

EFFECT OF EPOXIDES ON ULTRAVIOLET DEGRADATION OF POLYVINYL CHLORIDE

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(Received 10 July 1997, accepted 1 December 1997)

PVC-DOP system was formulated with some prepared epoxidized vegetable oils such as epoxidized linseed and soybean oils as well as epoxidized phenolic compound such as the prepared low molecular weight bisphenol A diglycidyl ether. Ba/Pb laurate as a light stabilizer was added in low concentration. Samples without epoxidized compounds were also formulated. The formulated PVC samples with and without a light stabilizer were tested and evaluated before and after exposure to UV lamp for 6 months at 20 °C. The effect of these epoxidized compounds on colour, mechanical properties and electrical volume resistivity of PVC samples before and after exposure to UV radiation was studied. It was found that the epoxidized linseed and soybean oils were generally good both as stabilizers and plasticizers. While bisphenol A diglycidyl ether was generally a good stabilizer but poor plasticizer. The epoxidized samples were also evaluated for use in electrical insulation fields.

Key words: PVC-DOP system, Epoxidized linseed oil, Epoxidized soybean oil, Bisphenol A diglycidyl ether, Ba/Pb laurate, UV degradation.

Introduction

The plastic industries have been working on formulating materials that are durable, long lasting and resistant to environmental degradation (EL-Hennaw 1983; Decker 1984 Kirk-Othmer 1985; Jacqueline and Kroschwitz 1990; Sadek *et al* 1993; Charles and Carraher 1996). Under exposure of PVC samples to UV radiations of wave length above 250 nm, a large amount of HCl is evolved, together with the formation of conjugated polyene sequences which are absorbed in the visible range and are therefore responsible for the discolouration of irradiated material. In addition to this dehydrochlorination, the polymer chains suffer both crosslinking and backbone scissions while carbonyl and hydroperoxide groups appear on the photo-oxidized PVC chains (Decker 1984).

The feature looks good for UV stabilizers and the concept of their use as sequestering agents or chelators was introduced in outdoor applications of PVC. Ultraviolet stabilizers such as phenylsalicylate, benzotriazoles, such as 2-(2'-hydroxyphenyl) benzotriazole, substituted acrylonitrile such as ethyl-2-cyano-3,3'-diphenyl acrylate, metallic complexes such as nickeldibutylthiocarbamate, and pigments such as carbon black (Charles and Carraher 1996). Epoxidized fats and oils, epoxidized fatty-acid esters, and epoxy resins such as bisphenol A diglycidyl ether were commonly used as stabilizers in conjunction with metal compounds (Sears and Darby 1982). Epoxidized soybean and linseed oils were the most frequently used plasticizer-stabilizers for vinyl resins

(Charles and Carraher 1996; Krochwitz 1991). They became the largest volume, fastest growing noncyclic plasticizers. Bisphenol A and hindered phenols were commonly added as stabilizers, especially in conjunction with specific plasticizers (Sears and Darby 1982).

The main objective of this work is to study the effect of the prepared epoxidized oils and bisphenol A diglycidyl ether in presence of Ba/Pb laurate, as UV stabilizer, on PVC degradation. Their influence on colour, mechanical properties and electrical volume resistivity of PVC composition was studied.

Experimental

To prepare epoxidized linseed oil or epoxidized soybean oil, peracetic acid (2 mol) was added dropwise in a period of 20 h at 30 °C to linseed oil or soybean oil (1 mol). The experiment was carried out according to the method described in (Motawie *et al* 1995 and 96). On the other hand low molecular weight bisphenol A diglycidyl ether was also prepared, thus sodium hydroxide solution (2.2 mol in 100 ml H₂O) was added dropwise to bisphenol A (1 mol) and epichlorohydrin (2 mol) at 65-70 °C. The experiment was carried out according to the described method (Motawie *et al* 1988; Motawie *et al* 1991 a and b Motawie 1993). Specifications of the prepared epoxidized compounds are given in Table 1.

Variable proportions of the prepared epoxidized compounds were added dropwise to a vigorously stirring mixture of 100g

Table 1
Specifications of the prepared epoxidized compounds

Epoxidized compounds	Average molecular weight	Epoxy group content, %	Epoxide equivalent / 100 g	Hydroxy group content, %	Iodine value, mg KOH/g
Epoxidized linseed oil	800	5.4	0.123	19.0	25
Epoxidized soybean oil	850	5.5	0.132	22.0	15
Bisphenol A diglycidyl ether	500	21.3	0.512	3.13	0

PVC (bulk density 0.45 g l⁻¹ and K value 70 produced by Egyptian Petroleum Company) and dioctylphthalate DOP (M.W. 391) at 25 °C. Sample without epoxidized compounds were also formulated, in such a way that in each formulation the total plasticizer content was 40 % (Table 2).

Table 2
Formulation of PVC-DOP-epoxide systems

Sample No.	Formulation, (for each 100 g PVC)		
	Epoxidized compound	DOP	
	Type	%	%
1	Without	0	40
2	Epoxidized linseed oil	10	30
3	" " "	20	20
4	" " "	30	10
5	" " "	40	0
6	Epoxidized soybean oil	10	30
7	" " "	20	20
8	" " "	30	10
9	" " "	40	0
10	Bisphenol A diglycidyl ether	10	30
11	" " "	20	20
12	" " "	30	10
13	" " "	40	0

After complete addition, the mixture was pressed under 100 kg/cm² at 150 °C for 20 min to give the required formulated samples without light stabilizer (samples 1-13 designated by K). While samples with a light stabilizer can be obtained after complete addition of Ba/Pb laurate (1%Pbw), as a light stabilizer to the above ingredients under the same conditions (samples 1-13 designated by K'). The formulated PVC samples were tested and evaluated before and after exposure to UV lamp (7 Watt Philips and placed at 5 cm from the samples) for 6 months at 20 °C.

The change in colour of the samples with and without a light stabilizer before and after exposure to UV radiation was followed up by the visual inspection. Tensile strength and percentage elongation of the formulated PVC samples were determined (ASTM D 638-77a 1989), using Instron tensile testing machine (Model 1026) at 23 ± 2 °C, with cross-head speed of 100 mm min⁻¹, chart speed 200 mm min⁻¹, and load range 0-500 newton. Also shore hardness test was carried out according to (ASTM D 2240 1986) by a Shore "A" Zewic Durometer. Electrical volume resistivity of the samples was determined at 20°C according to (ASTM D 257 1978) using direct current supply unit GMU 516/01 (Philips) and multimeter URLBN 1050 Rhode Schwarz.

Results and Discussion

Natural oils and other derivatives of natural products were commonly used as starting materials for producing epoxidized plasticizers. Linseed and soybean oils were the most common, since they were readily available and had a high degree of unsaturation (Nass 1976). Epoxidation of the vegetable oils was effected readily by peracids (Motawie *et al* 1995a). Changes that occurred during weathering of plasticized PVC-loss in flexibility, increased ease of cracking at low temperatures. The eventual brown colour formation depended significantly on the structure of plasticizer molecule as well as on the stabilizer system.

In the present work different ratios of DOP and epoxidized vegetable oils such as epoxidized linseed or soybean oils as well as epoxidized phenolic compounds such as bisphenol A diglycidyl ether were compounded with PVC. Ba/Pb laurate, as a UV stabilizer, was added giving light stabilized samples (samples 1-13 designated by K') for the purpose of comparison with other samples without Ba/Pb (samples 1-13 designated by K). Samples without epoxidized compounds were also formulated. The PVC samples were tested and evaluated before and after exposure to UV lamp for 6 months at 20 °C.

Table 3

The change in colour of the formulated PVC samples without and with Ba/Pb laurate, as a light stabilizer, before and after exposure to UV radiation for 6 months, at 20 °C

Sample No.	Formulation, (for each 100 g PVC)			Colour			
	Epoxidized compound	DOP		K		K'	
	Type	%	%	B	A	B	A
1	Without	0	40	Ly	y	Ly	Ly
2	Epoxidized linseed oil	10	30	pb	b	pb	pb
3	"	20	20	pb	b	b	b
4	"	30	10	b	db	b	b
5	"	40	0	b	db	b	b
6	Epoxidized soybean oil	10	30	py	y	y	y
7	"	20	20	py	y	y	y
8	"	30	10	y	dy	py	y
9	"	40	0	y	dy	py	y
10	Bisphenol A diglycidyl ether	10	30	Ly	dy	Ly	py
11	"	20	20	Ly	dy	Ly	py
12	"	30	10	py	dy	Ly	py
13	"	40	0	py	dy	Ly	py

K = Sample without light stabilizer B = Before exposure to UV radiation
 K = Sample with light stabilizer A = After exposure to UV radiation
 L = light P = pale b = brown y = yellow d = deep

The change in colour of formulated PVC samples with and without a light stabilizer before and after exposure to UV radiation was followed up by the visual inspection as shown in (Table 3).

The results given in (Table 3) indicated that samples without Ba/Pb laurate, as a light stabilizer, exhibited deterioration of colour after exposure to UV radiation (samples 1-13 designated by K). On the other hand this deterioration was not observed for stabilized samples with Ba/Pb laurate (samples 1-13 designated by k') which reduces colour formation by attacking double bond sequence in polyene product (Jacqueline and Kroschwitz 1990).

Tensile strength, percentage elongation and hardness of formulated PVC samples with and without a light stabilizer before and after exposure to UV radiation were studied as illustrated in Table 4.

The results in (Table 4) show that before exposure of PVC samples to UV radiation, the tensile strength and hardness were decreased steadily and percentage elongation was increased with increasing epoxidized oil concentrations for sample containing epoxidized oils (samples 2-9 designated by K) as compared with sample without epoxidized compound (sample 1 designated by K). On the other hand samples containing bisphenol A diglycidyl ether exhibit an opposite

Table 4

Mechanical properties of the formulated PVC samples without and with Ba/Pb laurate, as a light stabilizer, before and after exposure to UV radiation for 6 months, at 20 °C

S.No.	Epoxidized compound	DOP	Mechanical properties												
			Tensile strength, N/mm ²				Percentage elongation				Hardness, shore A				
			value	inc.	value	inc.	value	inc.	value	inc.	value	inc.	value	inc.	
	Type	%	%	B	A	B	A	B	A	B	A	B	A	B	A
1	Without	0	40	20	120	18	25	220	67	260	70	70	80	62	15
2	Epoxidized linseed oil	10	30	17	116	14	22	315	13	320	11	60	72	50	12
3	"	20	20	15	100	11	20	350	12	360	10	56	53.7	47	10
4	"	30	10	12	94	9	18	380	10	395	9	51	40	44	9
5	"	40	0	10	90	7	14	400	8	420	7	46	32	40	7
6	Epoxidized soybean oil	10	30	18	100	16	20	230	19	290	17	65	40	53	11
7	"	20	20	17	92	13	18	250	16	300	15	61	37	50	10
8	"	30	10	15	82	11	15	300	13	360	10	54	32	46	7
9	"	40	0	12	80	8	13	350	10	380	8	50	27	41	6
10	Bisphenol A diglycidyl ether	10	30	24	58	21	17	200	35	220	30	75	19	70	6
11	"	20	20	26	55	24	15	180	33	200	29	79	15	75	5
12	"	30	10	29	53.8	26	11	150	31	160	26	85	12.9	81	3.5
13	"	40	0	31	45.8	29	10	130	30	140	24	91	7.6	88	2

K = Sample without light stabilizer B = Before exposure to UV radiation K = Sample with light stabilizer A = After exposure to UV radiation

behaviour (samples 10-13 designated by K). This is due to the presence of phenyl group in the epoxy resin which in turn increases the tensile strength and decreases percentage elongation (Motawic *et al* 1988; 1991 a and b)). Thus the selection of these epoxidized samples as plasticizer can be arranged in the order according to their mechanical properties epoxidized : linseed oil > epoxidized soybean oil > bisphenol A diglycidyl ether.

After exposure to UV radiation the PVC samples began to lose their flexibility and became hard which in turn increased their tensile strength and hardness and decreased their elongation as shown in Table 4. Also the data given in Table 4 showed that increasing the epoxidized compound concentration decreased the increase degree in both tensile strength and hardness, and also decreased the decrease degree in percentage elongation as compared with sample without epoxidized compound (sample 1 designated by K). The results also revealed that for samples containing bisphenol A diglycidyl ether (samples 10-13 designated by K) the loss in flexibility after exposure to UV radiation was less than that for other samples containing epoxidized oils (samples 2-9 designated by K). This was due to the higher epoxide content in the composition. Epoxide groups at the end of aliphatic chains lead to the better heat stability (Sears and Draby 1982; Mc Guigan 1962).

Thus one can conclude that the selection of these epoxidized samples as UV stabilizers can be arranged in the order: bisphenol A diglycidyl ether > epoxidized soybean oil > epoxidized linseed oil.

The mechanism of stabilizer action was assumed to involve the removal of HCl as it is formed and keep it from aggravating decomposition by addition to the epoxide ring (Charles and Carrarher 1996). Stabilizers that are usually considered to scavenge HCl include metallic salts of organic acids or phenols. The most common are the mixtures of the salts of barium and cadmium with or without small amounts of zinc (Sears and Darby 1982).

The results in (Table 4) also show that before exposure, PVC samples containing Ba/Pb laurate as a light stabilizer, to UV radiation the tensile strength and hardness were decreased and percentage elongation was increased with increasing epoxidized oil concentration for samples containing epoxidized oils (samples 2-9 designated by K). As compared with sample without epoxidized compound (sample 1 designated by K') and samples without light stabilizer (samples 2-9 designated by K). While for samples containing bisphenol A diglycidyl ether (samples 10-13 designated by K'), both tensile strength and hardness were increased and percentage

elongation was decreased with increasing epoxidized phenolic compound, e.g. bisphenol A diglycidyl ether, due to the presence of phenyl group in the epoxy resin. As compared with samples containing epoxidized oils (samples 2-9 designated by K'). It was found that this increase in both tensile strength and hardness was less than that for the samples without Ba/Pb laurate as a light stabilizer (samples 10 - 13 designated by K).

After exposure to UV radiation, the PVC samples containing Ba/Pb laurate showed limited loss in their flexibility (Table 4). The degree of increase of tensile strength and hardness and the degree of decrease of percentage elongation were decreased with increasing epoxidized compound concentrations (samples 2-13 designated by K'). As compared with sample without epoxidized compound (sample 1 designated by K'), and samples without light stabilizer (samples 2-13 designated by K).

This indicated that Ba/Pb laurate may be retard degradation of the polymer, e.g. enhances the stabilization by a so-called synergistic effect. This explained the more effective stabilization by a mixture of carboxylic acid salt (Winkler 1949; Cowell and Joseph 1950; Krik-Othmer 1985).

The electrical volume resistivity or its reciprocal, electrical conductivity, is a clearly defined specific quantity and important to the insulation industry (Boening 1973; Charles and Carrarher 1996). The volume resistivity of formulated PVC samples without and with a light stabilizer before and after exposure to UV radiation was determined at 20 °C as given in (Table 5).

Volume resistivity values given in (Table 5) showed higher resistance at low plasticizer content for all samples, since ion mobility depends on the plasticity of the mass. Hence the volume resistivity of PVC compositions will vary greatly with choice and concentration of plasticizer as these affect the internal viscosity of the mass (Motawie *et al* 1991b; Manieh *et al* 1995). Samples containing bisphenol A diglycidyl ether give higher electrical resistance (samples 10-13 designated by K) with comparison to samples containing epoxidized oils (samples 2-9 designated by K).

After exposure of PVC samples to UV radiation the results in (Table 5) show that the degree of decrease of volume resistivity decreased with increasing epoxidized compound concentrations (samples 2-13 designated by K) in comparison with sample without epoxidized compound (sample 1 designated by K). This was because after exposure of PVC samples to UV radiation, HCl formed by incipient decomposition of the polymer can cause poor resistivity in the final product (Sears and Darby 1982). The data in Table 5

Table 5

Electrical volume resistivity of the formulated PVC samples without and with Ba/Pb laurate, as a light stabilizer, before and after exposure to UV radiation for 6 months, at 20 °C

Sample No.	Formulation, (for each 100 g PVC)				Electrical volume resistivity at 20 °C x 10 ¹⁰ Ω cm				
	Epoxidize compound			DOP		K		K'	
	Type			%	%	B	A	B	A
1	Without			0	40	22	92	8.6	40
2	Epoxidized linseed oil			10	30	15	91	3.5	32
3	"	"	"	20	20	12	90	5.3	25
4	"	"	"	30	10	9	90	2	16
5	"	"	"	40	0	6	89	1	9.5
6	Epoxidized soybean oil			10	30	18	70.5	4.4	26
7	"	"	"	20	20	14	69	2.5	22
8	"	"	"	30	10	11	60	1.9	14
9	"	"	"	40	0	9	55	1.2	7
10	Bisphenol A Diglycidyl ether			10	30	20	68	6.4	12
11	"	"	"	20	20	19.5	65	4.2	8
12	"	"	"	30	10	19	57	3.5	6
13	"	"	"	40	0	17	50	2.1	2

K = Sample without light stabilizer B = Before exposure to UV radiation
K = Sample with light stabilizer A = After exposure to UV radiation

also indicated that the degree of decrease of volume resistivity for samples containing bisphenol A diglycidyl ether (samples 10-13 designated by K) was less than that for other samples containing epoxidized oils (samples 2-9 designated by K). This can be attributed to the presence of phenyl group in the bisphenol A diglycidyl ether (Motawie *et al* 1991b).

Before and after exposure, the PVC samples containing Ba/Pb laurate as light stabilizer to UV radiation showed sharp decrease in volume resistivity (samples 2-13 designated by K') in comparison with samples without Ba/Pb laurate (samples 2-13 designated to K). Since lead stabilizers are ionic impurities, they might increase conductivity (Sears and Darby 1982).

The data also revealed that the degree of decrease of volume resistivity for samples containing Ba/Pb laurate is less than that for the samples without this stabilizer.

Conclusion

Epoxidized soybean or linseed oil is used not only as a plasticizer but also as a UV stabilizer for PVC resins.

Although, bisphenol A diglycidyl ether is a poor plasticizer, it is generally a good stabilizer for PVC resins.

Samples containing bisphenol A diglycidyl ether have higher electrical volume resistivity than samples containing epoxidized oils.

Incorporation of an epoxy compound with carboxylic acid

salt produces a synergistic UV stabilizing effect.

The epoxidized compounds are evaluated for use in electrical insulation field.

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