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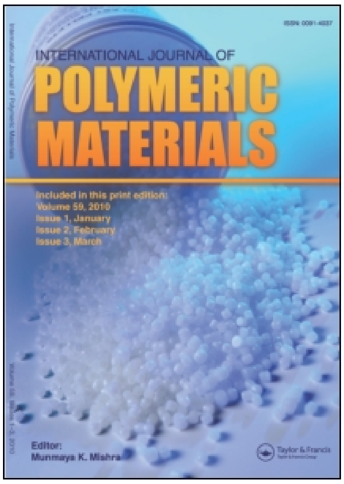

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Secondary Plasticizers for Polyvinyl Chloride (PVC) Epoxidized Esters†

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The synthesis of epoxy esters of 3-pentadecenyl phenol a low cost indigeneous raw material is described. These epoxy esters have further been evaluated as secondary plasticizers for PVC. Epoxidized 3-pentadecenyl-phenyl linoleate seems to be an attractive candidate as a secondary plasticizer amongst the epoxy esters evaluated.

INTRODUCTION

A great number of plasticizers have been available for PVC, but no single plasticizer structure satisfies the best possible combination of properties. It has become a common practice in the vinyl industry to use plasticizer blends to provide the optimum balance of properties to vinyl resin compositions.

Epoxides are primarily used as heat stabilizers. They also enhance light stability in vinyl compositions. As compatible liquids they contribute a plasticizing effect to vinyl resin compositions. Several epoxy compounds have been reported as plasticizers/stabilizers such as epoxidized soybean oil fatty acid phenyl esters,[1] epoxidized

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vegetable and fish oils,[2] acetoxy-epoxy derivatives of vegetable oils,[3] epoxidized acetylated caster oil[4] etc. Natural oils and other derivatives of natural products containing significant amount of unsaturation are commonly used as starting materials for producing epoxy plasticizers. In the present study the fatty acid esters of naturally occurring 3-pentadecenylphenol having significant amount of unsaturation have been used as the starting materials. The following epoxy esters have been synthesized and evaluated as secondary plasticizers in PVC.

I) Epoxidized 3-pentadecenylphenyl stearate.
II) Epoxidized 3-pentadecenylphenyl oleate.
III) Epoxidized 3-pentadecenylphenyl linoleate.

EXPERIMENTAL

Preparation of esters from 3-pentadecenyl phenol

3-pentadecenylphenyl stearate, 3-pentadecenylphenyl oleate and 3-pentadecenylphenyl linoleate were prepared as per the procedure reported in our earlier communication.[7]

Preparation of perbenzoic acid

Perbenzoic acid was prepared according to the procedure described in the literature.[5]

General method for the epoxidation of esters

In a 500 ml conical flask, a slight excess (1.2 moles per double bond) of perbenzoic acid was taken in cold chloroform. Then the respective ester was added to it at 0°C within 10 minutes time with constant stirring. The stirring was continued further for one hour at 0–5°C and finally the flask was kept in a refrigerator for a specific time (given in Table II for each ester). After a stipulated period the chloroform solution was washed with sodium bicarbonate solution till free from benzoic acid. After final washing with distilled water the chloroform solution was dried over anhydrous sodium sulfate. Finally it was filtered and the solvent was removed completely. The residual products could not be distilled even under reduced press-

TABLE I

Compounding recipe

No.	Ingredients	Parts
1	PVC Resin[a]	100
2	Plasticizer DOP/epoxidized ester (2/1)	Variable
3	White lead paste	8
4	Calcium stearate	1
5	Stearic acid	1

[a] A product of M/s. Sriram Vinyl, Kota, India having *K* value of 66.

ure. The oxirane oxygen content and elemental analysis are reported in Table II.

Compounding and testing

The compounding recipe used for evaluation of epoxidized esters as secondary plasticizers is given in Table I.

Initially the respective epoxidized ester was dissolved in a primary plasticizer, i.e. DOP, in the ratio 1:2 and then mixed in required proportions with the other ingredients of Table I in a mixer. The primary-secondary plasticizer mixture was blended in the proportions of 40, 50, 60 and 70 parts with 100 parts of PVC resin during evaluation studies. The compound was milled at 150°C for 6 minutes on a two roll mixing mill to give uniform sheets of thickness 0.01 to 0.025 inch.

The tensile strength, modulus, elongation and hardness were determined at room temperature according to ASTM designation D412-68 and D2240-68. The loss of plasticizer was determined according to ASTM designation D1203 (61 T) 1964. Volume resistivity was determined according to ASTM designation D-257-61 (1965).

DISCUSSION

Plasticizing efficiency of the plasticizer in plastics not only depends on the amount of plasticizer used but also on its chemical nature,

TABLE II

Epoxidized fatty acid esters of 3-pentadecenyl phenol

No.	Name of the compound	Ester used for epoxidation in g	Perbenzoic acid used for epoxidation in g	Total period required for epoxidation hours	Nature of the compound	Refractive index ηD^{25}	Oxirane content %	Analysis			
								Calcd.		Found	
								C %	H %	C %	H %
1	Epoxidized 3-pentadecenyl-phenyl stearate	10	7.2	90	Pale yellow	1.5053	4	78.25	11.04	78.56	10.92
2	Epoxidized 3-pentadecenyl-phenyl oleate	10	10.6	95	Pale yellow	1.5042	5.4	76.45	10.46	76.28	10.67
3	Epoxidized 3-pentadecenyl-phenyl linoleate	10	14.6	100	Pale yellow	1.5406	7.2	74.75	9.90	74.59	9.73

TABLE III

Physical properties of the PVC compounds F, G, H, and I

No.	Physical Properties	F (1)[a]	F (2)[b]	G (1)[a]	G (2)[b]	H (1)[a]	H (2)[b]	I (1)[a]	I (2)[b]
1	Hardness	75	78	70	73	71	73	80	81
2	Tensile strength (MPa)	17.72	18.89	18.55	20.13	19.03	20.41	17.51	18.55
3	100% Modulus (MPa)	13.58	15.65	14.41	16.55	14.89	17.03	13.24	15.72
4	Elongation %	230	160	240	200	250	200	200	190
5	% loss in heating with carbon black at 70°C for 24 h.	1.223	—	1.227	—	1.092	—	1.446	—
6	% loss on aging in oven at 100°C for 24 h.	7.476	—	7.235	—	6.537	—	8.011	—
7	% loss in 1% soap solution at 25°C for 24 h.	0.1236	—	0.1219	—	0.1134	—	0.1244	—
8	Volume resistance at 25°C (Ω cm)	1.530×10^{12}	—	2.473×0^{12}	—	4.564×10^{12}	—	6.372×10^{11}	—

F = 40 parts of mixture of DOP : Epoxidized 3-pentadecenylphenyl stearate
G = 40 parts of mixture of DOP : Epoxidized 3-pentadecenylphenyl oleate
H = 40 parts of mixture of DOP : Epoxidized 3-pentadecenylphenyl linoleate
I = 40 parts of dioctyl phthalate.

[a] Before aging

[b] After aging at 100°C for 24 h.

TABLE IV

Physical properties of the PVC compounds F–I, G–I, H–I, and I–I

No.	Physical properties	F–I (1)[a]	F–I (2)[b]	G–I (1)[a]	G–I (2)[b]	H–I (1)[a]	H–I (2)[b]	I–I (1)[a]	I–I (2)[b]
1	Hardness	73	74	66	69	67	69	76	79
2	Tensile strength (MPa)	16.68	17.51	16.13	16.76	17.51	18.96	16.96	17.51
3	100% Modulus (MPa)	13.03	15.03	12.68	14.41	13.93	15.72	12.62	14.48
4	Elongation %	250	240	260	250	270	250	260	230
5	% Loss in heating with carbon black at 70°C for 24 h.	1.686	—	1.613	—	1.540	—	1.877	—
6	% loss on aging in oven at 100°C for 24 h.	8.662	—	7.902	—	7.539	—	10.660	—
7	% loss in 1% soap solution at 25°C for 24 h.	0.1554	—	0.1404	—	0.1431	—	0.2101	—
8	Volume resistance at 25°C (Ω cm)	1.118×10^{12}	—	1.290×10^{12}	—	2.698×10^{12}	—	4.800×10^{11}	—

F–I = 50 parts of mixture of DOP: Epoxidized 3-pentadecenylphenyl stearate
G–I = 50 parts of mixture of DOP: Epoxidized 3-pentadecenylphenyl oleate
H–I = 50 parts of mixture of DOP: Epoxidized 3-pentadecenylphenyl linoleate
I–I = 50 parts of dioctyl phthalate

[a] Before aging

[b] After aging at 100°C for 24 h.

TABLE V

Physical properties of the PVC compounds F–II, G–II, H–II and I–II

No.	Physical properties	F–II (1)[a]	F–II (2)[b]	G–II (1)[a]	G–II (2)[b]	H–II (1)[a]	H–II (2)[b]	I–III (1)[a]	I–III (2)[b]
1	Hardness	64	66	64	67	64	67	65	68
2	Tensile strength (MPa)	15.31	16.89	15.44	16.55	16.62	17.74	13.96	16.34
3	100% Modulus (MPa)	11.93	13.86	12.06	14.06	13.03	14.00	10.13	11.24
4	Elongation %	280	260	280	260	280	260	270	240
5	% loss in heating with carbon black at 70°C for 24 h.	1.928	—	1.789	—	1.590	—	2.178	—
6	% loss on aging in oven at 100°C for 24 h.	10.520	—	9.684	—	8.190	—	11.100	—
7	% loss in 1% soap solution at 25°C for 24 h.	0.1624	—	0.1558	—	0.1525	—	0.2737	—
8	Volume resistance at 25°C (Ω cm)	9.495×10^{11}	—	1.147×10^{12}	—	1.484×10^{12}	—	3.8×10^{11}	—

F–II = 60 parts of mixture of DOP : Epoxidized 3-pentadecenylphenyl stearate
G–II = 60 parts of mixture of DOP : Epoxidized 3-pentadecenylphenyl oleate
H–II = 60 parts of mixture of DOP : Epoxidized 3-pentadecenylphenyl linoleate
I–II = 60 parts of dictyl phthalate.

[a] Before aging

[b] After aging at 100°C for 24 h.

TABLE VI

Physical properties of the PVC compounds F–III, G–III, H–III and I–III

No.	Physical Properties	F–III (1)[a]	F–III (2)[b]	G–III (1)[a]	G–III (2)[b]	H–III (1)[a]	H–III (2)[b]	I–III (1)[a]	I–III (2)[b]
1	Hardness	61	63	60	63	60	62	61	63
2	Tensile strength (MPa)	14.48	15.79	14.75	16.00	16.13	17.03	12.06	14.82
3	100% Modulus (MPa)	11.24	12.41	11.65	13.10	12.34	13.31	8.00	9.93
4	Elongation %	360	300	350	300	370	310	300	270
5	% loss in heating with carbon black at 70°C for 24 h.	2.118	—	1.988	—	1.938	—	2.4805	—
6	% loss on aging in oven at 100°C for 24 h.	10.88	—	10.20	—	10.20	—	11.54	—
7	% loss in 1% soap solution at 25°C for 24 h.	0.1719	—	0.1656	—	0.1656	—	0.3021	—
8	Volume resistance at 25°C (Ω cm)	4.035×10^{11}	—	9.520×10^{11}	—	9.520×10^{11}	—	2.583×10^{11}	—

F–III = 70 parts of mixture of DOP: Epoxidized 3-pentadecenylphenyl stearate
G–III = 70 parts of mixture of DOP: Epoxidized 3-pentadecenylphenyl oleate
H–III = 70 parts of mixture of DOP: Epoxidized 3-pentadecenylphenyl linoleate
I–III = 70 parts of dioctyl phthalate.

[a] Before aging

[b] After aging at 100°C for 24 h.

size and presence of functional groups. The compatibility of long chain compounds with PVC can be increased by the introduction of the three membered oxirane ring into the molecule.[6] It is reported that high oxirane content in fatty acid esters increases their compatibility with PVC and ultimately their thermal resistance and flexibility. The unsaturated fatty acid esters of 3-pentadecenyl phenol[7] and their chlorinated counter parts[8] have already been reported as plasticizer extenders for PVC. As the fatty acid esters of 3-pentadecenyl phenol have significant amounts of unsaturation, it was decided to introduce the three membered epoxide ring in these esters and evaluate them as plasticizers for PVC resin.

The epoxy fatty acid esters of 3-pentadecenyl phenol are high molecular weight yellowish liquids having medium viscosity. The oxirane content of these compounds ranges from 4 to 7.2% which is lower than the expected oxirane values. As has been reported earliers, the lower oxirane values may be due to the side reactions and destruction of the oxirane ring during the course of formation of the epoxy groups.[9] When compounded with PVC for use as primary

TABLE VII

Percentage retention of the physical properties after aging of the PVC compounds at 100°C for 24 h.

Compound No.	Hardness	Tensile strength	100% Modulus	Elongation
F	104	106	115	69
G	104	108	111	83
H	102	107	114	88
I	101	105	118	95
F–I	101	105	115	96
G–I	104	105	113	96
H–I	103	108	112	92
I–I	104	103	114	86
F–II	103	110	116	92
G–II	104	107	116	92
H–II	104	105	107	92
I–II	104	115	110	88
F–III	103	109	110	83
G–III	105	108	112	85
H–III	103	105	107	83
I–III	103	122	124	90

plasticizers they were found to be less compatible than DOP. Therefore they have been evaluated as secondary plasticizers.

The results in Tables III to VII indicate that the PVC compounds wherein epoxidized esters of 3-pentadecenyl phenol have been used as secondary plasticizers were superior in tensile strength, permanence, volume resistivity and percent retention of the physical properties after aging as compared to the PVC compounds where DOP alone is the plasticizer. Epoxidized 3-pentadecenylphenyl linoleate was the best of the group and as a secondary plasticizer for PVC. This observation can obviously be attributed to its high oxirane content (7.2% oxirane). The PVC compounds containing epoxy esters of 3-pentadecenyl phenol show decrease in hardness and increase in percent elongation as the proportion of the plasticizer-extender mixture increases.

CONCLUSION

The epoxidized product of 3-pentadecenylphenyl linoleate is the most attractive compound amongst the epoxidized esters studied as secondary plasticizer for PVC.

References

1. Kim, Jumsik, Park, Sang Hee and Lee, Chigiu, *Kungnip Kongop Yonguso Pogo* **19,** 129–32 (1969), (Korean), C. A. **75,** 6801 g (1971).
2. A. S. Danyushevkii, A. F. Vorobeva and A. I. Sergeeva, *Plasticeskie Massy* No. 11, 20–3, (1960), *C.A.* **55,** 14973a (1961).
3. A. Upendrarao, T. Chandrasekhararao and R. Subbarao, Fette, Seifen, *Anstrichem* **74**(4), 223–6 (Eng.) (1972), *C.A.* **77,** 77037a (1972).
4. R. K. Bhatnagar and A. K. Jain, *Indian* **105,** 490, (22nd August 1970), *C.A.* **76,** 60450a (1972).
5. *Organic Synthesis Collective,* Vol. I, 2nd edition (Edited by A. H. Blatt, Queens College Flushing N.Y.) 3rd printing Jan. 1946, p. 431.
6. L. P. Witnauer, H. N. Knight, W. E. Plam, R. E. Koos, W. C. Ault and D. Swern, *Ind. Eng. Chem.* **47,** 2304–10 (1955).
7. N. D. Ghatge and S. V. Vaidya, *Die Angewandte Makromolekulare Chemie* **43,** 1–10 (1975).
8. N. D. Ghatge, S. S. Mahajan and S. V. Vaidya (communicated).
9. J. Fath, *Mod, Plast.*, **37,** 8, 135 (1960).