Vinyl Epoxystearate: Preparation, Polymerization and Properties of Polymers and Copolymers*

LEONARD S. SILBERT,† ZELDA B. JACOBS,† WILLIAM E. PALM,
LEE P. WITNAUER, WILLIAM S. PORT, and DANIEL SWERN,
Eastern Regional Research Laboratory,‡ Philadelphia 18, Pennsylvania

In a previous paper,[1] a study was reported of the mechanical properties of copolymers of vinyl chloride containing various amounts of vinyl stearate. These properties were compared with those of compositions of polyvinyl chloride containing increasing amounts of external plasticizers (di-2-ethylhexyl phthalate and tricresyl phosphate). An approximate correspondence was found between the two systems of polymer modification, but they were not strictly comparable because of differences in chemical structure between the plasticizer and the comonomer used. The chemistry of the system is an important consideration, as evidenced by the fact[1] that, in a series of copolymers of vinyl chloride and homologous vinyl esters, those containing long-chain esters exhibited less flexural stiffness than those containing short-chain esters. In the present study, an effort was made to eliminate differences between the chemistry of the comonomer and of the external plasticizer by using two closely related compounds, vinyl epoxystearate as the comonomer and butyl epoxystearate as the plasticizer.

This paper reports the preparation of vinyl epoxystearate, some properties of polyvinyl epoxystearate, a comparison of the mechanical and thermal properties of copolymers of vinyl chloride and vinyl epoxystearate with those of compositions of polyvinyl chloride and butyl epoxystearate, and a comparison of the light and heat stability of these copolymers and compositions.

PREPARATION OF VINYL EPOXYSTEARATE

Vinyl epoxystearate was prepared by the preferential peracid epoxidation of the internal double bond of vinyl oleate.

Kinetic Studies

A study of the relative rates of epoxidation of the two double bonds in vinyl oleate was undertaken to determine whether advantage could be taken of the competing rates of reaction for the peracid to permit a practical synthesis. For this study, perbenzoic acid was used rather than commercial peracetic acid to avoid the difficulties in analysis which the presence of hydrogen peroxide and diacetyl peroxide in the latter would entail.

Although the epoxidation of a vinyl ester has not been studied previously, the reaction of other species of unsaturated compounds with perbenzoic acid is quite extensively reported in the literature.[2] Table I

TABLE I

SPECIFIC REACTION RATE CONSTANTS (k) FOR THE REACTION OF ALIPHATIC OLEFINS WITH PERBENZOIC ACID[2]

Olefin	Temp., °C.	$k \times 10^3$, l./mole min.
Oleic acid	0	384
Hendecenoic acid	0	16
Sorbic acid and derivs.	0	0.03–0.23
Sorbic acid and derivs.	20	0.2–1.52
Vinyl laurate[a]	30	7.13
Vinyl oleate[a]	30	1580

[a] This investigation.

shows the effect of groups adjacent to the olefinic bond on the specific rate for the reaction of some aliphatic olefins with perbenzoic acid. An inspection of these rates in consideration of the structure of the compounds led to the conclusion that the epoxidation rates for the two double bonds of vinyl oleate should be sufficiently different for the synthesis to be feasible. The data show that oleic acid (internal double bond) reacts with perbenzoic acid at 0°C. 24 times as fast as does hendecenoic acid (terminal double bond) and approximately 10,000 times as fast as does sorbic acid and its derivatives (double bond deactivated by conjugative resonance with the electronegative carboxyl group). It was reasoned, then, that because the vinyl ester double bond is terminal and moderately deactivated by the

$$CH_3—(CH_2)_7—CH=CH—(CH_2)_7—COO—CH=CH_2$$

$$\downarrow R—CO_3H$$

$$CH_3—(CH_2)_7—CH—CH—(CH_2)_7—COO—CH=CH_2 + R—CO_2—H$$
$$\underset{O}{\diagdown\diagup}$$

$$RCO_2H \diagup \qquad\qquad \diagdown R—CO_3H$$

$$CH_3—(CH_2)_7—CH—CH—(CH_2)_7—COO—CH=CH_2 \qquad CH_3—(CH_2)_7CH—CH(CH_2)_7COOCH=CH_2$$
$$\underset{OH}{|} \ \underset{O_2CR}{|} \qquad\qquad\qquad\qquad \underset{OH}{|} \ \underset{O_3CR}{|}$$

Fig. 1. Epoxidation of vinyl oleate and representative ring-opening reactions.

ester linkage, the specific reaction rate constant for a vinyl ester of a saturated fatty acid (*e.g.*, vinyl laurate) would be smaller than that for hendecenoic acid (double bond terminal, but not deactivated) but greater than that for sorbic acid (double bond strongly deactivated). This was confirmed experimentally in the reaction with perbenzoic acid at 30°C.: the specific reaction rate constant was found to be 1580×10^{-3}/l./mole min. for vinyl oleate (combined k for both double bonds) and 7.13×10^{-3} for vinyl laurate, a ratio of 220:1. It was concluded, therefore, that the preparation of vinyl epoxystearate by epoxidation of vinyl oleate was feasible.

Constitution of Products of Reaction Simultaneous with and Subsequent to Epoxidation

In determining the method of purification of crude vinyl epoxystearate, consideration had to be given to the nature of the possible products which would be formed by reactions occurring simultaneously with and subsequent to epoxidation. Figure 1 outlines the formation of vinyl epoxystearate and ring-opened products obtained from the reaction of benzoic and perbenzoic acids with the oxirane ring. In earlier studies,[3] it was found that oxirane ring opening in epoxystearic acid by acetic acid occurred at the rate of 1% per hour at room temperature. Both benzoic acid, which is a relatively strong acid, and perbenzoic acid should be capable of opening the ring to produce hydroxy ester and hydroxy perester, respectively. The reactions which the vinyl ester double bond are believed to undergo simultaneously with epoxidation of the internal double bond are shown in Figure 2. Experiments in support of these conclusions were performed on vinyl laurate (rather than vinyl oleate) in order to isolate the reaction of the peracid on

$$RCO_2CH{=}CH_2$$

$$R'CO_3H \nearrow \qquad \searrow R'C{=}O$$

$$RCO_2CH{-}CH_2 + R'CO_2H \qquad R'CCH_2CHO_2CR$$
$$\underset{O}{\diagdown\diagup} \qquad\qquad\qquad \underset{O}{\|}$$

$$(I)$$

$$\Big\downarrow R'CO_2H \qquad\qquad \Big\downarrow RCO_2CH{=}CH_2$$

polymer

$$RC{\diagup}^{O}{\diagdown}\ \ {\diagup}CHCH_2O_2CR'$$

$$(II)$$

$$\Big\downarrow$$

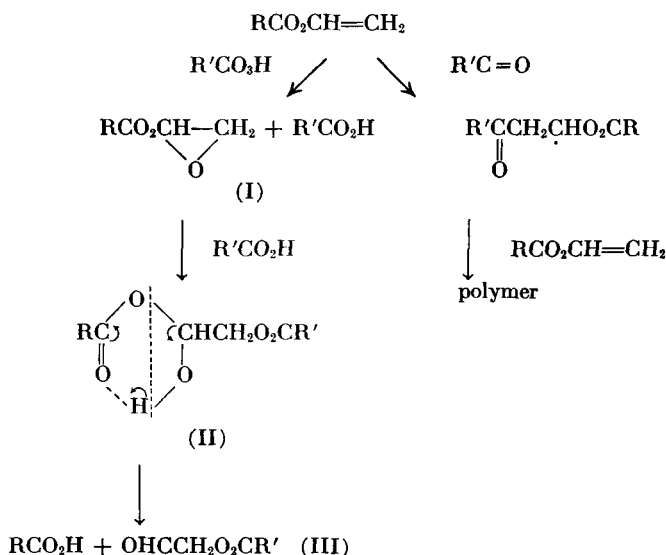$$RCO_2H + OHCCH_2O_2CR' \quad (III)$$

Fig. 2. Reactions of vinyl esters with peracids.

the vinyl group.   The following observations were made and conclusions drawn in support of the mechanism shown in Figure 2:

(1) The rate of disappearance of vinyl laurate (as measured by iodine number) was greater than the rate of consumption of peracid.   When the reaction mixture of vinyl laurate and perbenzoic acid (in benzene) was poured into methanol, a viscous liquid separated.   Both observations are consistent with the postulate of vinyl polymer formation: the free radical formed from the decomposition of a single peracid molecule would initiate the polymerization of many vinyl ester molecules; polyvinyl laurate is insoluble in methanol.   A smaller quantity of polymer was formed in the epoxidation of vinyl oleate probably because of the inhibitory effect of the allyl system of the internal double bond.[4]

(2) The reaction product of peracetic acid and vinyl laurate (in acetic acid) was found to have a high acid number after it was washed with water to remove the unused peracetic and acetic acids.   It is postulated that the acidity is due to water-insoluble lauric acid.   The oxirane content of the product (as well as that from the reaction of perlauric acid and vinyl laurate) is zero.

(3) A qualitative demonstration of the presence of glycolaldehyde in the reaction mixture of peracetic acid and vinyl laurate was made by means of a positive color test.[5]   Glycolaldehyde is believed to have arisen from the hydrolysis of its acetic acid ester (III, $R' = CH_3$).   Confirmation of this view was obtained by the isolation of III ($R' = C_{11}H_{23}$) as its 2,4-dinitrophenylhydrazone from the reaction mixture of perlauric acid and vinyl laurate and of perlauric acid and vinyl 2-ethylhexanoate.   This derivative was shown to be identical with the 2,4-dinitrophenylhydrazone from the product of the periodate oxidation of α-monolaurin, an unequivocal method of obtaining III ($R' = C_{11}H_{23}$).

PROPERTIES OF POLYMERS AND COPOLYMERS FROM VINYL EPOXYSTEARATE

Polyvinyl Epoxystearate

Conventional methods for free radical initiation of polymerization were applicable to the polymerization of vinyl epoxystearate.   The results of the light scattering, osmotic pressure, and viscosity measurements are given in Table II.   Polyvinyl epoxystearate has about the same weight-average degree of polymerization as polyvinyl caprate prepared under approximately the same conditions,[6] but its number-average is higher.   A comparison of the weight-average and number-average molecular weights indicates a wide distribution of molecular sizes.   An increase in polymerization temperature from 50 to 75°C. produced only a slight decrease in the average molecular size with apparently little effect on distribution.   The molecular weight, however, was markedly decreased by solvent transfer, the weight-average molecular weight being reduced from greater than 200,000 to approximately 80,000.

Intrinsic viscosities reported in Table II were taken from plots of reduced viscosity (η_{sp}/C) *versus* concentration. Measurements were made in the

TABLE II
MOLECULAR WEIGHT AND SOLUTION VISCOSITY CHARACTERISTICS OF POLYVINYL EPOXYSTEARATE SAMPLES

Expt. No.	Method	Temp., °C.	Molecular weight $M_n{}^a$	$M_w{}^b$	Viscosity $[\eta]$	$k'{}^c$
1........	Suspension	50	95,300	309,000	0.270	0.62
2........	Suspension	75	73,100	245,000	0.230	0.57
3........	Solution	79–80	—	82,000	0.045	2.1

[a] Determined by osmotic pressure in tetrahydrofuran solution.
[b] Determined by light scattering in tetrahydrofuran solution.
[c] From Huggins' equation.[7]

concentration range 0.5 to 2 g./100 ml. A linear relationship between η_{sp}/C and C was obtained which could be represented by Huggins' equation:[7]

$$\eta_{sp}/C = [\eta] + k' [\eta]^2 C$$

The intrinsic viscosities of the polyvinyl epoxystearate samples were low and were approximately of the same order of magnitude as those of polyvinyl palmitate, laurate, and caprylate.[6]

Copolymers of Vinyl Chloride and Vinyl Epoxystearate

Copolymers of vinyl chloride containing various amounts of vinyl epoxystearate were prepared by the suspension procedure[1] used for the preparation of copolymers of vinyl chloride and vinyl stearate. The mechanical and thermal properties of these copolymers were compared with compositions of polyvinyl chloride containing 5 to 20 mole per cent of butyl epoxystearate which were prepared by conventional milling and molding proce-
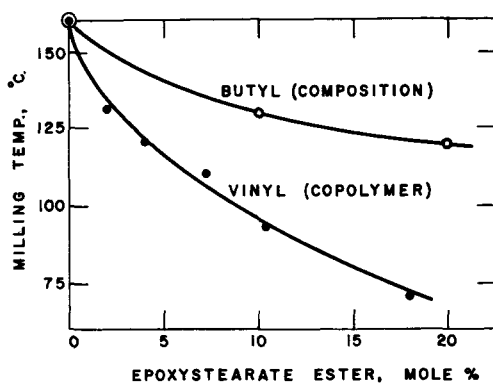
Fig. 3. Effect of epoxystearate ester content on milling temperatures of compositions of polyvinyl chloride and butyl epoxystearate and of copolymers of vinyl chloride and vinyl epoxystearate.

dures.   In general, while there was a parallelism in the change of the value
of the various properties with increase in epoxystearate content, quantita-
tive differences were observed between the two modes of plasticization.

Crystallinity.   The milling temperature decreased as the per cent
plasticizer was increased, but, as is shown in Figure 3, a more gradual
change was observed for butyl epoxystearate plasticized samples than for
the copolymers.   It is postulated that the milling temperature corresponds
to the temperature at which crystallite crosslinks are melted out.   If this
interpretation is correct, it would follow that the external plasticizer has a
smaller effect on the crystallinity of the polymer than does an internal
plasticizer.   Such difference in effect on crystallinity may arise because of the
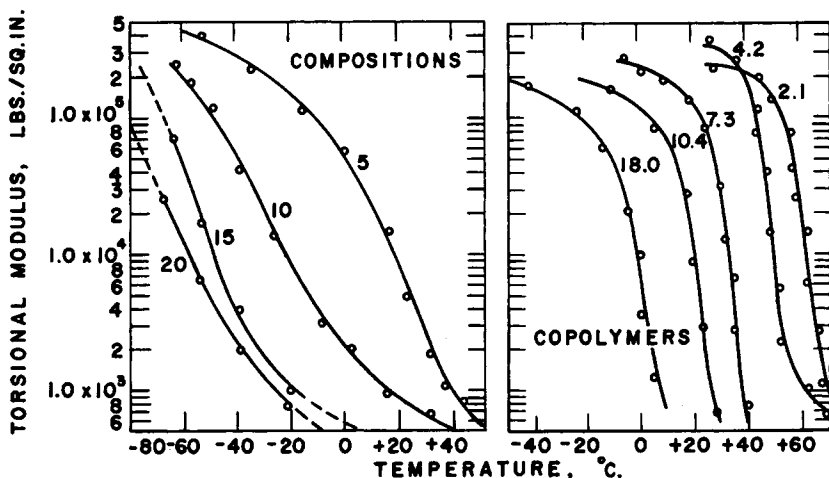
Fig. 4. Effect of temperature on the torsional modulus of polyvinyl chloride-
butyl epoxystearate compositions and vinyl chloride-vinyl epoxystearate
copolymers.   Numbers denote percentage of plasticizer or comonomer.

necessarily random distribution of the comonomer during copolymerization
as compared with the more preferential segregation of the plasticizer in the
noncrystalline regions of the polymer.

Torsional Modulus.   The effect of temperature and per cent plasti-
cizer or comonomer on torsional modulus are shown in Figure 4.   An in-
crease in either plasticizer or comonomer content caused a decrease in the
modulus, but the temperature coefficients of the modulus for the copoly-
mers were greater than those of the compositions.   One possible explana-
tion for this behavior is that plasticization is a dynamic process controlled
by the rate of diffusion of plasticizer as discussed by Aiken et al.,[8] and in this
sense the copolymers are not plasticized at all but are merely weakened
polyvinyl chlorides.   On the other hand, it is possible that plasticization
requires a long-time association of plasticizer with a chain segment com-
pared with the timescale for segmental motion, but that, in the time re-
quired for measurement of the modulus, diffusion of the plasticizer can

occur permitting the motion of several segments per plasticizer molecule, and thus an external plasticizer is more efficient than an internal plasticizer. If diffusion of the plasticizer (in the composition) proceeds more rapidly than does the segmental motion of the copolymer at a given temperature and, if the controlling step in plasticization is diffusion, then in a dynamic shearing experiment the modulus of the composition should not approach the modulus of the copolymer except at a test rate approaching the rate of diffusion.

Stability to Heat and Light. In heat and light stability tests, copolymers of vinyl chloride and vinyl epoxystearate showed greater resistance to degradation (as evidenced by discoloration) than did unplasticized polyvinyl chloride, but the stability of compositions of polyvinyl chloride and butyl epoxystearate and other epoxidized fatty acid derivatives was greater than that of the copolymers. Some results of these tests are given in the "Experimental" section below.

EXPERIMENTAL

Reagents

Vinyl oleate and *vinyl laurate* were prepared by the procedure of Swern and Jordan.[9] A commercial grade of vinyl oleate met the following specifications: n_D^{30} 1.4538, I.V. 165.7; in a 12-hour copolymerization test attained n_D^{55} 1.4490.[10]

Peracetic acid was a commercial 40% acetic acid solution in which free sulfuric acid was neutralized with sodium acetate prior to use. *Perbenzoic acid* was prepared by the Kolthoff-Lee-Mairs[11] modification of Braun's[12] procedure. *Perlauric acid* was prepared by the method of Parker et al.[13] The peracid contents of these preparations were determined by the procedure described by Swern.[14]

Vinyl chloride was obtained in cylinders and purified by distillation using a cold-finger condenser cooled by solid carbon dioxide. *Vinyl 2-ethylhexanoate*, b_{52} 103°, n_D^{30} 1.4211–13, was distilled from a commercial product. *Vinyl acetate* was obtained by distillation of the commercial product; the fraction boiling at 72–72.5°C. at atmospheric pressure was used. *Tetrahydrofuran* was purified by simple distillation and stored in the cold under nitrogen.

Polyvinyl alcohol (98.5 to 100% hydrolyzed, $\bar{M}_n$ 40,000), *benzoyl peroxide* and *butyl epoxystearate* were obtained from commercial sources, and were used without further purification. Solvents and precipitants were of reagent grade and were not further purified.

Vinyl Epoxystearate

Preparation by Perbenzoic Acid Oxidation. Vinyl epoxystearate was prepared from vinyl oleate in benzene solution by the incremental addition of perbenzoic acid at a rate to maintain the reaction temperature at

20°C.   The unreacted perbenzoic acid was destroyed with potassium iodide solution, and the benzene solution was washed with potassium iodide solution, dilute sodium thiosulfate, sodium bicarbonate, and water.   After the benzene had been dried and distilled off under vacuum, the crude vinyl epoxystearate was dissolved in methanol (3 ml. of solvent per gram), treated with carbon black to adsorb small quantities of insoluble polymer, and then crystallized three times from methanol at 5°C.   The yield of pure monomer after three crystallizations was 18–22%.

Table III illustrates the results of three experiments conducted under different conditions.   When the molar concentration of perbenzoic acid was increased, the reaction time was decreased and the oxirane oxygen value was increased.   The 1:1.2 mole ratio of vinyl oleate to perbenzoic acid yielded a crude reaction product having an oxirane oxygen value 93% of theory.

TABLE III

EFFECT OF CONCENTRATION AND MOLE RATIO OF PERBENZOIC ACID ON EPOXIDATION OF VINYL OLEATE

Molar ratio vinyl oleate to perbenzoic acid	Molar concn. vinyl oleate	Reaction time, hrs.	Perbenzoic acid consumed, % of theor.	Crude product oxirane oxygen %[a]
1:1	0.050	24	96.0	4.43
1:1	0.180	2	94.5	4.45
1:1.2	0.222	1.5	97.8	4.60

[a] Calculated for vinyl epoxystearate 4.93%.

Preparation by Peracetic Acid Oxidation.   For larger scale studies vinyl epoxystearate was prepared from vinyl oleate (made from a commercial grade of oleic acid which had been crystallized at low temperatures to separate polyunsaturated acids) and peracetic acid.   Epoxidation of the vinyl oleate was conducted with a 1:1.25 mole ratio of vinyl oleate to peracetic acid at 0.5–0.6 molar concentration in glacial acetic acid at 20°C.   The reaction was permitted to proceed for a period of four to five hours consuming 97–98% of the calculated quantity of peracetic acid.   Oxirane analysis of the isolated crude compound was 90% of theory.   Two crystallizations from methanol gave a product with an oxirane analysis within 96% of the theoretical value.   The crude vinyl epoxystearate was also purified by a flash distillation at 0.01–0.1 mm. pressure at a head temperature of 130–150°C.   The purity of the distillate, as determined by its oxirane oxygen content, was 90–91% and the yield was 30–48%.   The product polymerized at a retarded rate (compared with the twice-crystallized monomer) whereas the crude monomer did not polymerize.

Properties of Pure Vinyl Epoxystearate.   Purified vinyl epoxystearate [Iodine Value 78.5 (calc. 78.3) and oxirane oxygen 4.85% (calc. 4.93%)] has the following physical characteristics: m.p. 22.2–22.6°C., n_D^{30} 1.4529, dn/dt −0.00037 (30–50°C.), d_4^{30} 0.9133 ± 0.0003 g./ml.

The rate of bulk polymerization at 70°C. in the presence of 0.25% benzoyl peroxide was used as a measure of purity of vinyl epoxystearate. Figure 5 compares the rate of copolymerization by vinyl epoxystearate with that of vinyl stearate as reflected by the increase in their refractive indices. The initial refractive index (at 50°C.) for the solution of vinyl epoxystearate and initiator was 1.4461; that of vinyl stearate (at 55°C.) was 1.4364.
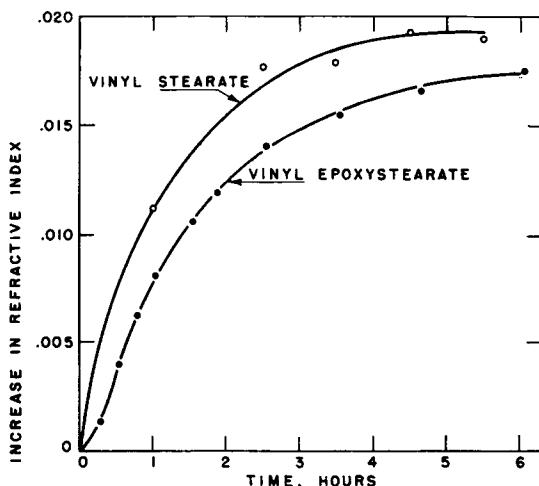

Fig. 5. Comparison of the homopolymerization rates of vinyl stearate and vinyl epoxystearate.

Polyvinyl Epoxystearate

Preparation. *Experiment 1.* Vinyl epoxystearate (50 g.) was polymerized by the suspension technique in 100 ml. of 1% aqueous polyvinyl alcohol in the presence of 0.0290 g. (0.078 mole per cent based on the monomer) benzoyl peroxide in a nitrogen atmosphere at 50°C. for 48 hours. The mixture was extracted with benzene, the polyvinyl alcohol solution was discarded, and the benzene solution was dried over anhydrous sodium sulfate. The dried solution was made up to 250 ml. for analysis: Iodine Value 60.0, oxirane oxygen, 4.82%. From the iodine value, a 23% conversion was calculated. The polymer was isolated by two precipitations from benzene solution into methanol.

Experiment 2. The reaction was repeated at 75°C. for a reaction time of six hours. The yield was 50%. The polymer was isolated by four precipitations from benzene solution into methanol. Its oxirane oxygen content was found to be 4.72%, Iodine Value 3.50, n_D^{50} 1.4647, dn/dt −0.00033.

Experiment 3. A solution of 100 g. of vinyl epoxystearate and 0.50 g. benzoyl peroxide in 300 ml. methyl ethyl ketone was refluxed in a nitrogen atmosphere for 19 hours. The solution was concentrated and the polymer was isolated by precipitation. After further purification by precipitation, the polymer was dried *in vacuo*.

Molecular Weight. The molecular weights of the polymers of Experiments *1–3* were determined by light scattering and osmometry. Light scattering measurements, at angles from 135 to 22° to the primary beam, were made with a Brice-Phoenix photometer, using a cylindrical scattering cell[15] at wave lengths 436 and 546 mμ. Results reported were averaged for the two wave lengths. The maximum difference between the molecular weights at the two wave lengths was 6%. The refractive increment was determined in a differential refractometer, the average dn/dc was 0.071 ± 0.001 at λ 546 and 0.073 ± 0.001 at λ 436 for the concentration range 0.5 to 2% and for the three polymers studied. Osmotic pressure determinations were made at 30° in a Fuoss-Mead type osmometer, using a denitrated nitrocellulose membrane. The intrinsic viscosities given were deduced from measurements on an Ostwald-type viscometer at 30°C. All solutions used were first clarified by centrifugation and then passed through ultrafine sintered glass filters. The solvent used in all measurements reported was tetrahydrofuran.

Copolymers of Vinyl Epoxystearate and Vinyl Chloride

Composition. A series of copolymers of vinyl chloride containing various amounts of vinyl epoxystearate was prepared in suspension.[1] The composition of the monomer mixtures and of the copolymers formed from them are shown in Table IV. The oxirane oxygen content of the

TABLE IV
COMPOSITION AND ELEMENTAL ANALYSIS OF COPOLYMERS OF VINYL CHLORIDE AND VINYL EPOXYSTEARATE

Mole % vinyl epoxystearate			Oxirane oxygen	
In monomer mixt.	In copolymer[a]	% Cl	Found	Calc.[a]
2.5	2.1	51.06	0.54	0.50
5	4.2	46.31	0.90	0.91
10	7.3	40.21	1.45	1.62
15	10.4	35.47	1.80	1.85
20	18.0	26.11		

[a] From Cl analysis.

copolymers listed in Table IV demonstrate that there is substantially no opening of the oxirane ring during polymerization. Some mechanical and thermal properties of these copolymers and also of compositions of polyvinyl chloride containing corresponding amounts of butyl epoxystearate are given in Table V.

Evaluation of Physical Properties. An ASTM method[16] was used for determining the tensile strength of the samples. Also determined was the Clash-Berg T_f temperature,[17] which is the temperature at which the torsional modulus of elasticity is 135,000 p.s.i. and corresponds to a brittle temperature.

TABLE V

Mechanical and Thermal Characteristics of Vinyl Chloride Copolymers and Polyvinyl Chloride Compositions

Vinyl chloride copolymer, mole % vinyl epoxystearate	Polyvinyl chloride compn., mole % butyl epoxystearate	Tensile strength, p.s.i.	Elongation %	100% modulus, p.s.i.	Clash-Berg[17] T_f, °C.	Stiffness at 23°C. p.s.i.	Milling temp., °C.
2.1	—	5030	0	—	49	240,000	132
4.2		4540	0	—	41	330,000	121
	5	3350	260	1960	−17	9,240	—
7.3		3080	140	3000	19	88,000	110
	10	2190	320	870	−55	960	130
10.4		2100	280	1370	− 1	2,350	93
	15	1305	650	550	−72	370	—
18.0		650	200	225	−32	90	71
	20	890	1080	380	−75	225	120

Resistance of the copolymers toward thermal degradation was measured by heating the samples in an oven at 160°C., and comparing their change in color as a function of time with that of a polyvinyl chloride composition containing 35% epoxidized diacetylated cottonseed oil under the same conditions. A copolymer containing 37% (by weight) of vinyl epoxystearate darkened as much in 4 hours as the composition did in seven hours. When compared among themselves, the copolymers showed increasing stability with increasing oxirane content.

Stability toward ultraviolet radiation alone was estimated by exposing solvent-cast films (6% in tetrahydrofuran) to radiation from a Hanovia type 7420 mercury arc lamp at a distance of 30 inches from the light source for 24, 48, and 72 hours at 30°C. To avoid heat effects, the experiment was conducted in a hood with air sweeping across the surface of the film to prevent a temperature rise. The copolymers tested contained 2.1, 4.2, and 7.3 mole per cent vinyl epoxystearate. Unplasticized polyvinyl chloride and polyvinyl chloride stabilized with butyl epoxystearate (in amounts equivalent to the epoxy content of the copolymers) were used for comparison. For the same exposure periods the copolymers showed decreasing color with increasing vinyl epoxystearate content. All the copolymers were better than unplasticized polyvinyl chloride, but none of them approached the compositions containing butyl epoxystearate, which did not change in color throughout the test. The effect of light on color and solubility of molded specimens was determined by exposing them in an Atlas Twin Arc Weather-Ometer. The specimens were necessarily heated during this exposure; temperatures ranged from 70–75°C. The specimens were examined at regular intervals for changes in color and solubility. The copolymers showed better stability to color changes as the epoxystearate content increased. All the copolymers became insoluble in tetrahydrofuran after 48 hours.

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Synopsis

Vinyl epoxystearate was synthesized by the reaction of vinyl oleate and percarboxylic acids. An investigation of the kinetics of the epoxidation of the two unsaturated bonds in vinyl oleate showed that the epoxidation of the internal double bond proceeded at 220 times the rate of the vinyl bond. Polyvinyl epoxystearate was prepared by conventional methods. Like polyvinyl esters of other long-chain fatty acids, polyvinyl epoxystearate exhibited low intrinsic and specific viscosities. The mechanical and thermal properties of copolymers of vinyl chloride and vinyl epoxystearate were compared with those of compositions of polyvinyl chloride and butyl epoxystearate. Vinyl epoxystearate had a greater effect on the milling temperature of the copolymer than butyl epoxystearate had on that of the composition, but the opposite effect was observed on the temperature coefficient of the torsional modulus. In heat and light stability studies, it was found that butyl epoxystearate (or other external epoxy plasticizers) was more efficient than vinyl epoxystearate.

Résumé

L'époxystéarate de vinyle a été synthétisé par réaction de l'oléate de vinyle et des acides percarboxyliques. L'étude de la cinétique de l'époxydation des deux double liaisons de l'oléate de vinyle a montré que l'époxydation de la double soudure interne progresse 220 fois plus rapidement que la soudure vinylique. L'époxystéarate de polyvinyle a été préparé par les méthodes habituelles. De même que les esters polyvinyliques à longue chaîne latérale l'époxystéarate de polyvinyle manifeste des faibles viscosités intrinsèques et spécifiques. Les propriétés mécaniques et thermiques des copolymères

de chlorure de vinyle et d'époxystéarate de vinyle ont été comparées à celles de mélange de chlorure de polyvinyle et d'époxystéarate de butyle. L'effet de l'époxystéarate de vinyle sur la température de compounding du copolymère était plus prononcé que celui du butylépoxystéarate sur la température de compounding de la composition. L'effet contraire a été observé concernant le coefficient thermique du module de torsion. Du point de vue de la stabilité thermique et de la stabilité à la lumière, on a trouvé que le butylépoxystéarate (ou tout autre plastifiant contenant un lien époxyde externe) est plus efficace que l'époxystéarate de vinyle.

Zusammenfassung

Vinylepoxystearat wurde durch die Reaktion von Vinyloleat und Percarboxylsäure hergestellt. Eine Untersuchung der Kinetik der Epoxydation der zwei ungesättigten Bindungen in Vinyloleat zeigte, dass die Epoxydation der internen Doppelbindung 220 Mal so schnell als die der Vinylbindung fortschritt. Wie Polyvinylester anderer langkettiger Fettsäuren zeigte Polyvinylepoxystearat niedrige Grenz- und spezifische Viskositäten. Die mechanischen und thermischen Eigenschaften von Copolymeren von Vinylchlorid und Vinylepoxystearat werden mit denen von Verbindungen von Polyvinylchlorid und Butylepoxystearat verglichen. Vinylepoxystearat hatte eine grössere Wirkung auf die Mahltemperatur des Copolymers als Butylepoxystearat auf die der Zusammensetzung, aber es wurde die gegenteilige Wirkung auf den Temperaturkoeffizienten des Torsionsmoduls beobachtet. In Hitze- und Lichtbeständigkeitsuntersuchungen wurde gefunden, dass Butylepoxystearat (oder andere externe Epoxy-Weichmacher) wirksamer als Vinylepoxystearat war.