.7 Static Heat Stability

Circular test pieces (30 mm diameter) were punched from the samples prepared in 2.2.1 placed in a circulating air oven maintained at 177 ±1 °C and allowed to age. In order to monitor the required degree of ageing, test-pieces were removed at intervals of 5, 10, 15, 30, 45, 60, 75, 90 and 130 minutes. The concomitant colour changes with the ageing process were observed using a Minolta spectrophotometer, as specified in section 2.8 below.

2.8 Colour Measurements

Gloss measurements of samples were made from a KONICA MINOLTA Multigloss -268 reflectometer. Five measurements were taken from the surfaces of each sample and the mean was recorded as representing the gloss value. The values recorded represent two angles of incidence, notably 20° and of 60°. A Minolta spectrophotometer was used for surface colour analysis under the following conditions:

Table 1. Samples prepared from Mee oil derivatives, the stabilising system and sample numbers

	Oil derivative	Formulation/Stabilising system	Sample number
Mee Oil	$E_{100}M$	$F_2 (E_{100}M)_5$	5.1
		$F_2 (E_{100}M)_{10}$	5.2
		$F_2 (E_{100}M)_5(Ca/Zn)_2$	5.3
		$F_2 (E_{100}M)_{10}(Ca/Zn)_2$	**5.4**
	$E_{100}HM$	$F_2 (E_{100}HM)_5$	6.1
		$F_2 (E_{100}HM)_{10}$	6.2
		$F_2 (E_{100}HM)_5(Ca/Zn)_2$	6.3
		$F_2 (E_{100}HM)_{10}(Ca/Zn)_2$	6.4
Standard		$F_2 ((Ca/Zn)_2$	0

Condition 1 Mode : L UV : 100%, Illuminant 1 : D65
Observer: 10° (Specular included (SCI))

2.9 Kinetic Studies

Tensile dumb-bells similar to those used for characterising the tensile properties were utilised for studying kinetic behaviour. In principle, the procedure involved ageing test-pieces over a range of temperatures (100,110, 120 and 130 ºC) and times, as described in our previous paper[13].

3. RESULTS AND DISCUSSION

3.1 Characterisation of Mee Oil and its Derivatives

Fatty acid compositions of oil evaluated by their GC-MS and other pertinent properties of oil are stated in **Table 2**. The epoxidation increases the polarity and the stability of vegetable oils improving their compatibility with polymers such as PVC. Four epoxidised oil derivatives were prepared as illustrated in **Figure 1** and products were characterised for their iodine value and oxirane content (see **Table 3**). Other physical properties such as density and molar mass were also determined. The fatty

acid profile of the oil and the general structure of each glyceride were taken into consideration when estimating the molar masses of the oils and their epoxidised products. Solubility parameters of oil derivatives were calculated from the molar attraction constant values *G*, using Small's equation (Equation (1)).

$$\delta = \frac{d}{M} \sum G \tag{1}$$

where δ is the solubility parameter, *d* is the density, *M* is the molar mass.

It is commonly observed that a non-polar polymer will dissolve in a liquid or a mixture of liquids having a solubility parameter that does not differ by more than ±1.8 $(cal\ cm^{-3})^{1/2}$ from that of the polymer[16]. The d values obtained for epoxidised oil derivatives were in good agreement with the miscibility criterion. Moreover, these values are comparable with those of conventional plasticisers such as di-2-(ethyl) hexylphthalate (δ =8.8) used in PVC formulations.

3.2 Plasticising Effect of Oil Derivatives

The effectiveness of plasticiser action is determined by the processing

characteristics, the optimum amount of oil derivative which can be incorporated without exudation and the permanency. The addition of vegetable oil derivatives is clearly a novel idea and hence there are no standard or similar formulations with which the present results can be compared. Therefore the performance of the Mee oil derivatives as a plasticiser was compared with samples containing a popular ester plasticiser, such as DOP according to the formula F_1. The formula (F_1) used in the preparation of test samples of PVC included the use of a very efficient general stabiliser, dibasic lead phthalate (DBLP) having a molecular formula $C_6H_4 (COO^-)_2 Pb^{2+}$.

Our first attempt in the present study was to prepare a sample with 30 phr level of **E100M** as a plasticiser. This effort proved to be futile due to the processing difficulties of the blend, and brittle properties were encountered with the compression-moulded product thus obtained. It is evident from this initial trial that none of the oil derivatives, when incorporated alone as a plasticiser, showed appreciable plasticising effect on PVC. However, favourable effects were observed when these oil derivatives were mixed with a minimum level of 30 phr of DOP. Therefore, an optimum level of DOP was always taken as 30 phr throughout the present study; with this optimum level fixed for DOP, various additional levels of oil derivatives were used in the preparation of all other samples. This implies that these oil derivatives could act as secondary plasticisers.

Three major tensile properties (E-modulus, tensile strength, and percentage elongation) were measured

Table 2. General properties and composition of Mee oil

Property	Mee oil	Percentage fatty acid composition
Appearance	Pale yellow	Palmitic acid (16:1) : 18
Specific gravity	0.9125	Stearic acid (18:0) : 25
Refractive index	1.4610	Oleic acid (18:1) : 40
Iodine value	62	Linoleic acid (18:2) : 17
Saponification value	195	Linolenic acid (18:3) : Traces
Viscosity (cP:21 ºC,30 rpm)	203	

Table 3. Characterisation of oil derivatives

| Oil derivative	Nature/ Colour	Density g/cm⁻³	Iodine value	Epoxidation %	Oxirane content %	Molar mass g/mol	Solubility parameter δ (cal/cm³)¹ᐟ²
$E_{100}M$	Yellow oil	**0.9396**	**14**	**78**	**3.64**	325.4	9.90
$E_{50}M$	Yellow oil	**0.9042**	**35**	**31**	**1.25**	320.0	10.06
$E_{100}HM$	Yellow oil	**0.9363**	**09**	**87**	**3.5**	288.4	8.44
$E_{50}HM$	Yellow oil	0.9201	**30**	**54.5**	**1.52**	284.5	8.48

for samples prepared with incorporation of different levels of oil derivatives. The results are shown in **Table 4**. If an oil derivative imparts a plasticising effect when mixed with a system already containing 30 phr of DOP, the percentage elongation of samples thus prepared should be higher than that of the sample prepared with 30 phr DOP alone. Similarly tensile strength and elastic modulus should be lower than that of the sample containing only 30 phr of DOP. Comparative results in **Table 4** shows that the percentage elongation of the samples designated with formula numbers 1,2.3, and 10, in which varying levels and types of epoxidised oil derivatives were incorporated with 30 phr level of DOP, was higher than the percentage elongation of the sample with formula number 12 (contains only 30 phr level of DOP). Tensile strength and elastic modulus of all samples were both lower in comparison to sample number 12, apart from the exceptional behaviour of E-Mod of sample 9. Furthermore, there was a decreasing trend of elastic modulus when the level of 100% epoxidised Mee oil was increased and this is the only Mee oil derivative that could be incorporated up to 50 phr level into PVC, without any processing difficulties. Furthermore, oil derivatives prepared by hydrolysis followed by epoxidation (numbers 8 to 11) showed poor performance both in properties and processing when incorporated in PVC with DOP.

Moreover, Melt flow indices (MFI) and softness numbers were measured on samples in which $E_{100}M$ is incorporated and the results are shown in **Figure 2** together with the corresponding values for F_1 $(DOP)_{30}$ and F_1 $(DOP)_{50}$. It was observed that MFI of the samples had increased when higher levels of the epoxidised oil derivative were incorporated. The highest value, 29, was observed for $F_1(DOP)_{30}$ $(E_{100}M)_{50}$. Increasing MFI by raising the level of oil derivative can be attributed to the reduction of crystallinity and diminution of entanglements of polymer chains,

Table 4. Mechanical properties of PVC blends prepared

No.	Formulation	Tensile stress (MPa)	E-Mod(MPa)	%Elongation
1	F_1 $(DOP)_{30}(E_{100}M)_{10}$	**19**	**16**	**193**
2	F_1 $(DOP)_{30}(E_{100}M)_{20}$	**15.2**	**11.3**	**188**
3	F_1 $(DOP)_{30}(E_{100}M)_{30}$	**20**	**15**	**208**
4	F_1 $(DOP)_{30}(E_{100}M)_{40}$	**7.4**	**6.6**	**140**
5	F_1 $(DOP)_{30}(E_{100}M)_{50}$	**4.5**	**5.1**	**111**
6	F_1 $(DOP)_{30}(E_{50}M)_{10}$	**11.4**	**8.8**	**170**
7	F_1 $(DOP)_{30}(E_{50}M)_{20}$	**11.2**	**24**	**94**
8	F_1 $(DOP)_{30}(E_{100}HM)_{10}$	**20.4**	**24**	**148**
9	F_1 $(DOP)_{30}(E_{100}HM)_{20}$	**11**	**156**	**50**
10	F_1 $(DOP)_{30}(E_{50}HM)_{10}$	**17**	**20**	**194**
11	F_1 $(DOP)_{30}(E_{50}HM)_{20}$	**5**	**63**	**108**
12	F_1 $(DOP)_{30}$	26.4	120	186
13	F_1 $(DOP)_{50}$	16.6	8.8	231

Figure 2. Variation of softness number and MFI with increasing the level of oil derivative
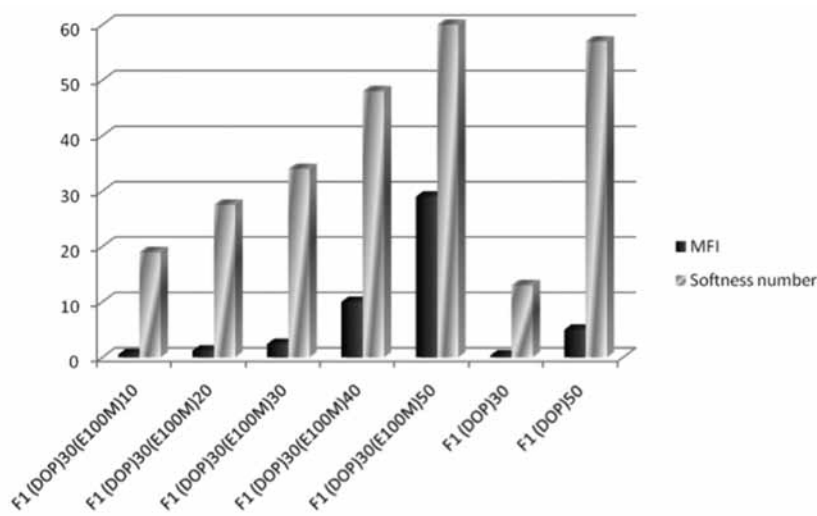
and hence reduction of the overall intermolecular forces between chains due to trapping of plasticiser molecules. In addition, it is also expected that if an oil derivative has fewer interactions with the polymer chains, when the chains are separated by the oil derivative, they move freely, resulting in a higher MFI value. Therefore it may be concluded that epoxidised Mee oil interacts to a lesser degree in PVC compared to that of DOP. Generally, as we would expect the softness number of plasticised PVC

increases with increasing plasticiser level. This trend was observed with samples prepared with $E_{100}M$, which suggests possible plasticising effects of the oil derivative (see **Figure 2**). Moreover the SN values obtained for $F1(DOP)_{30}(E_{100}M)_{10}$ were larger than that for $F_1(DOP)_{30}$, indicating the plasticising effect of the oil derivatives in PVC. Nevertheless, the corresponding SN value for $F1(DOP)_{30}(E_{100}M)_{20}$ was smaller than that of $F_1(DOP)_{50}$ even though the two samples contained

the same amount of plasticiser. This finding implies that the oil derivative (that is $E_{100}M$) has a lower plasticising efficiency relative to DOP.

It was observed that there was a significant variation of the carbonyl (C=O) stretching frequencies of FTIR spectra of the PVC samples containing different oil derivatives. Though there were slight variations in C-Cl stretching frequency, it was not considered significant among the samples prepared. Comparison of the change in carbonyl stretching frequencies between pure DOP, pure oil derivative and in the PVC matrix enabled us to assess the effectiveness of the interaction between oil derivatives and PVC. Carbonyl stretching frequencies obtained from the respective FTIR spectra for the samples, pure oil derivatives, DOP and so forth, are given in **Table 5**.

Change in carbonyl stretching frequency can be correlated to the extent of interaction of the carbonyl group with other groups in the matrix. Possible types of interactions may be dipole-dipole, van der Waals or intermolecular/ intra-molecular hydrogen bonding. Decreasing the C=O stretching frequency (red shift) compared to the pure compound indicates progressive weakening of the carbonyl bond, due to interactions of C=O group with other groups in the matrix. The stronger the interaction, the lower is the C=O frequency relative to the pure compound. On the other hand, if the frequency is shifted to a higher wave number (blue shift), the C=O bond is strengthened, thus reducing the strength of interactions with the carbonyl groups.

When comparing the changes in carbonyl-stretching frequency of pure DOP and other samples in **Table 5**, it was observed that in most cases, the wavenumber shifted to a lower value. In the case of $\mathbf{F_1(DOP)_{30}}$ and $\mathbf{F_1(DOP)_{50}}$, the change in carbonyl frequency was 4 ±0.5 cm^{-1}. The observed drop of the C=O stretching frequency is due

to the interaction of carbonyl groups in the plasticiser with PVC matrix, where dipole-dipole attractions were formed between the C=O groups of the plasticiser and C-Cl groups in PVC. A significant reduction of carbonyl stretching frequency, compared to that of the pure oil derivative, was observed in samples incorporated with $E_{100}M$. Furthermore, differences between stretching frequencies of the pure oil derivative and the PVC sample showed a lower degree of negativity with increasing levels of oil derivative in PVC. This suggests that interactions between oil derivatives and the PVC matrix became weaker when higher levels of oil derivatives were incorporated. As a result, the oil derivatives became less compatible and tend to exude from the material. Nevertheless, the relative position of the carbonyl group is controlled by the overall effect of interactions present in the matrix.

These observations lead to the conclusion that 100% epoxidised Mee oil could act as an effective secondary plasticiser.

3.3 Stabilising Effect of Oil Derivatives

3.3.1 Static Heat Stability
Four test samples were prepared from each oil derivative as described in section 2.2.2; **Table 1** summarises the composition and identities of each sample. To gauge the extent of

degradation it was necessary to include a reference sample in the present study; thus, the control sample contained only Ca/Zn stearates as the stabiliser which, for convenience, was labelled **zero.** The neutralisation effect of a stabiliser is primarily determined by its ability to prevent discoloration of PVC. In terms of discoloration (see **Figure 3a**), it was clear that the presence of oil derivatives had an inhibitive effect on thermal degradation of PVC. Moreover, the stabilising effect of $E_{100}M$ was significantly greater as compared with a standard metal soap stabilising systems (Sample 0) such as those based on Ca/Zn stearates. A synergistic effect was observed when both the metal soap system and the oil derivatives were used in combination. Standard Ca/Zn stearate system is stable only up to 30 minutes; thereafter degradation occurred with celerity through dehydrochlorination, resulting in the formation of a black brittle material at the latter stages of the degradation cycle. In passing, the reader should note that the appearance of the material changes from colourless to black under severe degradation. The black colour is due to the formation of conjugated polyenes and the concomitant hardening is due to extensive crosslinking between linear chains[5]. When only the oil derivative was incorporated as the stabiliser, the rate of degradation was reduced and there was no indication of surface blackening even after a period of 90 minutes. This observation suggests

Table 5. Change in carbonyl stretching frequencies in FTIR spectra

Sample	C=O Str.Freq/cm^{-1}	Difference with pure oil component	Difference with Pure DOP
Pure DOP	1724.07	-	-
F1(DOP)50	1720.3	-	- 3.77
F1(DOP)30	1719.62	-	- 4.45
$E_{100}M$	1741.45	-	
$F_1(DOP)_{30}(E_{100}M)_{10}$	1721.3	- 20.24	- 2.77
$F_1(DOP)_{30}(E_{100}M)_{20}$	1721.86	- 19.59	- 2.21
$F_1(DOP)_{30}(E_{100}M)_{30}$	1721.21	- 20.24	- 2.86
$F_1(DOP)_{30}(E_{100}M)_{40}$	1722.60	- 18.85	- 1.47
$F_1(DOP)_{30}(E_{100}M)_{50}$	1725.83	- 15.62	+1.76

that the oil derivative increased the induction time of the degradation mechanism. These results are further confirmed by the variation of lightness (L) with time. It may be deduced from **Figure 3b** that the rate of discoloration was significantly lower in all samples compared to the standard Ca/Zn stabiliser system (Sample 0) over a period of about 90 minutes.

3.3.2 Kinetics of Degradation of PVC Incorporating Epoxidised Mee Oil

Elastic modulus, tensile strength and percentage elongation at break, were measured for unaged and aged specimens at temperatures of 100 °C, 110 °C, 120 °C and 130 °C for samples prepared with 100% epoxidised Mee oil derivative (E100M); this oil derivative was chosen because it was identified as the most promising one, having good plasticising effects with effective stabilising action. Aging at each temperature was continued until the elastic modulus had reached a steady-state value. Force-extension variations of samples before aging and that for samples 5.2 and 5.4 with different times of aging at 130 °C are given in **Figure 4**. As regards values before aging, the lowest elastic modulus and

Figure 4. Force-extension variation of samples (a) Before aging, (b) At different times of aging at 130 °C
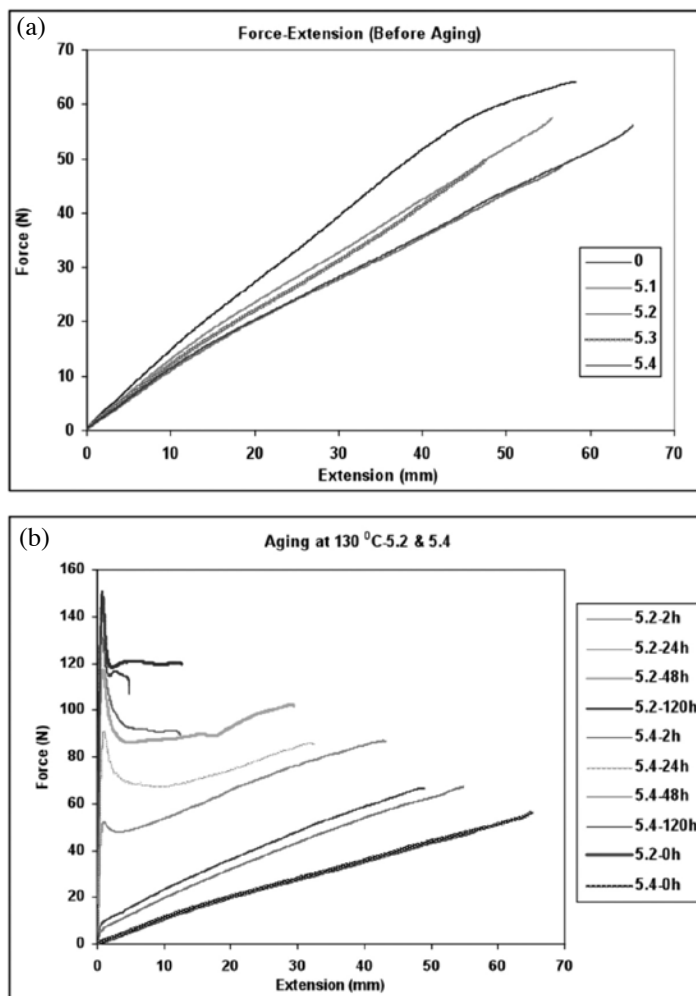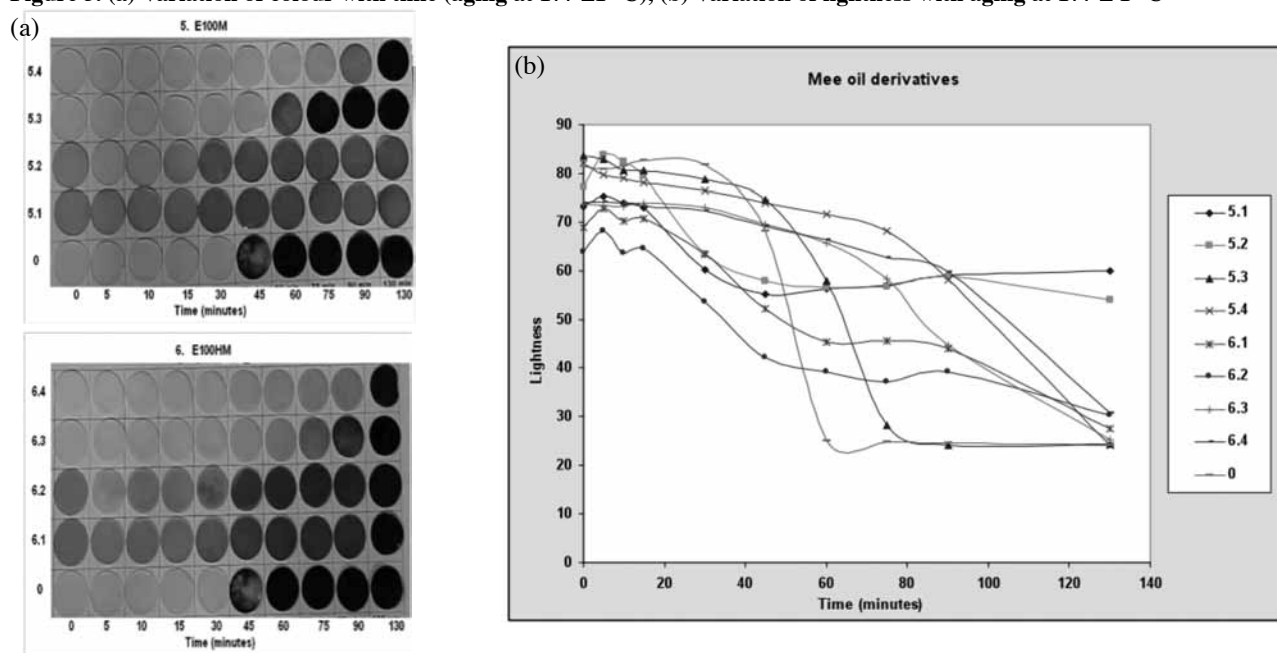

Figure 3. (a) Variation of colour with time (aging at 177 ±1 °C), (b) Variation of lightness with aging at 177 ± 1 °C

the highest elongation at break was exhibited by sample 5.4, in which Ca/Zn stearates and $E_{100}M$ (10 phr) were incorporated, while the lowest tensile strength was exhibited by sample 5.2. These observations suggest that the presence of EMO produces a positive plasticising effect on PVC. A reduction in tensile strength could be attributed to the weak interactions between PVC chains and EMO.

Figure 5 illustrates the variation of logarithm of elastic modulus with time of aging for all four temperatures; these significant relationships clearly provide an opportunity for modelling the behaviour kinetically. The relationships imply direct proportionality between the slope at any point on the curve and the difference between the asymptotic value of *log E* (log E_Y) and the *log E* value at the point at which the slope is taken.

That is,

$$\frac{d}{dt}(\log E) \propto (\log E_\infty - \log E)$$

This leads to the derivation of Equation (2):

$$\ln(\log E_\infty - \log E) = -kt + c \qquad \textbf{(2)}$$

where E = E- modulus
E_a = E-modulus at steady state
k = proportionality constant which can be considered as the rate constant
c = constant of integration

The form of equation 2 indicates linearity of a plot of *ln (log E_∞-log E)* against aging time *(t)*. The gradient *k*, confers the rate constant of the change in elastic modulus due to the degradation process.

Plots of *ln (log E_∞-log E)* against aging time *(t)* at different temperatures for the complete series of samples investigated are given in **Figure 6**. In all cases, smooth curves were drawn for plots of log *E* vs. time;

Figure 5. Variation of *Log E* with time of aging

(a)

(b)

(c)

(d)
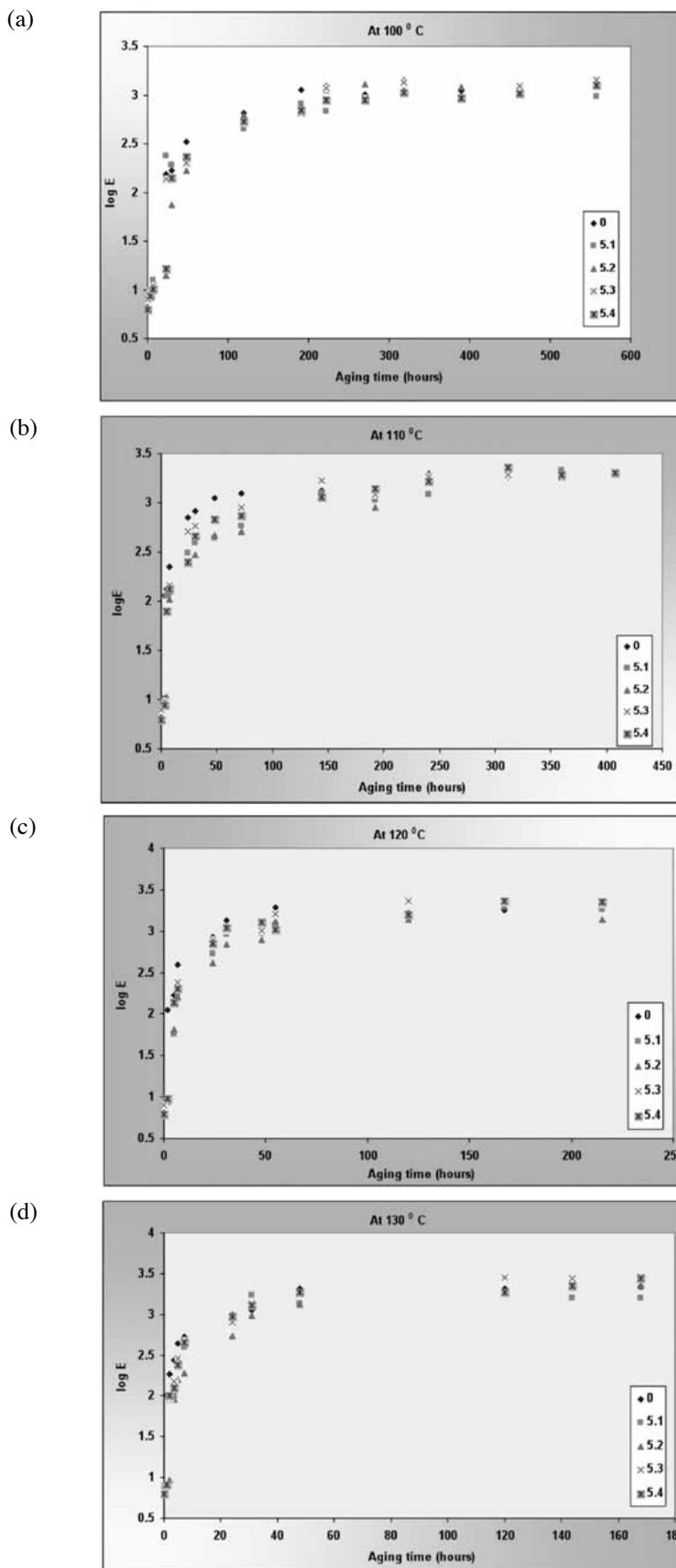
then by using these ideal curves, values of log E were interpolated at various times. As for log E_α, this represents the steady-state or plateau value of the plot of log E *vs.* time. log E_α values were easily identified and readily determined for traces that attained steady-state conditions. However, some curves were found to increase steadily with time and therefore extrapolation techniques, similar to those described in our previous paper[13], were employed to estimate log E_α values. All plots showed excellent agreement with Equation (4.2). The linear equations thus obtained, together with their R^2 values, are given in **Table 6**.

The temperature dependency of the rate constant is given by the Arrhenius equation (Equation (3))

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A \tag{3}$$

where k is the rate constant, T is the absolute temperature, A is the pre-exponential factor, R is the universal gas constant and E_a is the activation energy.

The Arrhenius plots were constructed with appropriate rate constants, and the activation energies and pre-exponential factors were calculated from the gradients and the intercepts respectively. The equations representing the Arrhenius relationship, the calculated activation energies and pre-exponential factors are given in **Table 7**.

The activation energy of a chemical reaction reflects the kinetic stability of any system. High activation energies are indicative of reactants being kinetically stable and may imply no reaction or a reaction taking place at a very slow rate. It is expected that the addition of a heat stabiliser to PVC should result in higher values of activation energy for dehydrochlorination; and, the more effective the stabiliser system,

Figure 6. Straight line plots obtained for the equation 2 for samples at four different temperatures
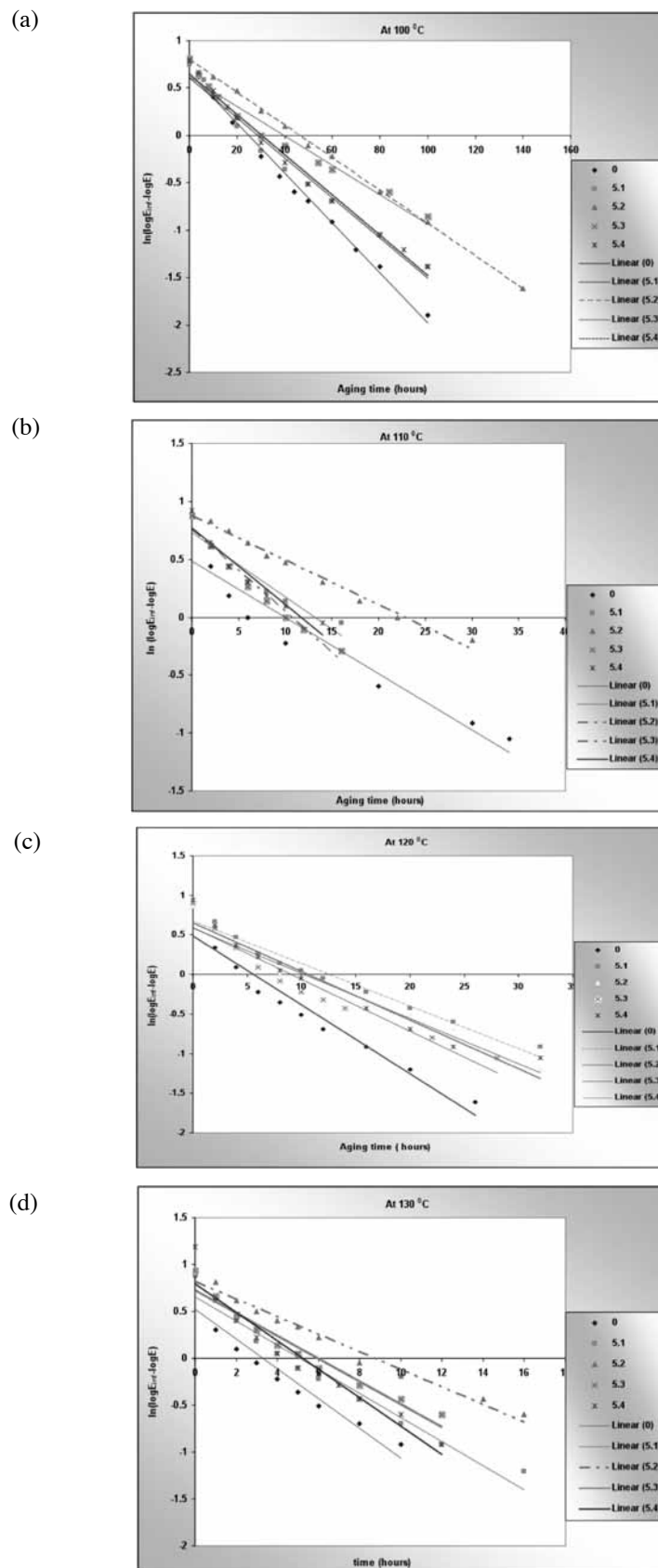
(a)

(b)

(c)

(d)

Table 6. Rate equations and rate constants at different temperatures

Temperature °C	Sample	Rate Equation $\ln(\log E_\infty - \log E) = -kt + c$	R^2 value	Rate constant (k) (hour^{-1})
100	00	Y = - 0.0264 x + 0.6602	0.9932	**0.0264**
	5.1	Y = - 0.0211 x + 0.6086	0.9791	**0.0211**
	5.2	Y = - 0.0172 x + 0.7945	0.9993	**0.0172**
	5.3	Y = - 0.0156 x + 0.6169	0.9610	**0.0156**
	5.4	Y = - 0.0214 x + 0.6595	0.9878	**0.0214**
110	00	Y= - 0.0486 x + 0.4819	0.9100	**0.0486**
	5.1	Y= - 0.0559 x + 0.7349	0.9092	**0.0559**
	5.2	Y= - 0.0383 x + 0.8729	0.9879	**0.0383**
	5.3	Y= - 0.0714 x + 0.7601	0.9684	**0.0714**
	5.4	Y= - 0.0662 x + 0.7333	0.9283	**0.0662**
120	00	Y = - 0.0869 x + 0.4834	0.9440	**0.0869**
	5.1	Y = - 0.078 x + 0.6781	0.9644	**0.0780**
	5.2	Y = - 0.0731 x + 0.68	0.9569	**0.0731**
	5.3	Y = - 0.0934 x + 0.7619	0.9618	**0.0934**
	5.4	Y = - 0.0971 x + 0.8434	0.9638	**0.0971**
130	00	Y = - 0.1592 x + 0.5252	0.9158	0.1592
	5.1	Y = - 0.1284 x + 0.6536	0.9638	**0.1284**
	5.2	Y = - 0.0938 x + 0.8196	0.9781	**0.0938**
	5.3	Y = - 0.1219 x + 0.7358	0.9536	**0.1219**
	5.4	Y = - 0.1515 x + 0.7968	0.9301	**0.1515**

Table 7. Linear relationships to Arrhenius plots, calculated activation energies and pre-exponential factors

Sample	Equation	R^2 value	E_a (kJ mol^{-1})	Pre-exponential Factor (hour^{-1})
0	Y=-8973 x + 20.4	0.9995	**74.6**	7.3×10^8
5.1	Y=-8678 x + 19.6	0.9566	**72.2**	3.1×10^8
5.2	Y=-8660 x + 19.3	0.9632	**72.0**	2.3×10^8
5.3	Y=-4127 x + 8.1	0.9999	**34.3**	3.4×10^3
5.4	Y=-9452 x + 21.7	0.9390	**78.6**	2.6×10^9

the higher the values of activation energy. In the present work the highest activation energy obtained was 78.6 kJ mol^{-1} when a 10 phr level of EMO and Ca/Zn system was used as the heat stabiliser. The activation energy obtained for the standard Ca/Zn system (sample 0) was 74.6 kJ mol^{-1}. It is important to note that all kinetic calculations were based upon the assumption that a single activation energy persists over the temperature range 100-130 °C; i.e., it was assumed that the activation energy was independent of the temperature in the present range.

From the data in **Table 7**, it is evident that the pre-exponential factors vary with the activation energies; this may be attributed to the occurrence of dissimilar mechanisms. However the compensation relation connected with pre-exponential factors is ascertained by the kinetic compensation effect according to Equation (4)[13]:

$$\ln A = \frac{E_a}{RT_{iso}} + \ln k_{iso} \quad (4)$$

where k_{iso} and T_{iso} are the isokinetic rate constant and the isokinetic temperature respectively.

In **Figure 7** the dependence of ln *A* *vs.* E_a is shown for the system under consideration; clearly an excellent linear relationship is observed. The relationships for the system may be represented by the following expression:

$$\ln A = 0.3031 E_a - 2.2973 \quad (5)$$

The isokinetic temperature; which may be regarded as the temperature at which the rate constants of all reactions of the series have the same value, was calculated from the gradient of the above equations (Equations (4) and (5)) and found to be 397 K (124 °C). Also, the calculated isokinetic rate constant from the intercept was 2.81×10^{-5} s^{-1}.

4. CONCLUSIONS

Overall analysis of the results concluded that the oil derivatives obtained from the direct epoxidation of virgin Mee oil performed better compared to oil derivatives obtained from epoxidation of hydrolysed products. This conclusion was supported by the evaluated solubility parameter values. It was found that 100% epoxidised oil derivative ($E_{100}M$) was the only oil derivative which could be added to high levels, typically 50 phr. The addition of high levels of $E_{100}M$ led to a gradual increase in the plasticising efficiency, flexibility, percentage elongation, softness, and MFI. It was found the values of the foregoing properties were enhanced by higher levels of $E_{100}M$. Therefore $E_{100}M$ may be considered as an effective secondary plasticiser; perhaps more so than the other oil derivatives. However, all the prepared oil derivatives could be added at levels of 10 phr to enhance the plasticising effect of 30 phr DOP, as confirmed by their tensile properties.

Figure 7. Kinetic compensation effect of EMO
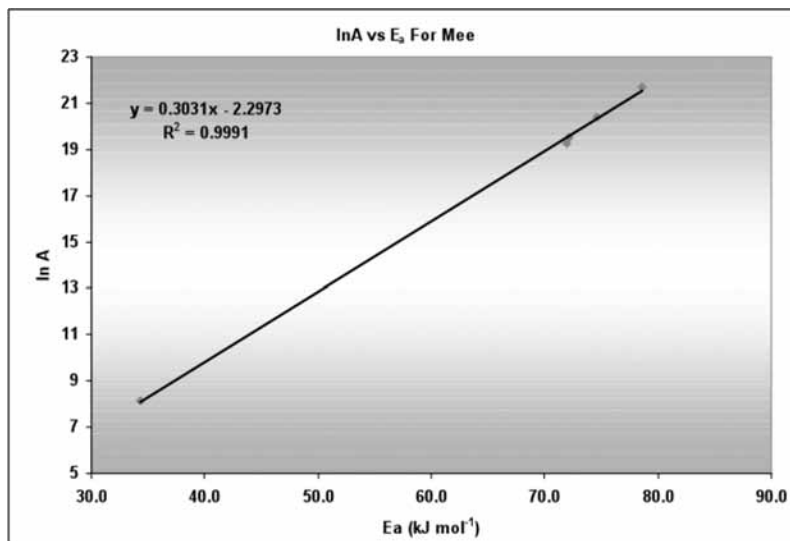
The present study was also concerned with investigating the effectiveness of Mee oil derivatives as heat stabilisers in PVC. Affiliated colour variation of the samples prepared under artificial aging conditions at 177 ± 1 °C showed that the stability engendered by EMO was very significant. The stability provided by EMO in terms of changes in elastic modulus during high-temperature ageing was modelled kinetically after having determined that the loss of plasticiser during degradation was negligible using FTIR. It was found that the kinetic model obeyed a law of the form ***ln (log E_a – log E) = kt + C***. Activation energy values for the change in elastic modulus of PVC suggested that 10 phr of ENO/and Ca/Zn system was capable of retarding the degradation of PVC, having the highest activation energy of 78.6 kJ mol⁻¹. The activation energy and pre-exponential factor were linked by the compensation relation describing the reaction ability of the system.

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