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Epoxidized Esters of Palm Kernel Oil as an Effective Plasticizer for PVC: A Study of Mechanical Properties and Effect of Processing Conditions

One of the most commonly used vegetable oil plasticizer in polyvinyl chloride (PVC) is epoxidized soybean oil (ESBO). On the contrary, epoxidized palm oil is among the least used, because of its low compatibility with PVC. This work reports that epoxidized and esterified palm kernel oil (EEPKO) has the potential to be used as a plasticizer for PVC. In this study, it was found that a maximum of 65 phr of EEPKO could be incorporated within the PVC resin. In addition, subjecting this EEPKO plasticized PVC (p-PVC) at a processing temperature of 200°C resulted in much reduced plasticizer loss. EEPKO lowers the glass transition temperature of PVC from 79°C to –23°C. The optimum mechanical properties, namely tensile strength, elongation at break and hardness, were obtained for p-PVC processed at 200°C.

1 Introduction

The ever increasing concern over the use of potentially toxic and often hazardous conventional plasticizers, such as bis(2-ethylhexyl) phthalate (DEHP), di(isodecyl) phthalate, di(undecyl) phthalate, undecyl dodecyl phthalate, di(2-ethylhexyl) adipate, etc (Storey et al., 1989; Semsarzadeh et al., 2002; Navarro et al., 2010; Ovchinnikov et al., 1971; Tawfik et al., 2006), in polyvinyl chloride (PVC) has led to considerable research into the possibility of using epoxidized vegetable oils as potential alternatives. For example, in many studies it has been described that conventional plasticizers are liable of producing carcinogenic, toxic and adverse effects, especially in animal and human tissues (Agarwal et al., 1989; Treinen and Heindel, 1992; Shea, 2003; Warren et al., 1982; Tickner et al., 2001). Moreover, the conventional plasticizers are petroleum based, and therefore, their long term availability is uncertain. As a result, over the last couple of decades several vegetable oils have emerged in the plasticizer and stabilizer market. These mostly include epoxidized soybean oil, sunflower oil, linseed oil and others (Bouchareb and Benaniba, 2008; Karmalm et al., 2009a, 2009b; Gall and Greenspan, 1955; Bueno-Ferrer et al., 2010; Demertzis et al., 1991; Gibbons and Kusy, 1996; Gil et al., 2006; Baltacioglu and Balköse, 1999; Benaniba et al., 2001; Benecke et al., 2004). However, the most disturbing problem associated with the use of external plasticizers has been their evaporation, leaching and migration into their immediate surroundings and has remained largely unsolved until date (Kastner et al., 2012; Campbell and McConnell, 1980; Lau and Wong, 2000; Tsumura et al., 2001; Hammarling et al., 1998; Tsumura et al., 2002; Horn et al., 2004).

Esters, phosphates and epoxides are the most suitable plasticizers for PVC. Due to the polar nature of PVC, ester type plasticizers are mostly used. However, vegetable oil based plasticizers are mostly epoxides and their use is highly desirable, since this may drastically reduce and potentially eradicate the use of petroleum based conventional plasticizers. Moreover, the use of the so-called "green plasticizers" is associated with certain critical advantages. These include: a) they are renewable, b) products derived from them are more readily biodegradable than the corresponding product made from petroleum based substances, hence their impact on environment is less (Erythropel et al., 2012), c) interaction between these polar plasticizer and polar PVC leads to reduction of concentration of the existing polar bonds in PVC, and results in imparting desirable flexibility to the otherwise rigid PVC (Rosli et al., 2003), and d) their non-toxic and non-hazardous nature.

Among the various vegetable oil plasticizers, epoxidized soybean oil (ESBO) has been the most preferred because of its dual plasticizer-cum-stabilizer function. Although there have been several efforts in developing epoxidized palm oil (EPO) based plasticizers (Rosli et al., 2003; Gan et al., 1995), their low compatibility with PVC have hindered their extensive use. However, epoxidized esters of palm olein prepared from butyl alcohol have been found to be suitable plasticizers for PVC (Gan et al., 1995). Moreover, the solubility parameter value of 1.96×10^4 $(Jm^{-3})^{1/2}$ of PVC is in close proximity to the value of 1.88×10^4 $(Jm^{-3})^{1/2}$ of epoxidized palm oil (Gan

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et al., 1995). It was reported that palmitates present in palm oil were found to be largely responsible for the poorer compatibility of the epoxy esters of palm olein prepared from higher alcohols (Gan et al., 1995).

Considering the problems associated with poor compatibility, and environmental and thermal stability (Demertzis et al., 1991; Staples et al., 1997), it was intuited that epoxidized palm kernel oil (EPKO), that is oil derived from the kernel of palm fruit, shall serve as a potential plasticizer for PVC. Moreover, considering the polar nature of PVC, it was conceived that esterification of EPKO shall lead to better compatibility with PVC (Bouchareb and Benaniba, 2008; Gan et al., 1995; Fenollar et al., 2009; Yousef et al., 2001). In addition, the inherently lower palmitic acid content of PKO (as compared to ordinary palm pulp oil) shall pose lesser hindrance towards compatibility. Furthermore, presence of lower degree of unsaturation than other commonly used vegetable oils shall lead to self-controlled degree of epoxidation and decreased oxidative degradation. The inherently lower iodine value shall also provide assistance as have been frequently reported (Bouchareb and Benaniba, 2008; Karmalm et al., 2009a; Gan et al., 1995). The approximate contents of fatty acids present in PKO as compared to ordinary palm oil are presented in Table 1. From the table it can be clearly seen that the total unsaturation content of PKO is only 17.6 % in comparison to 45.7 % unsaturation in ordinary palm oil. It is to be noted that these amounts of unsaturation are much lower compared to other vegetable oils used as plasticizers, such as linseed oil (89 %), sunflower oil (88.4 %), soybean oil (84.5 %), jatropha oil (78.9 %) and flax seed oil (91 %). EEPKO also have the potential to serve as a stabilizer by virtue of possessing epoxide groups (Baltacioglu and Balköse, 1999; Benaniba et al., 2001; Fenollar et al., 2009; Lee et al., 1995; Starnes et al., 2006).

2 Experimental

2.1 Materials

Formic acid (90 %) and hydrogen peroxide (50 %) were used for epoxidation. Butyl alcohol (AR) was obtained from Merck. It was then distilled from magnesium activated with iodine in a dry nitrogen atmosphere. Polyvinyl chloride, DEHP and palm kernel oil were obtained from Sigma Aldrich. The oil used was refined, bleached and deodorized following the reported standard procedure (Satue et al., 1995; Man and Hussin, 1998; Young, 1983; Goh et al., 1985; Badri et al., 2001). It was dried under reduced pressure in order to remove the moisture and volatile components prior to use. The commercial PVC resin Lacovyl PB 1172 H possessed an ISO viscosity or kwert (k)-value (parameter that characterizes the viscosity of a material, and is a measure of the molecular weight of the PVC resin) of 70, as measured according to ISO standard 1628-2 by the supplier. The PVC used was a suspension resin.

2.2 Preparation of Esters and Epoxidation

Butyl esters of PKO were prepared by alcoholysis by butyl alcohol, using KOH as catalyst (Gan et al., 1995). Epoxidations were carried out *in situ* by the method of peroxyformic acid. Typically, 50 g of the oil was mixed with 12 g of formic acid in a 125 ml Erlenmeyer flask. Epoxidation was started by gradually charging hydrogen peroxide (H_2O_2) into the mixture over a period of 4 h. A mole ratio of $1 : 1.5$ (C=C : H_2O_2) was used at a constant temperature of 50 °C. Here, moles of unsaturated ester refer to moles of ethylenic unsaturation present in the ester (Fong and Salimon, 2012). After complete addition of H_2O_2, the reaction was allowed to continue for another 4 h. After the completion of the reaction, the mixture was cooled down and neutralized by water. Diethyl ether was used to enhance the separation of the oil product from water phase. The final product was dried by heating at 40 °C. Table 2 compiles the various properties of EEPKO.

Properties	Values
Oxirane oxygen mole%	3.1
Acid value	1.2
Iodine value	0.5
Specific gravity (kg m^{-3}) at 28 °C	943

Table 2. Properties of EEPKO

Type of fatty acid	Palm kernel oil content %	Ordinary palm oil content %
Saturated caprylic acid (C8)	3.3	–
Saturated capric acid (C10)	3.4	–
Saturated lauric acid (C12)	48.2	–
Saturated myristic acid (C14)	16.2	1.0
Saturated palmitic acid (C16)	8.4	43.5
Saturated stearic acid (C18)	2.5	4.3
Monounsaturated oleic acid (C18)	15.3	36.6
Polyunsaturated linoleic acid (C18)	2.3	9.1
Others	0.4	5.5

Table 1. Comparison between saturated and unsaturated fatty acid content of palm kernel oil and ordinary palm (pulp) oil

2.3 Sample Preparation

100 phr (parts per hundred of resin) of PVC was thoroughly mixed with different phr of plasticizer in a rotative mixer for 20 min at a rotating speed of 5 rpm to prepare PVC dispersion in liquid plasticizer matrix. After complete mixing, the respective pastes were placed in a vacuum chamber to remove air bubbles. Three sets of samples were prepared as presented in Table 3. The total plasticizer content for each sample was maintained constant. Each sample was then processed in a compression mold at 120 °C, 140 °C, 160 °C, 180 °C and 200 °C under a load of 10 000 kg with a molding time of 10 min. Sheets of $9 \times 9 \times 0.5$ cm^3 were obtained.

2.4 Plasticizer Loss and Change of Glass Transition Temperature (T_g) of PVC

Room temperature (25 °C) plasticizer loss was measured from the observed difference in the weight of each test piece recorded over a period of 14 days. The formula used for determining the plasticizer loss for all the samples was:

$$\% \text{ Plasticizer loss} = [(W_0 - W) \times 100]/W_0, \qquad (1)$$

where W_0 is the initial weight of the plasticized PVC (p-PVC) and, W is the weight of the p-PVC obtained at the end of the test.

Rectangular strips of p-PVC, with dimensions approximately 3×8 cm^2 and having a weight of approximately 5 g, were cut from the original sample and used as test specimens for all

Set No.	Sample No.	PVC phr	DEHP phr	EEPKO phr
01	01	100	5	10
	02	100	5	20
	03	100	5	30
	04	100	5	40
	05	100	5	50
	06	100	5	60
02	01	100	–	15
	02	100	–	25
	03	100	–	35
	04	100	–	45
	05	100	–	55
	06	100	–	65
03	01	100	15	–
	02	100	25	–
	03	100	35	–
	04	100	45	–
	05	100	55	–
	06	100	65	–

* Constituents Ca/Zn stearate = 1 phr and Stearic acid = 1 phr have been used for all the formulations

Table 3. Details of sample formulations

the plasticizer loss analysis. Elevated temperature loss was determined according to a BS method (BS 746, Appendix E) (BS 746, 1976), in which the test pieces were suspended vertically in a wire gauge placed in the centre of an oven for 7 days at a constant temperature of 100 °C.

Migration test in n-hexane was carried out following the ASTM D 5227-01 standard (ASTM D 5227-01, 2001). Typically, the samples were immersed in n-hexane at a constant temperature of 50 °C, and after 2 h the weight loss was measured. This method presumes that the weight of the residue extract present in n-hexane (obtained after evaporation of n-hexane) is equal to the amount of plasticizer extracted from the sample. Again, the loss in weight of the sample can be presumed to be equal to the amount of plasticizer extracted. For this purpose, a square piece of 2.5 g weight of each sample was immersed in 1 000 ml of *n*-hexane. After 2 h, the sample was transferred to a covered beaker and subjected to vacuum drying at 80 °C for 2 h, and then cooled to room temperature. The samples were then finally weighed to determine the loss of plasticizer from the samples. The glass transition temperatures (T_g) were determined with a Perkin Elmer DSC-7 apparatus using aluminum open crucibles. Approximately 12 mg of each sample was heated in a static nitrogen atmosphere in the temperature range of 20 °C to 550 °C and at a constant heating rate of 10 °C min^{-1}.

2.5 Tensile Strength, Elongation at Break and Hardness

Tensile strength and elongation at break were determined using an Instron Universal Testing Instrument, according to ISO 527-2 (ISO 527-2, 2012). A 20 mm min^{-1} crosshead speed was used. Tests were done at 27 °C and the reported values are the average obtained from five test samples. For the hardness test, the test specimens were first conditioned at a temperature of 27 °C and relative humidity of 85 % for 24 h. Shore hardness was determined using a durometer, type A (Shore instrument) according to ASTM D 2240 method (ASTM D 2240-00, 2000).

3 Results and Discussion

3.1 Influence of Processing Temperature and Analysis of Plasticizer Loss

PVC plastisols, that is the paste formed by the combination of PVC resin and plasticizer, is a suspension of small and fine individual resin particles and sometimes aggregates dispersed in a liquid plasticizer matrix. Heating of this liquid plastisol results in increased interaction between the PVC and the plasticizer molecules. At first, plasticizer enters inside some voids within the aggregates and subsequently initiates solvation/swelling of some individual PVC particles to form a homogeneous structure (Semsarzadeh et al., 2002; Wang and Chen, 1991; Hong and Huang, 1999). Upon continuation of the heating process and by the time the T_g of PVC is reached, the resin particles absorb the plasticizer to such a great extent that the plastisol becomes a solid paste (Boudhani et al., 2007; García and Marcilla, 1998; Kwak, 1995a; Marcilla and García, 1997a, 1997b, 1998). Fenollar et al. (2009) reported that for-

mation of gel structure above the T_g and disappearance of free plasticizer peak in the DSC calorimetric curves indicate total plasticizer absorption. It has been suggested that a small fraction of the present epoxy rings open upon reaction at labile hydrogen sites in the PVC to form an ether linkage with the chlorinated epoxy (Fig. 1) (Bouchareb and Benaniba, 2008). However, at this stage the cohesion among the particles is poor leading to consequent poor mechanical properties. It is reported that a homogeneous matrix forms upon heat treatment above 190 °C when fusion of PVC microcrystallites takes place (Kwak, 1995b; López et al., 2004). Upon subsequent cooling, a solid material, consisting of small primary particles, gets

formed. A certain degree of cohesion might exist between these smaller particles, resulting in imparting flexibility to the solid material. It should be noted that larger visible particles

Fig. 1. The reaction occurring between the epoxide rings of the oil with PVC, Bouchareb and Benaniba (2008)
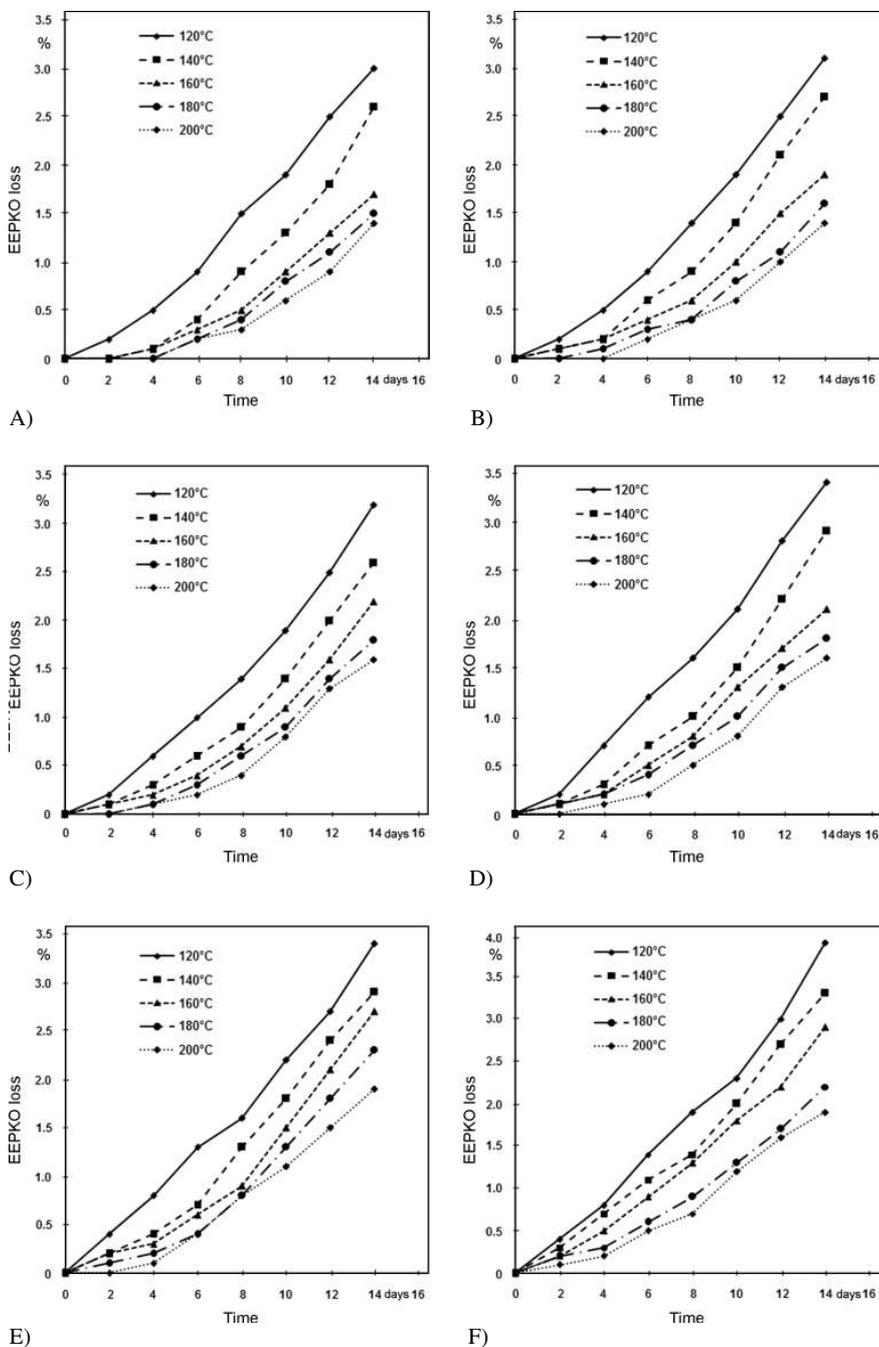

A)

B)

C)

D)

E)

F)

Fig. 2. Room temperature plasticizer losses from the samples of set-1 (containing a fixed 5 phr of DEHP) represented as percentage against the time frame of the analysis represented in days. (A) sample-1, (B) sample-2, (C) sample-3, (D) sample-4, (E) sample-5, and (F) sample-6

will have been largely destroyed due to the material processing. Therefore, considering the above processes, it is possible to establish a relation between processing temperature and overall properties of PVC plastisol at room temperature. It should be noted that varying the heat treatment temperature from 120 °C to 200 °C resulted in a difference of only 0.1 % of incorporated plasticizer among the samples, which can be neglected. Therefore, the total amount of initially incorporated plasticizer was assumed to be equal for all the samples and equal to the total plasticizer fed, for calculating the plasticizer loss percentages.

Loss of plasticizer from p-PVC does not only cause deterioration of p-PVC compounds, but is also associated with an even more serious contamination problem (Agarwal et al., 1989; Treinen and Heindel, 1992; Shea, 2003; Warren et al., 1982; Tickner et al., 2001; Kastner et al., 2012; Campbell and McConnell, 1980; Lau and Wong, 2000; Tsumura et al., 2001; Hammarling et al., 1998; Tsumura et al., 2002; Horn et al., 2004). Therefore, analysis of plasticizer loss is very critical before claiming the application potential of any plasticizer. Keeping this in mind, the samples were first subjected to room temperature plasticizer evaporation analysis. It was observed

Fig. 3. Room temperature plasticizer losses from the samples of set-2 (containing only EEPKO) represented as percentage against the time frame of the analysis represented in days. (A) sample-1, (B) sample-2, (C) sample-3, (D) sample-4, (E) sample-5, and (F) sample-6

that for both set of samples containing EEPKO (Table 3) the plasticizer loss was in the range of 1.8 % to 3.8 % in the 14 days time frame of the experiment. The %EEPKO loss vs. time curves of the first set of samples, i.e. with a fixed 5 phr of DEHP along with varying amount of EEPKO (Fig. 2), were closely similar to that obtained for the second set (Fig. 3). From both figures it can be seen that the samples corresponding to a processing temperature of 200 °C showed the minimum plasticizer loss of about 1.8 % after 14 days, possibly due to network formation via interactive associations (Fenollar et al., 2009). However, by comparing the individual results obtained among samples in set-1 (Fig. 2), and those among set-2 (Fig. 3), it can be easily seen that percent plasticizer loss increases with increasing plasticizer content. Although these loss values are on a higher side (compared to the 1.3 % plasticizer loss observed for the sample containing 65 phr of DEHP), but considering the new plasticizer system dealt in here and in the ongoing work in this laboratory, lot of scope for further developments can be realized. Nevertheless, this obtained results, as of now, hinted at the efficiency of EEPKO to be able to complement a primary plasticizer, like DEHP, in p-PVC compounds.

Next, it was interesting to see the percentage plasticizer loss at an elevated temperature. This was necessary in order to realize an accelerated and long term condition which the p-PVC compound might have to face in service life. The results obtained after continuously exposing the samples at a temperature of 100 °C for 7 days are represented in Fig. 4. Closely matching curves were observed between samples of set-1 and set-2, indicating that complete replacement of DEHP by EEPKO does not result in reduced compatibility. In addition, from Fig. 4A and B it can be clearly seen that the amount of plasticizer loss increased with increasing plasticizer content. This result is expected and is comparable to that obtained from Figs. 2 and 3. In this respect it should be noted that upon testing samples containing higher than 65 phr of plasticizer, it was observed that a very high amount of plasticizer got lost possibly due to over loading of the plasticizer beyond the tolerable limit permitted by the compatibility between the plasticizer and PVC within the range of applied temperature. This, in effect, led to decline in mechanical integrity as can be expected. Therefore, a maximum of 65 phr plasticizer could be incorporated. Samples processed at 180 °C and 200 °C, similarly yielded superior results, i.e. lower plasticizer loss. The percent

plasticizer losses recorded for the samples containing 65 phr plasticizer (both set-1 and set-2) were below 15 %, corresponding to a processing temperature of 200 °C, as against 9 % plasticizer loss observed for the sample containing 65 phr of DEHP and processed at 200 °C.

The problem associated with migration of plasticizers by the process of extraction in organic mediums has already been discussed in previous sections. The migration loss of EEPKO by exposure to n-hexane at 50 °C for a period of 2 h was determined. The results shown in Fig. 5 undoubtedly express the extent of compatibility exhibited by EEPKO towards PVC. Here too, higher amount of EEPKO present within PVC resulted in larger loss of plasticizer. The percent EEPKO that got migrated from the sample containing 65 phr EEPKO and processed at 200 °C was 16 %. This migration value remained almost constant upon increasing the exposure time from 2 h to 4 h, thus indicating good plasticizer absorption and high swollen particle interactions that restrict plasticizer mobility and migration. Therefore, better extent of network formation via interactive associations (at higher processing temperature) plays a crucial role in trapping the plasticizer molecules within its network, thus hindering its leaching (Fenollar et al., 2009). These results are motivating enough to utilize EEPKO as a plasticizer in PVC formulations in future.
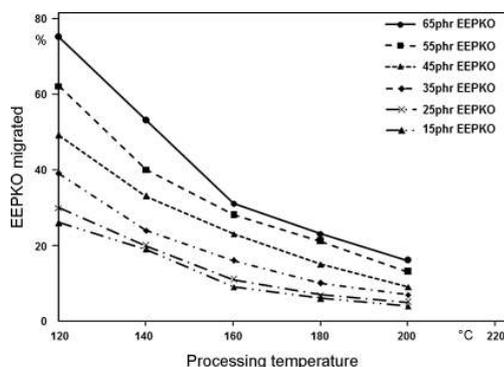

Fig. 5. Determination of percentage of EEPKO migrated from p-PVC to n-hexane (at 50 °C for 2 h), from the percentage of weight loss of the p-PVC compound
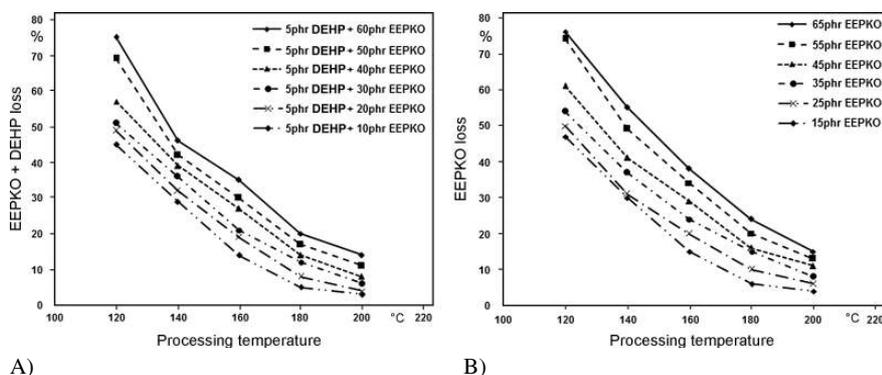

A)

B)

Fig. 4. Analysis of plasticizer loss at 100 °C for 7 days of (A) samples of set-1 containing fixed phr of DEHP, and (B) samples of set-2 containing only EEPKO

3.2 Determination of T_g of EEPK-Plasticized PVC

An effective plasticizer acts principally as a flexible spacer between polymer chains and consequently reduces its rigidity. This phenomenon, in effect, shall result in lowering of the glass transition temperature of the polymer. Therefore, determination of change of T_g of PVC upon addition of plasticizer EEP-KO is demanding, since this is necessary to realize the working efficiency of EEPKO (Bueno-Ferrer et al., 2010; Beirnes and Burns, 1986). From the curves in Fig. 6 it can be seen that T_g of p-PVC processed at 200 °C decreases with increasing amount of plasticizer incorporation. Similar trends were obtained for samples processed at 180 °C and 160 °C. However, samples processed at 140 °C and 120 °C showed insignificant effect on T_g. This is because of lesser extent of interaction present between the plasticizer and the PVC resin, and the correspondingly larger plasticizer loss exhibited by them. It was interesting to note that the samples containing both DEHP and EEPKO yielded a slightly better result compared to the samples containing only EEPKO. Incorporation of a total of 65 phr of DEHP and EEPKO resulted in the lowest T_g value of –32 °C, whereas that obtained for the corresponding sample containing only EEPKO gave a value of –23 °C. Therefore, presence of DEHP is responsible for causing much lower T_g value. This was further evidenced from the Tg value of the p-PVC sample containing 65 phr of only DEHP. This sample produced a T_g value of –51 °C. Beirnes and Burns also reported that incorporation of 70 phr DEHP in PVC resulted in a T_g of –60 °C (Beirnes and Burns, 1986). Probably for this reason, the presence of DEHP in the samples used in this work showed lower T_g value compared to those containing only EEPKO. It should also be noted that the DSC plots of p-PVC exhibited typical broad glass transition ranges, with the maximum of 70 °C broad transition obtained for the samples with 65 phr plasticizer. This large transition range is a result of overlapping of two individual glass transitions, where the higher T_g is assigned to noncrystalline syndiotactic PVC sequences and the lower temperature transition to the more easily solvated atactic chain segments. This observation is similar to that observed by Beirnes and Burns (1986).
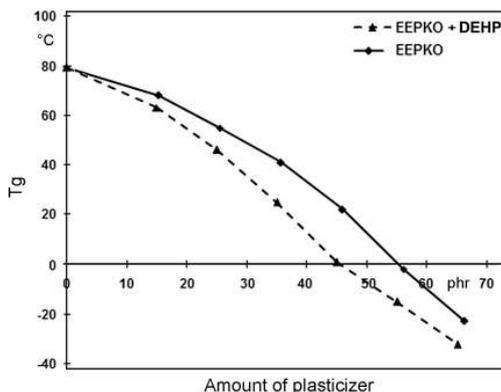
3.3 Estimation of Solubility Parameter and Compatibility

Determining the solubility parameters (δ) of the prepared oil derivatives and comparing them with PVC and conventional commercial plasticizers is very important in order to understand the compatibility of the plasticizers with PVC. This critical parameter can be represented as:

$$\delta = (E_{coh}/V)^{1/2}, \tag{2}$$

where E_{coh} is the cohesive energy, and V is the molar volume.

The value of δ can also be calculated using Small's equation (Sears and Darby, 1982), whereby:

$$\delta = \Sigma F/V, \tag{3}$$

where, F are the molar attraction constants (Small's constants) and ΣF represents E_{coh} of Eq. 2.

In this work, Eq. 3 was utilized to calculate the δ values of the different important epoxidized fatty acid esters which forms a constituent part of palm kernel oil, PVC and DEHP. The calculated values are represented in Table 4. Good compatibility with PVC can be ensured if the δ values of the plasticizer constituents are close to the value of 1.96×10^4 $(Jm^{-3})^{1/2}$ obtained for PVC. From the table it can be clearly seen that the δ values of epoxidized esters are closer to that of PVC, essentially indicating good compatibility between them.

3.4 Determination of Tensile Strength, Elongation at Break and Hardness of p-PVC

The practical utility of a formulation can be realized from its property analysis. Tensile strength and elongation at break are two of such properties that provide a glimpse of the mechanical behavior of a compound. In this analysis it was observed that tensile strength decreases with increasing amount of plasticizer incorporation. This was according to anticipation due to increasing extent of flexibility induced by the plasticizer. Samples containing fixed phr of DEHP (Fig. 7A) exhibited slightly better values than those containing only EEPKO (Fig. 7B). However, samples containing only DEHP showed the best performance, although only by a minute amount (Fig. 7C). From the curves in Fig. 7, it can be realized that samples processed at higher temperatures of 180 °C and 200 °C showed comparatively lesser tensile strength reduction, due to better network

Fig. 6. Variation of the glass transition temperature of p-PVC processed at 200 °C with amount of plasticizer incorporation

Components	Solubility parameter $(Jm^{-3})^{1/2}$ at 25 °C
Laurates	1.76×10^4
Myristates	1.72×10^4
Palmitates	1.83×10^4
Stearates	1.98×10^4
Oleates	1.81×10^4
PVC	1.96×10^4
DEHP	1.82×10^4

Table 4. Solublity parameter values of the EEPKO constituents, PVC and DEHP

formation via interactive association that have taken place in those samples. Processing at 180 °C yielded a value of 6 MPa corresponding to 65 phr of total plasticizer (EEPKO and DEHP), whereas processing at 200 °C gave a value of 10 MPa (Fig. 7A). These values are slightly better than the values of 2 MPa and 5 MPa corresponding to their EEPKO counterparts, respectively (Fig. 7B). A comparative analysis of the three plasticizer systems analyzed in this study has been provided in Fig. 7D. The samples processed at 200 °C, using the different plasticizer systems, have been comparatively analyzed. It can be clearly seen from the figure that both only EEPKO and EEPKO and DEHP plasticizer systems have resulted in imparting superior tensile strengths of the p-PVC samples at lower plasticizer concentrations. However, at 65 phr plasticizer concentration, DEHP-plasticized PVC yielded better tensile strength.

Elongation at break curves represented in Fig. 8A and B clearly shows an increase in elongation at break values with increasing plasticizer content. Here too, the maximum elongation of 412 % was observed corresponding to 65 phr EEPKO content processed at a temperature of 200 °C. Increased flexibility along with the presence of better interaction between the plasticizer and the PVC resin resulted in such an enhanced value. However, in contrast to earlier observations, here the presence of only EEPKO yielded a superior result over the presence of both EEPKO and DEHP. The latter set of samples exhibited a maximum elongation at break value of 385 %. Presence of only DEHP resulted in the least elongation at break value (Fig. 8C). The samples processed at 200 °C, using the different plasticizer systems, have been comparatively analyzed for their elongation at break values (Fig. 8D). It can be clearly seen from the figure that at 65 phr plasticizer concentration, EEPKO-plasticized PVC yielded better elongation at

break value, compared to only DEHP and EEPKO and DEHP plasticizer systems.

Shore A hardness values as represented in Fig. 9A and B show a similar trend as that obtained for tensile strength. Formulations containing both EEPKO and DEHP yielded a minutely larger reduction in hardness of p-PVC (Fig. 9A) compared to the formulations containing only EEPKO. Presence of only DEHP resulted in a maximum reduction in the hardness value (Fig. 9C). The maximum reduction for all the samples took place corresponding to the combination of 65 phr plasticizer and 200 °C processing temperature. However, while comparing the three plasticizer systems studied in this work, it can be realized that EEPKO-plasticized PVC exhibited the least reduction in hardness at almost all plasticizer concentrations, and the difference widened at 65 phr plasticizer concentration (Fig. 9D).

From the above discussions it is clear that: (a) EEPKO exhibits a good compatibility with PVC, as proved by the solubility parameter, plasticizer loss, plasticizer migration and T_g depression analysis; (b) EEPKO can complement other conventional plasticizer like DEHP in PVC formulations; (c) a higher degree of network formation via interactive associations is necessary to prevent plasticizer loss and to exhibit better mechanical properties; and (d) the optimum mechanical properties of EEPKO/p-PVC blends are obtained for samples processed at 200 °C. Furthermore, from the enhancement of properties observed at a processing temperature of 200 °C, followed by a drop in these properties upon increasing the temperature, it can be safely said that polymer degradation (if any) was negligible up to a temperature of 200 °C. This fact can also be realized from the color of the p-PVC sample (containing 65 phr of plasticizer), as presented in Fig. 10, clearly showing the
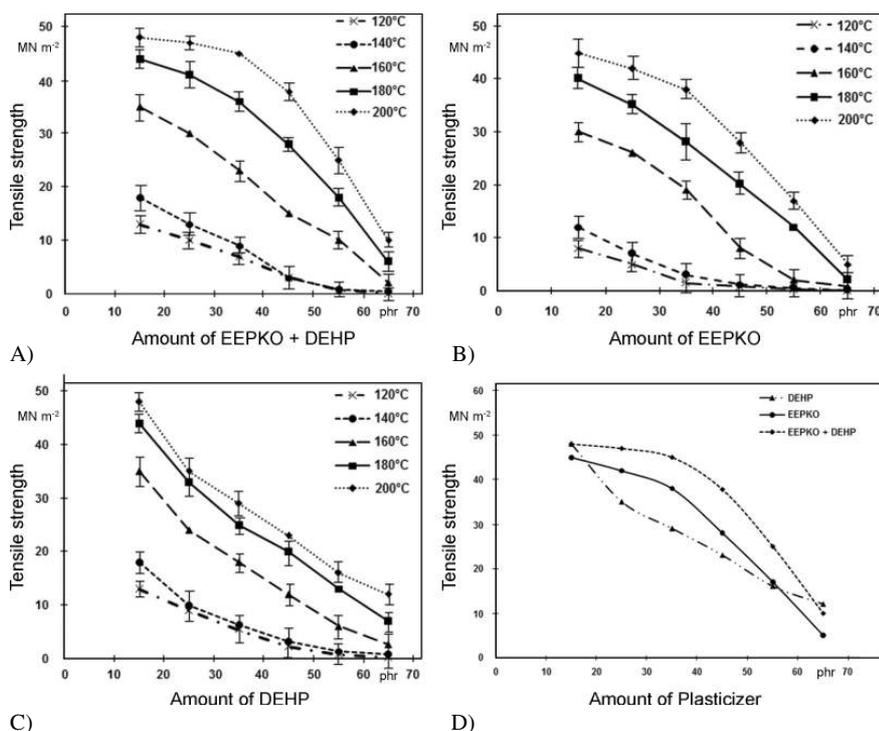

Fig. 7. Variation of tensile strength of p-PVC with different amounts of plasticizer and at different processing temperatures. Formulations containing (A) both EEPKO and DEHP, (B) only EEPKO, and (C) only DEHP. (D) comparison of tensile strength of the p-PVC samples, containing three different plasticizer formulations (i.e. only DEHP, only EEPKO and both EEPKO and DEHP), processed at 200 °C
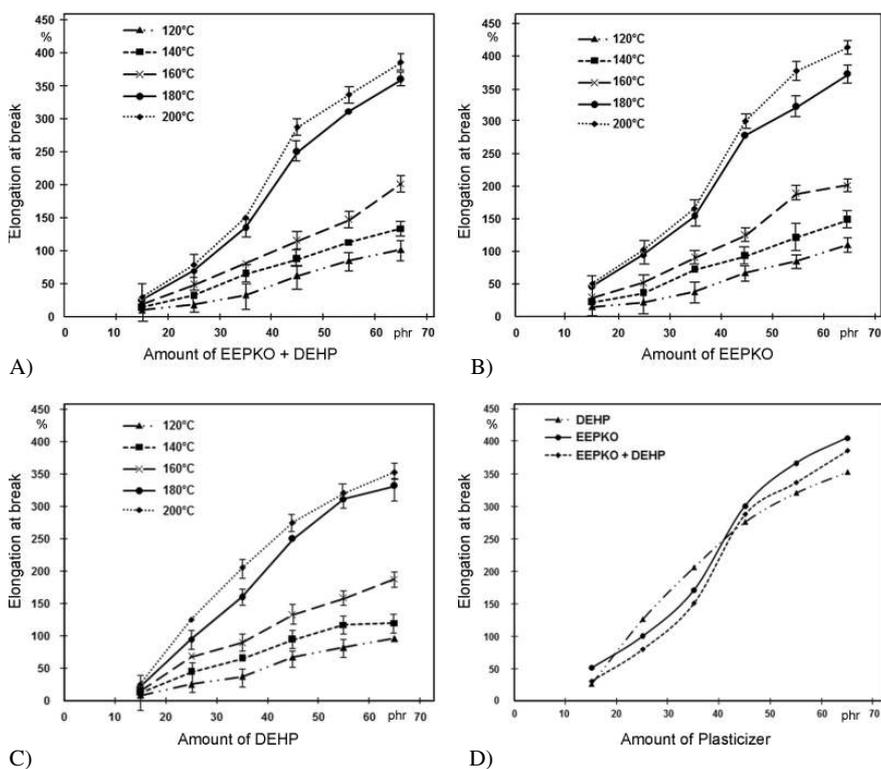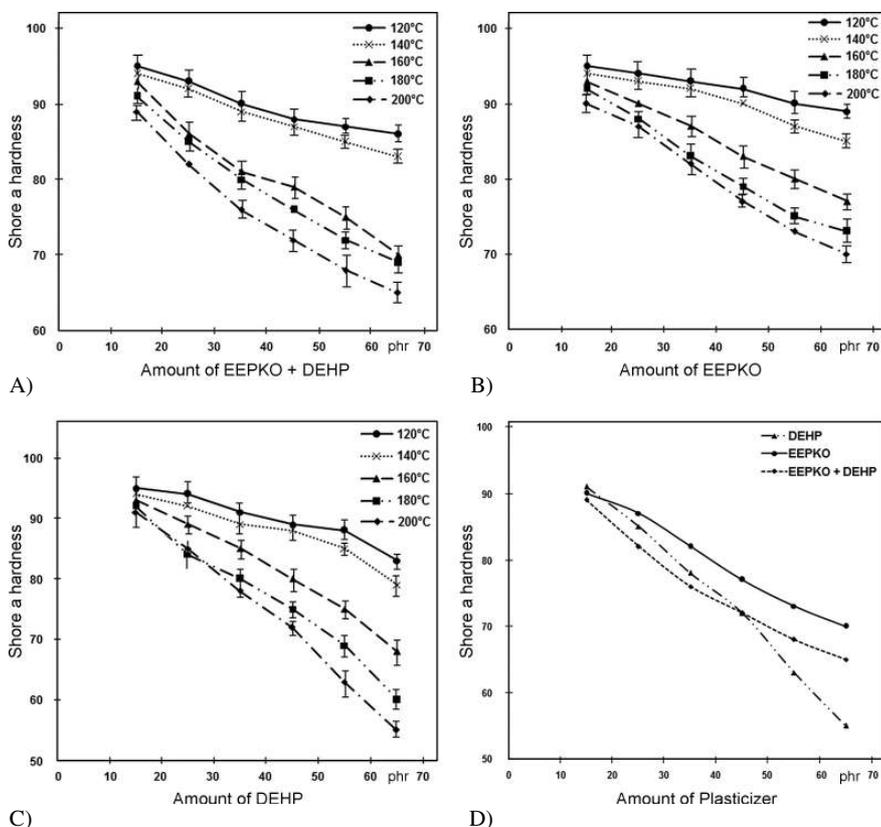
Fig. 8. Variation of elongation at break values of p-PVC with different amounts of plasticizer and at different processing temperatures. Formulations containing (A) both EEPKO and DEHP, (B) only EEPKO, and (C) only DEHP. (D) comparison of elongation at break of the p-PVC samples, containing three different plasticizer formulations (i. e. only DEHP, only EEPKO and both EEPKO and DEHP), processed at 200 °C

Fig. 9. Variation of shore A hardness of p-PVC with different amounts of plasticizer and at different processing temperatures. Formulations containing (A) both EEPKO and DEHP, (B) only EEPKO, and (C) only DEHP. (D) comparison of shore A hardness of the p-PVC samples, containing three different plasticizer formulations (i. e. only DEHP, only EEPKO and both EEPKO and DEHP), processed at 200 °C
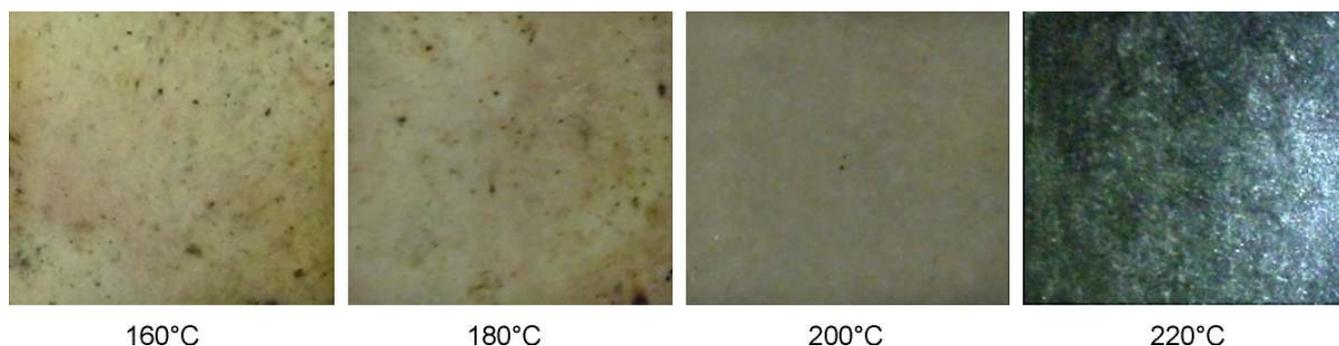
Fig. 10. The effects of processing temperature on the color of the p-PVC sample, containing 65 phr of plasticizer

transition of color from light yellow to black upon increasing the processing temperature from 160 °C to 220 °C. It can be realized from the figure that beyond 200 °C the blackening of the sample indicated probable degradation. Nevertheless, the degree of network formation via interactive associations achieved at this temperature was not complete as can be seen from Fig. 7, 8, and 9 and has been reported previously by Fenollar et al. (2009), and further enhancement of extent of interactive associations was not possible due to degradation of PVC at higher temperatures.

4 Conclusions

The potential of epoxidized and butyl alcohol esterified palm kernel oil to function as an efficient plasticizer in PVC was exploited in this work. The used plasticizer resulted in enhanced mechanical properties. The values obtained for various parameters are closely comparable to that obtained from the use of traditional plasticizers and other commonly used vegetable oil plasticizers, as can be seen from the references mentioned against them. Moreover, different processing temperatures resulted in different mechanical properties of p-PVC, with an optimum reached at 200 °C. A higher processing temperature resulted in severe deterioration of properties, presumably due to polymer degradation. The percent plasticizer losses recorded for the different samples processed at 200 °C were better than those processed at a lower temperature. The glass transition temperature of the sample prepared with 65 phr plasticizer showed a typical 70 °C broad peak centered around –23 °C. It showed a tensile strength of 6 MNm⁻², an elongation at break value of 410 %, and a shore A hardness of about 70. Apart from these inspiring results there are several other advantages of using EEPKO as green plasticizers: (a) It is a relatively inexpensive commodity; (b) its transesterification and epoxidation are relatively simple processes; (c) epoxy esters are known to impart a good heat stabilization effect; and (d) as these esters are derived from the natural triglycerides, they are likely to be more suitable for application in food grade PVC products. However, much further improvements, in terms of migration of plasticizer, are required before EEPKO can be used in food grade PVC products. Work on this particular aspect is being presently carried out in this laboratory.

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