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Full Length Research Paper

Effect of beta irradiation on plasticized polyvinyl chloride

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Various polyvinyl chloride (PVC) formulations were compounded with two types of plasticizers-diocthylphthalate (DOP) and epoxidized rubber seed oil (ERSO). The samples were subjected to beta irradiation at a rate of 2.4 mGy/h to total dose of 14.4 mGy. The mechanical properties and the plasticizer permanence such as leaching and migration of plasticizers from the various samples were evaluated. The tensile strength and elongation at break were observed to increase with increase in concentration of the plasticizer up to 40 parts per hundred resins (phr). Absorbance values of sample films were recorded with UV spectrophotometer using the unplasticized film as standard. The irradiated samples were observed to have higher absorbance values than the nonirradiated samples. Both plasticizers were observed to be effective in stabilizing the radiolytic degradation of PVC. This study shows that the conventional plasticizer (DOP) can be replaced at low concentrations (up to 40 phr) without markedly compromising the plasticizer efficiency.

Key words: Polyvinyl chloride, plasticizer, epoxidized rubber seed oil, diocthylphthalate, beta irradiation.

INTRODUCTION

Polyvinyl chloride (PVC) is a rigid polymer with extensive application. Its range of utilization is significantly expanded by compounding with additives such as plasticizer to improve processing and enhance some desirable properties. Plasticized PVC has achieved widespread commercial use. it can be used to make flexible hoses and tubing, flooring, covering and packaging materials, etc. The most widely used blood bag material up till now has been plasticized polyvinyl chloride (Lee et al., 1999). The plasticizer minimizes the dipolar interactions which exist in the polymer chains promoting mobility. This facilitates processing and increases flexibility and toughness in the final product by internal modification of the polymer molecule (Ticker et al., 2001).

Plasticizers are mainly the phthalate esters, of which dioctylphthalate (DOP) is the most widely used general purpose plasticizer for the manufacture of flexible plastics especially PVC. It is employed as commercial additive in PVC formulations for the manufacturing of food packages, baby toys and medical devices. It is Lipophilic or fat loving compound and so tends to concentrate in fatty tissues (Rock, 1990). It has good resistance to heat, ultraviolet light, hydrolysis and is insoluble in water.

The most debated issues regarding the use of plasticizer has been the leaching and migration of plasticizers, especially of the phthalates from commodity plastics (Rahman and Brazel, 2002). A number of phthalates have been banned from certain applications by the European Union (Hileman, 2005). As a result of the health implication of phthalate based plasticizers, there is need for more environmentally friendly alternative. In the last few years, we have engaged in rubber seed oil projects such as application of divalent soaps of rubber seed oil as heat stabilizers of powdered PVC (Egbuchunam et al., 2007; Ikhouria et al., 2002) and epoxidation (Ikhouria et al., 2007; Bakare et al., 2005). Epoxidized rubber seed oil has been found to be very useful as plasticizer of PVC.

In order to ensure the absence of microorganisms in PVC plasticized products, the technique of sterilization by ionizing radiation has been applied as an international standard. The aim of this study is to examine the effect of beta-irradiation on epoxidized rubber seed oil (ERSO)

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Table 1. Recipe for the formulation of Polyvinyl chloride films.

		Materials (phr)	
Sample	**PVC**	**DOP**	**ERSO**
I	100	30	-
II	100	40	-
III	100	50	-
IV	100	60	-
V	100	70	-
VI	100	-	30
VII	100	-	40
VIII	100	-	50
IX	100	-	60
X	100	-	70

plasticized PVC, dioctylphthalate (DOP) plasticized PVC and to compare the efficiency of the traditional phthalate based plasticizer (DOP) with the more environmentally friendly additive (ERSO).

EXPERIMENTAL

Materials

PVC powder of molar weight 100,000 g/mol was obtained from BDH Ltd, Pooles, England and was used without further purification. Dioctylphthalate (DOP) (Merck) was used as plasticizier. Rubber seed oil (RSO) was obtained from Rubber Research Institute of Nigeria, Iyanomon. Tetrahydrofuran (THF), of analytical grade was used with no further treatment.

Epoxidation of rubber seed oil

40 g of rubber seed oil (RSO) was placed in a 500 ml flask containing 0.09 mol acetic and 0.007 mol sulphuric acid, condenser, thermometer and stirrer. The mixture which was at room temperature was cooled to 10°C and 46.1 g of 30% hydrogen peroxide previously equilibrated at the reaction temperature was added drop-wise with continuous stirring for about 1 h. This precaution was taken because of the exothermic nature of epoxidation reaction. Thereafter, the temperature of the reaction was raised to 60°C and maintained at this temperature for a period of 8 h. The reaction mixture was cooled to room temperature, the oil extracted with ethyl acetate, washed with water until acid free and dried over sodium sulphate. The solvent was removed in vaccum at 60°C leaving the epoxidized rubber seed oil (RSO) (Egbuchunam et al., 2007).

Preparation of PVC films

PVC films consisting of DOP plasticizer (Samples I to V) and ERSO plasticizer (Samples VI to X) were formulated by solvent evaporation. 2 g of powdered PVC and the plasticizers (DOP/ ERSO) in various proportions, recipe given in Table 1 were dissolved in THF and poured in glass Petri dishes. The solvent was evaporated at room temperature and the films dried in vacuum until constant weights were observed. Unplasticized PVC films were made in the same method.

Irradiation technique

Differently compounded PVC films were exposed to Beta irradiation at 14.4 m/Gy from a $^{90}Sr/^{90}Y$ source with a dose rate of 2.4 m Gy/h. Both irradiated and nonirradiated films were taken for analysis (Martins-Franchetti et al., 2002).

UV spectroscopy

Absorbance values of film samples were recorded on a Unicam Heλious Alpha UV spectrophotometer with serial no.UVA-072519, made in England. The unplasticized film was used as reference.

Mechanical tests

The mechanical properties of the samples (tensile and elongation at break) were assessed at room temperature according to ASTM D882, standard test method for tensile properties of thin sheeting (http://www/instron.us/wa/solutions). The test was carried out on a fully automated table-top testing machine of Instron model 3369 at a cross-head speed of 20 mm/min. Three determinations were made for each sample and the average value taken.

Leaching

Leaching of plasticizers from plasticized PVC samples was studied using the method described in (Rahman and Brazel, 2002). In a typical experiment, thin rectangular samples (approximately 30 × 10 mm) were placed in 100 ml of ionized water in a flask. Samples weights were taken every other day for 12 days.

Migration test

The migration of plasticizers from plasticized to unplasticized PVC films were carried out at room temperature over a two weeks period. Rectangular plasticized PVC sheets (33×7 mm) were sandwiched between two unplasticized sheets of the same shape and maintained in close contact between glass microscope slides secured by binder clips. The amount of plasticizer that migrated to the unplasticized sheet was determined by gravimetric method (Rahman and Brazel, 2002).

RESULTS AND DISCUSSION

UV-Visible spectra

The UV absorption spectra of the two plasticizers samples are shown in Figure 1. It is observed that the shape of the absorption band is quite the same. Similar trend was observed with the other concentrations. Comparison of the irradiated and non irradiated DOP samples is shown in Figure 2. Similar trend was observed with the ERSO plasticized films. The irradiated samples were observed to have higher absorbance values than the nonirradiated samples. This could be due to the degradation associated with PVC irradiation with the

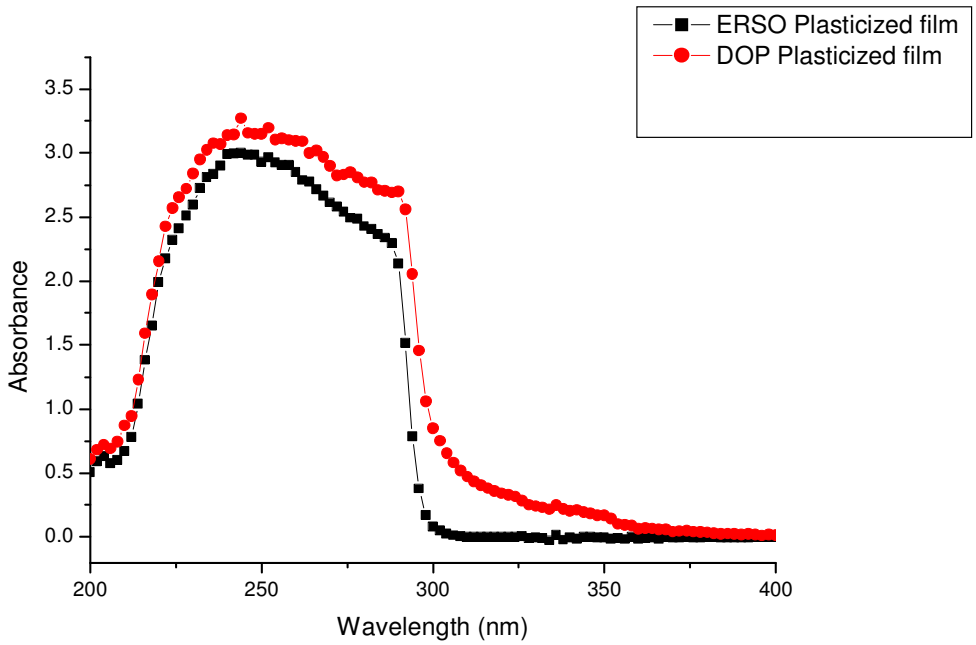

Figure 1. Variation in the absorbance values of DOP and ERSO plasticized films (40 phr).

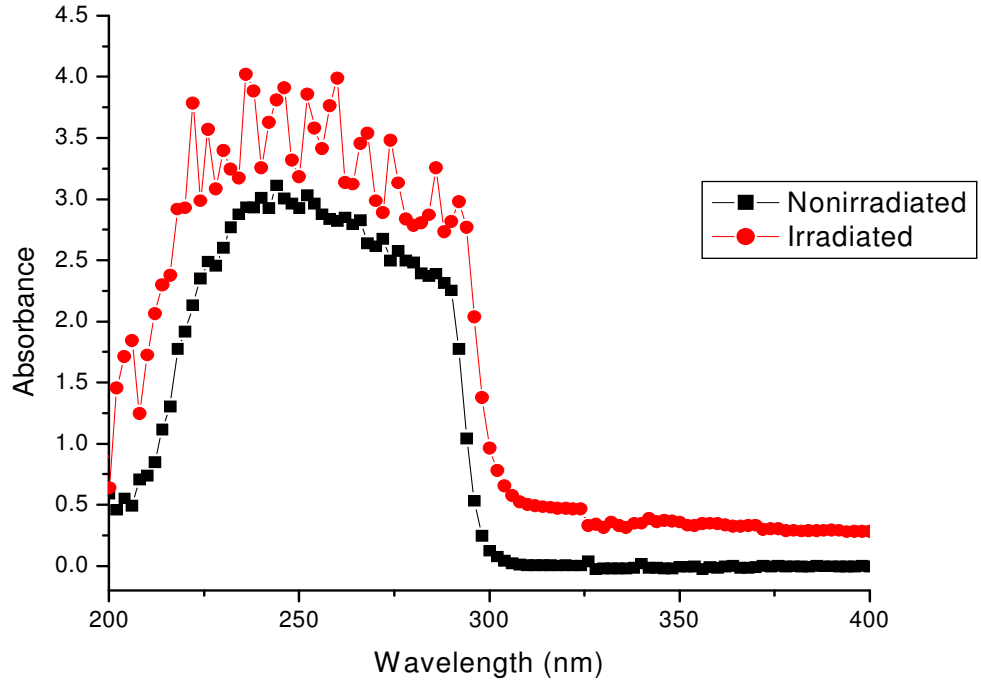

Figure 2. Variation in the absorbance values of the irradiated and nonirradiated films (60 phr).

release of HCl. The irradiation resistance in PVC seems to be mildly induced by the addition of the epoxidized oil. This could be due to the fact that the chlorine initially formed could be scavenged by the epoxy group, since epoxidized oil can scavenge HCl.

Mechanical properties

The mechanical properties of the PVC films with different plasticizers and different plasticizers concentrations were evaluated. The variation in tensile strength with

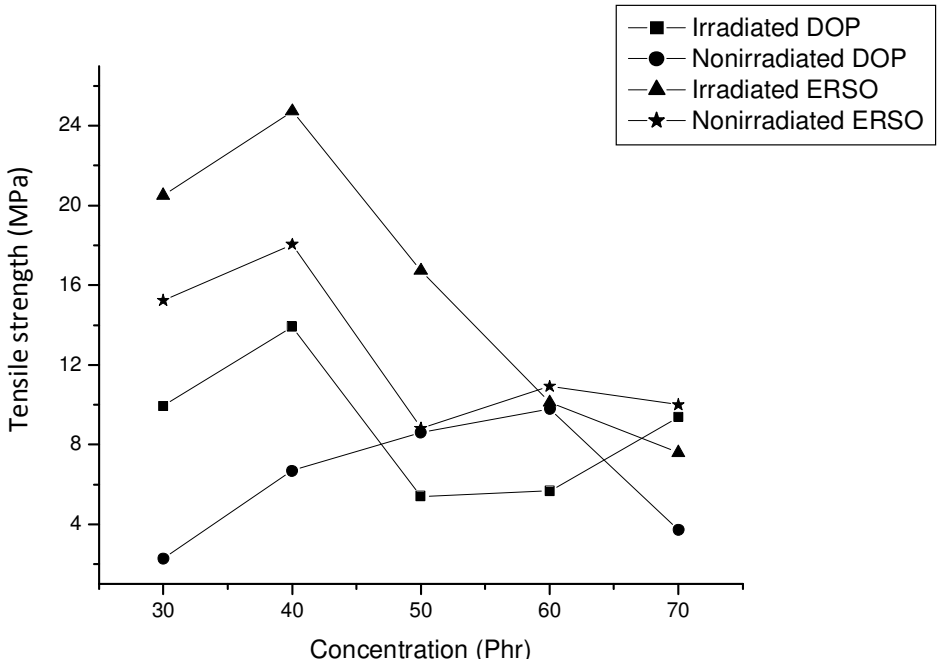

Figure 3. Variation in tensile strength with increase in plasticizer concentration.

concentrations for the irradiated and nonirradiated samples for DOP and ERSO plasticizers is shown in Figure 3.

It can be observed that an increase in plasticizer concentration has a general non-linear effect on the tensile strength for all the films, either irradiated or nonirradiated for both plasticizers. They were all observed to increase with concentration up to 40 phr. The increase in strength with the plasticizer may be attributed to its polarity which increased the cohesive energy density, such that materials tend to be held together more tightly resulting in reduced mobility and flexibility (Vinhas et al., 2003). At concentrations higher than 40 phr, an irregular trend was observed. The reason for this may be that the plasticizer concentration is too high to get a perfect blend with the PVC. It has been established that incompatible blends reduce the cohesive strength of the matrix and the extent of reduction in polymer properties is related to blend morphology with blends having finer dispersity showing less reduction in properties (Folkes and Hope, 1993). However, the tensile strengths for the irradiated samples were observed to be lower than those of the nonirradiated for both plasticizers. This could possibly be due to chain scission and double bond formation.

The variation of the elongation at break with the plasticizer concentration is shown in Figure 4. There is an increase in the elongation with increase in the plasticizer concentration for the nonirradiated samples. This is expected as the increase in the amount of plasticizer can lead to the insertion of some polar bonds between macromolecular chains resulting in increase in elongation (Jimenez et al., 2001). The plasticizer stabilizes PVC by slowing down the hydrochlorination reaction and absorption of the evolved hydrogen chloride. It breaks up the primary bonds that holds the polymer chains together and forms secondary polymer – plasticizer bonds (Rahman and Brazel, 2002). It impacts flexibility by acting effectively as an internal lubricant between PVC chains (Odian, 2004). However, a slight change was observed with the irradiated samples of both plasticizers. This could possibly be due to chain scission and double bond formation. Elongation at break is an important parameter for analyzing the flexibility imparted by the plasticizers. The extent to which the different plasticizer imparted flexibility to PVC varied to some extent, but the overall performance of ERSO in producing flexible PVC films, compared to the traditional plasticizer was quite satisfactory.

Plasticizer permanence

The tendency of a plasticizer to be removed from a system is very real because the polymer and the plasticizer molecules are continuously undergoing association and segregation. It is desirable that once compounded, the plasticizer should be retained permanently in the polymer. However, this is not always the case as plasticizers are not chemically bound to the polymer. There is often plasticizer loss resulting from leaching and migration. The permanence of a polymeric plasticizer in a flexible PVC compound depends mainly on structure, molecular weight/ viscosity and polarity.

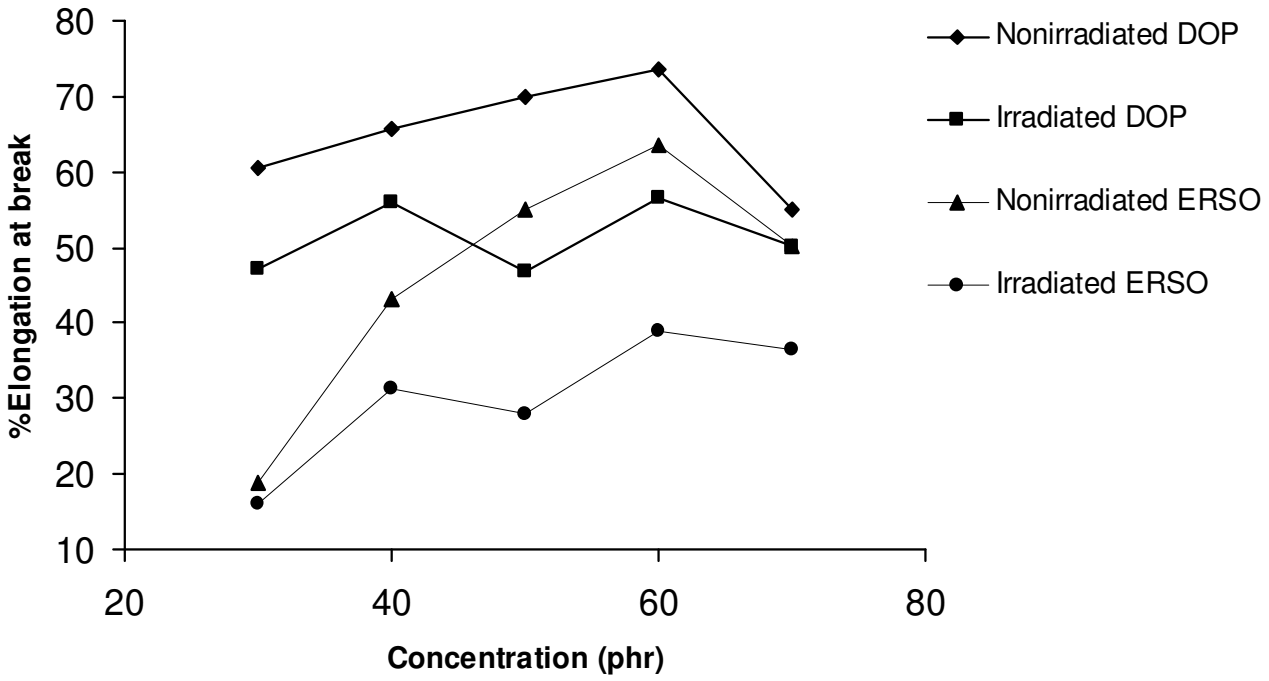

Figure 4. Variation in elongation at break with plasticizer concentration.

Leaching tests of plasticizers from the PVC films were conducted and slight weight change was observed in all the samples. This shows that Beta irradiation under the studied irradiation dose has no effect on the leaching tendency of the plasticizers.

Migration is the movement of a plasticizer within and from a PVC compound into a substrate to which it is held in intimate contact. It has been established that plasticizer migration is highly dependent on the diffusivity of the plasticizer in its host polymer and diffusivity is inversely influenced by strong polymer –plasticizer interaction (Hileman, 2005). The migration test conducted on the compounded PVC films showed minor variation in weights for the different formulations. This could be an indication of the compatibility of the plasticizers with PVC.

Conclusion

This study shows the effect of beta irradiation on plasticized PVC. It was observed that plasticized PVC with dioctylphthalate (DOP) and epoxidized rubber seed oil (ERSO) can degrade when exposed to beta irradiation. The extent to which the ERSO plasticizer imparts flexibility to the PVC films compared favourably with the traditional phthalate plasticizer, DOP. This study shows that the ERSO can be considered as a promising possibility for substitution for the conventional plasticizer especially at low concentrations (≤ 40 phr) without compromising the plasticizer efficiency.

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