

F. E. OKIEIMEN<sup>1</sup>  
T. O. EGBUCHUNAM<sup>2</sup>  
D. BALKÖSE<sup>3</sup>

<sup>1</sup>The University of Benin,  
Department of Chemistry & Centre  
for Biomaterials Research, Benin  
City, Nigeria

<sup>2</sup>Department of Chemistry, College  
of Education, Warri, Nigeria

<sup>3</sup>The Department of Chemical  
Engineering, Izmir Institute of  
Technology, Urla-Izmir, Turkey

SCIENTIFIC WORK

UDC 678.743+544.773.42-  
-036.5:621.6.023

## THE EFFECT OF BIO-BASED PLASTICIZER ON THE PERMANENCE AND WATER VAPOUR TRANSPORT PROPERTIES OF PVC PLASTIGELS

*Novel formulations of PVC plastisols based on blends of bio-based and synthetic plasticizers were prepared and characterized. A traditional phthalate plasticizer, dioctylphthalate, was replaced in the plastisols studied by the epoxidized rubber seed oil (4.5 % oxirane content). The plastisols formed were processed into plastigels and characterized in terms of permanence properties using leaching and migration tests and water vapour barrier properties. It was found that the permanence properties of PVC/DOP plastigels were maintained in the presence of up to 50 % ERSO, and that blending with DOP did not impair the water barrier properties of PVC plastigels.*

*Key words: biobased plasticizer, PVC, permeability, permanence.*

Poly (vinyl chloride), (PVC), is the second most widely used thermoplastic polymer. A large proportion (about 40 %) of total PVC production goes into flexible consumer products, such as wire and cable insulation, flooring, wall covering, packaging materials, medical applications, etc [1]. For these applications, and before molding or extrusion, PVC is blended with a suitable plasticizer, a material required to weaken the intermolecular bonds in the polymer and increase its workability, toughness and flexibility [2]. Plasticizers act by breaking up the secondary bonds holding the polymer chains together and forming relatively weaker polymer-plasticizer bonds and thus impart mobility to the polymer chain and/or polymer chain segments. Plasticizing efficiency is generally considered to be a function of organic/inorganic moiety, functional groups present in the plasticizer molecule, the structure, a chain length, a molecular weight, etc [3]. Thus, different plasticizers confer different plasticization effects because of the differences in the strength of plasticizer-polymer and plasticizer-plasticizer interactions.

Many of the commercial grade plasticizers are phthalate anhydride derived and they include diisononyl phthalate, di-2-ethylhexyl phthalate, diisodecyl

phthalate, etc. The applications of these and many other plasticizers are associated with a number of challenges: limited compatibility with polymer matrix, poor stability in high temperature environments and/or when exposed to UV radiation, reduced lubricity at low temperatures, flammability, etc [4]. More recent concerns regarding phthalate plasticizer application include toxicity in consumer products made of phthalate plasticized PVC [5,6]. There has therefore been a growing interest in the search for alternatives to phthalate plasticizers that have little or no environmental/public health concerns. Alternatives that have been proposed and studied widely include esters of aconitic acid (1,2,3-propenecarboxylic acid) [7] and ionic liquids [8-10]. Epoxidized triglycerides and their esters have similarly been studied as secondary plasticizers and additives for PVC [11-15]. In addition to good miscibility with the polymer, other attributes of a good plasticizer include high boiling temperatures to prevent or minimize losses during processing and a low rate migration out of the polymer to avoid loss of properties, and contamination of products which it comes in contact with [1,6]. It is thus desirable that once a plasticizer is compounded with PVC, it should be more or less permanently retained in the polymer matrix. But because plasticizers are not chemically bound to the polymer, there is loss of plasticizer to some extent resulting from leaching and migration. Several workers, [17,18] have reported on different methods to increase the leaching and migration resistance of plasticized PVC compounds. The effects of

Corresponding author: F. E. Okieimen, The University of Benin, Department of Chemistry & Centre for Biomaterials Research, Benin City, Nigeria.

E-mail: fexokieimen@yahoo.com

Paper received: 25 July 2007.

Paper revised: 9 December 2007.

Paper accepted: 8 January 2008.

blends of plasticizers on the permanence properties (leaching and migration) in PVC compounds remain to be extensively studied. In this report, the effect of a bio-based plasticizer, epoxidized rubber seed oil on some properties (mechanical, permanence and water vapour barrier properties in PVC-dioctyl phthalate (PVC-DOP) plastigels is reported.

## MATERIALS AND METHODS

Dioctyl phthalate (Merck, refractive index 1.4399 and density 0.993 g/cm<sup>3</sup>) was used as primary plasticizer. PVC (Petvinil P. 38/74,  $\bar{M}_v$  50,000) was used without purification. The epoxidized rubber seed oil (ERSO) was prepared in our laboratory. The detailed procedures for the preparation and determination of the oxirane content of the epoxidized seed oil have been reported previously [19].

### Preparation of PVC plastigels

PVC plastisols were prepared by blending PVC, DOP and ERSO in proportions given in Table 1. Thin films of plastisols were prepared by using a 90- $\mu$  film applicator and then gelled for 15 min in an air circulating oven at  $140 \pm 2$  °C to obtain the plastigels. The plastisol formulated to contain 100 % ERSO did not form homogenous film and so was not included in the studies.

Table 1. Recipe for the formulation of PVC/DOP/ERSO plastisols

Materials (phr)	I	II	III	IV	V
PVC	100	100	100	100	100
DOP	80	60	40	20	0
ERSO	0	20	40	60	80
Plastigel sample thickness, $\mu$ m	98.8	150.3	169.4	141.2	159.7

### Plasticizer permanence properties

#### Leaching test

Leaching of plasticizers from the PVC/DOP/ERSO plastigel samples was carried out using the method described by Rahman and Brazel [4]. In a typical experiment, thin rectangular samples (approx. 30x10 mm<sup>2</sup>) having weights of between 0.04-0.07 g were placed in 100 ml of deionized water in a flask. The flask was maintained at 50 °C. Sample weights were taken for 10 days.

#### Migration test

The migration of plasticizers from plasticized to unplasticized PVC films was carried out at room temperature over a two-week period. A rectangular plasticized PVC sheet (33x7 mm<sup>2</sup>) surface area and weigh-

ing between 0.03-0.06 g were sandwiched between two unplasticized PVC sheets of the same shape and maintained in close contact between the glass microscope slides secured by clips. The amount of the plasticizer that migrated to the unplasticized sheets was determined by gravimetry [4]. The unplasticized PVC films that were in contact with the plasticized films were examined by UV spectrophotometry.

#### Water vapour permeability test

The water vapour barrier property of PVC/DOP/ERSO plastigels was measured using a permeation cell [20]. The apparatus consisting of three parts has been described elsewhere [21]. In a typical experiment, the plastigel sample was placed in the hole of the apparatus and sealed between the rings. After the relative humidity in the upper part of the cell had reached 5 %, the inlet and outlet valves of the permeation cell were closed and the monitoring program started. The temperature and relative humidity data were monitored and recorded at 10 s interval for 12 h by a Datalogger SK-L 200 TH. The water vapour transport apparatus gives values of changes in the relative humidity at the sample surface from which permeability is calculated. Relative humidity is given by

$$RH\% = \frac{P_u}{P_L} \times 100 \quad (1)$$

where  $P_L$  and  $P_u$  are the saturated water vapour pressure at ambient temperature and the pressure at the sample surface after a certain period of time. The plots of  $\ln [(P_L - P_{ui}) / (P_L - P_u)]$  versus time, where  $P_{ui}$  is the initial pressure at the sample surface, allow the values of permeability to be obtained from the slopes of the initial linear portions of the plots [20]. The slope of the plot is given by

$$\frac{1}{\text{Slope}} = \frac{LV}{PART} \quad (2)$$

where  $L$  is thickness of the sample (cm),  $V$  is volume of water in the apparatus (cm<sup>3</sup>),  $P$  is permeability (g mol H<sub>2</sub>O/cm.S.K.Pa),  $A$  is area of the sample exposed to air (cm<sup>2</sup>),  $R$  is universal gas constant (cm<sup>3</sup> Pa mol<sup>-1</sup> K<sup>-1</sup>), and  $T$  is temperature (K).

## RESULTS AND DISCUSSION

### Plasticizer permanence

#### Leaching of plasticizers

Leaching tests of plasticizers from the PVC/DOP/ERSO plastigels were conducted with deionized water at 50 °C over a period of 10 days. The weight loss of a plasticizer as a function of time is

shown in Figure 1. It can be seen that all the samples showed a considerable resistance to leaching, with the maximum weight loss within the duration of the tests less than 7 %. Plastigel samples I and II (containing 0 and 25 % ERSO, respectively) showed marginal net weight gain ( $\leq 4$  %), while sample IV (containing 75 % ERSO) showed between 2 and 6 % weight loss during the 10-day test period.

#### Migration of plasticizers

The migration of plasticizers from the PVC/DOP/ERSO plastigel samples unto unplasticized PVC films was studied at room temperature over a two-week period. The levels of the plasticizer migration are given in Table 2. The results show a very low plasticizer migration from the plastigel samples; the sample I (containing no ERSO) showed the highest migration level (0.92 %) while the sample II (containing 25 % ERSO) showed 0.22 % plasticizer migration and the sample containing 75 % ERSO showed no plasticizer migration. UV spectrophotometric studies were carried out on the unplasticized PVC films used for the migration studies. The UV spectra (Figure 2)

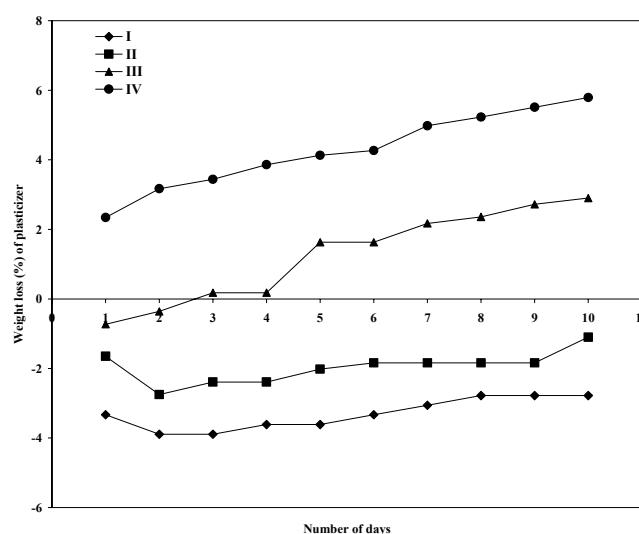


Figure 1. Percentage of plasticizers lost due to leaching in deionized water from PVC/DOP/ERSO plastigels at 50 °C

Leaching and migration of plasticizers in flexible polymer products represent a major challenge in the research in the plasticizer industry. Whether the plasticizers leach out to a liquid or migrate to a gaseous or solid substance, polymers fail to retain their flexibility, while the loss of plasticizers leaves the polymers inappropriate for the desired application [4]. The permanence properties showed by PVC/DOP/ERSO plastigels are thought to be partly due to the relatively high molecular weight of ERSO and its thermal behavior.

show the absorption bands of between 250-300 nm, which were absent in the spectrum of the unplasticized film (which was cast from the solution of PVC in THF) and also in the spectrum of ERSO (Figure 3) assigned to DOP and indicates that ERSO may have higher compatibility with PVC than DOP. The estimated value of the solubility parameter of ERSO (18.9) is somewhat closer to the value for PVC (19.4) than that for DOP (18.2) [21]. It is thought that in the blend of ERSO/DOP, the plasticizer with lower compatibility could bloom from the plasticized material. This may account for the observed relative migration of DOP from the ERSO/DOP/PVC plastigels.

Table 2. Migration of plasticizers from PVC/DOP/ERSO plastigels

Composition of plasticizers % ERSO	Percentage of plasticizer migrated
0	0.92
25	0.22
50	0.45
75	0.00

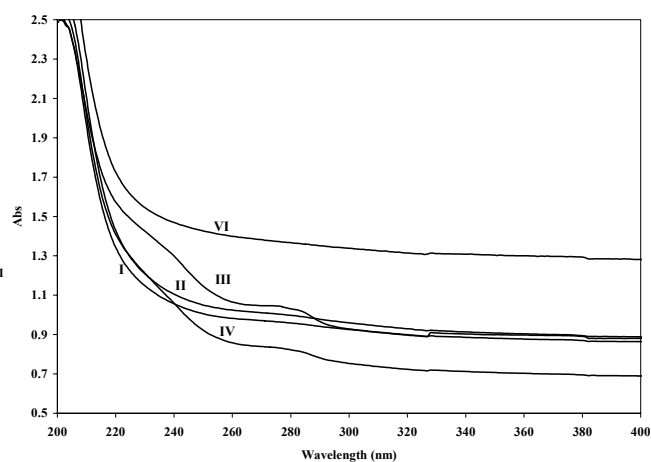


Figure 2. UV spectra on PVC films after migration test. (I) 0 % ERSO (II) 25 % ERSO (III) 50 % ERSO (IV) 75 % ERSO (VI) unplasticized PVC

The results of the studies show that the permanence properties of ERSO in PVC/DOP plastisols can compare favourably with those of phthalate plasticizers. In addition, the plasticizers coming out of the polymers often pose health and environmental risks [22].

#### Water vapour permeability

Plastisols are used in various applications such as membranes, tubes, coil coatings, etc., in which the water vapour permeability is considered to be an important performance criterion exposed to rain and high

humidity environment. The resistance to water vapour permeation by PVC/DOP/ERSO plastigels was measured in terms of the time taken for the onset of permeation (time lag) and a permeability coefficient which gives an assessment of the barrier property of the material. Typical output from the apparatus (plot of RH versus time) and the plot of  $\ln [(P_L - P_{ui}) / (P_L - P_u)]$  versus time are shown in Figures 4 and 5, respectively.

The time taken for the incipient uptake of the water vapour (time lag) was recorded automatically by the permeation equipment. It was found that the

sample I showed the shortest time lag (17.5 min) while the sample II gave the longest time lag (29.5 min). The lower values of the time lag of 20.5 and 26.5 min were obtained for samples III and IV, respectively. The variation of the water permeability coefficient with ERSO content of the plastigels is shown in Figure 6. The values of permeability coefficients are generally about the same order of magnitude. These results show that the barrier (against water vapour) properties of PVC/DOP plastigels are not compromised by the incorporation of ERSO as secondary plasticizer.

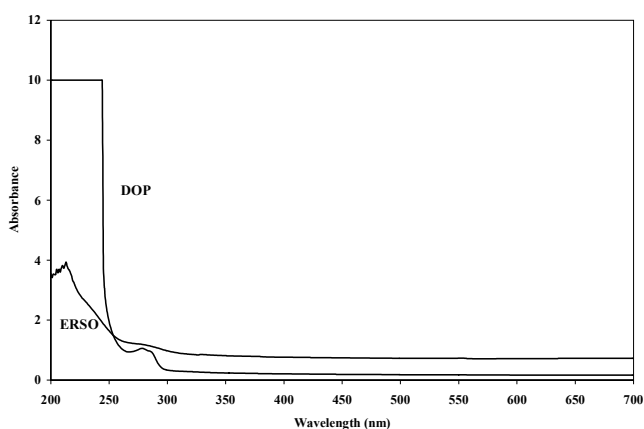


Fig. 3. UV spectra on DOP and ERSO

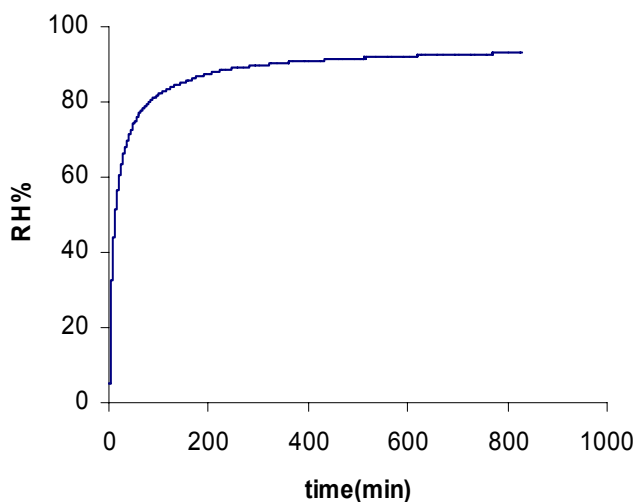


Fig. 4. Plot of RH versus time

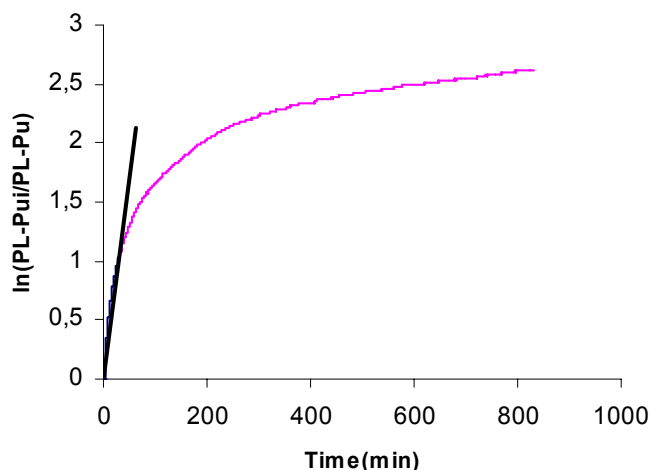


Figure 5. Plot of  $\ln [(P_L - P_{ui}) / (P_L - P_u)]$  versus time

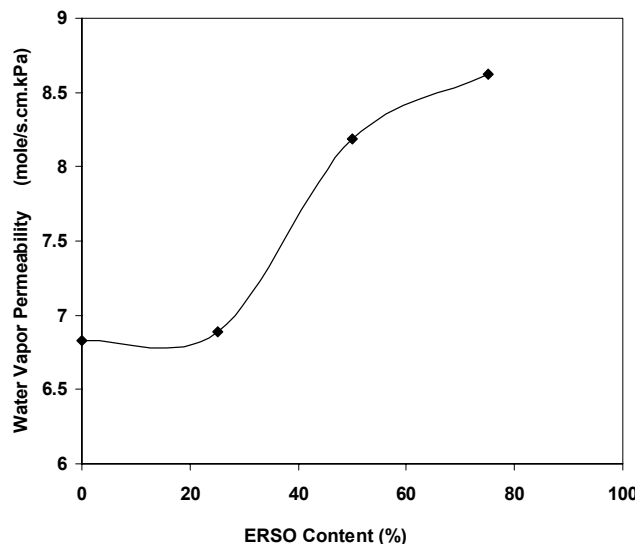


Figure 6. Water vapour permeability of PVC/DOP/ERSO plastigels as a function of the ERSO content of the plastigel blend

**CONCLUSION**

In this study, the effect of blends of DOP/ERSO on the permanence and water vapour transport pro-

perties of PVC/DOP/ERSO plastigels was studied. At low to moderate ( $\leq 50\%$  ERSO) levels of incorporation of ERSO, moderate improvements in some of the measured properties of the plastigels were observed.

### Acknowledgements

TOE is grateful to Prof. Devrim Balköse, Head, Department of Chemical Engineering, Izmir Institute of Technology, Izmir, Turkey for guidance and assistance during the course of this work and to the Council and management, College of Education, Warri, Nigeria, for the study leave.

### REFERENCES

- [1] B. Shah, V.V. Shertukde, *J. Appl. Polym. Sci.* **90** (2003) 3278
- [2] N. Gil, M. Saka, I. Negulescu, *J. Appl. Polym. Sci.* **102** (2006) 1366
- [3] L.G. Krauskopf, in: *Encyclopedia of Poly (vinyl chloride)* vol. 2 (L.I. Nass and C.A. Heiberger Eds), Marcel Dekker Inc., New York, 1988.
- [4] M. Rahman, C.S. Brazel, *Prog. Polym. Sci.* **29** (2004) 1223
- [5] G. Latini, *Biol. Neonates* **78** (2001) 269
- [6] B. Hileman, *Chem. Eng. News* **83** (2005) 11
- [7] E.J. Roberts, L.F. Martin, F.C. Magne, R.R. Mod, *Rubber World* (1954), p. 801.
- [8] M.P. Scott, M. Rahman, C.S. Brazel, *Eur. Polym. J.* **39** (2004) 1947
- [9] M. Rahman, C.S. Brazel, *Polym. Preprints* **45** (2004) 301
- [10] M. Rahman, H.W. Shoff, C.S. Brazel, in: *Ionic liquids in Polymer Systems. Solvents, Additives and Novel Applications* (C.S. Brazel and R.D. Roger, eds) ACS Symposium Series, Vol 913, American Chemical Society, Washington DC, (2005), p. 103.
- [11] L.H. Gan, K.S. Ooi, S.H. Goh, I.M. Gan, Y.C. Leong, *Eur. Polym. J.* **31** (1995) 719
- [12] Y. Itoi, M. Inoue and S. Enomoto, *Bull. Chem. Soc. Jpn.* **59** (1986) 3941
- [13] M.T. Benaniba, N. Belhaneche-Besemra and G. Gelbard, *Polym. Degrad. Stab.* **74** (2001) 501
- [14] F.E. Okieimen, *Industr. Crops Products* **15** (2002) 71.
- [15] M.A. Semsarzadeh, V.V. Shertukde, *J. Appl. Polym. Sci.* **90** (2003) 3278
- [16] R. Bert, Y.M. Huang, J.W. Rhim, *J. Appl. Polym. Sci.* **41** (1990) 534
- [17] C. Huang, *Polym-Plast Technol. Engng.* **33** (1995) 615
- [18] S.Y. Kwak, *J. Appl. Polym. Sci.* **55** (1995) 1683
- [19] I.O. Bakare, F.E. Okieimen, C. Pavithran, *Eur. J. Lipid Sci. Technol.* **107** (2005) 330
- [20] O. Topcuoglu, S.A. Altinkaya, D. Balköse, *Prog. Org. Coatings* **56** (2006) 330.
- [21] T.O. Egbuchunam, PhD thesis, University of Benin (2007).
- [22] M.L. Marin, J. Lopez, A. Sanchez, J. Vilaplana, A. Jimenez, *Bull. Environ. Contam. Toxicol.* **60** (1998) 68.