Evaluation of Fatty Vinyl Ether Polymers and Styrenated Polymers for Metal Coatings[1, 2]

B. G. BRAND and H. O. SCHOEN, Battelle Memorial Institute, Columbus, Ohio; and L. E. GAST and J. C. COWAN, Northern Regional Research Laboratory,[3] Peoria Illinois

Abstract

A further evaluation of fatty vinyl ether polymers as potential coatings for metals (particularly cans) includes studies on 12 linseed and soybean polymers containing isobutyl vinyl ether and cyclopentadiene. Baked films with and without driers from these homo-, co-, and terpolymers and their styrenated derivatives were examined for flexibility, adhesion, chemical resistance and hardness. Film properties were related to chemical composition of the polymers, including the effect of styrenation, linseed vs. soybean polymers and content of cyclopentadiene. Films possessed excellent flexibility, adhesion and hardness. Surprisingly, for most polymers, the hardest films were obtained without driers.

Introduction

A PREVIOUS STUDY on the end-use evaluation of copolymers and terpolymers of vinyl ethers of conjugated linseed fatty alcohols showed that certain of these materials might be useful for metal coatings (1). Evaluation tests demonstrated that this class of materials possessed unusual adhesion, chemical resistance, flexibility and hardness, but that no single polymer possessed all these desirable properties. However, since properties of copolymers and terpolymers can be altered by varying their composition, improved properties were sought by preparing additional polymers.

Experimental

Preparation of Polymeric Products. Medium-mol-wt copolymers and terpolymers of fatty vinyl ethers were prepared by polymerizing the appropriate monomers in toluene solution at room temp with stannic chloride catalyst (3). Similarily, low-mol-wt products were prepared, except chloroform was the solvent (2). Styrenation of selected products was carried out in terpene solvents at 145–165C (4). The products prepared for this study are shown in Table I.

Evaluation of Polymeric Products. Compatability tests were run on the polymer solutions listed in Table I with five commercial resins at 1:1 volume ratio. The commercial resins used were epoxy (Epon 828) (5), urea formaldehyde (Uformite F-240), urethane (Spenkel F-77-60MS), silicone (DC-840) and styrene-butadiene (Pliolite S-5).

Chemical resistance tests were run on approx 1 mil films applied to steel panels 4 x 8 x .032 in. (Q panels). The films were baked at the specified cycle with a drier system, when used, consisting of 0.5% lead and 0.01% cobalt as naphthenates. The test was conducted by placing a 1.5-in. diam watch glass, convex side down, on the surface of the film and introducing the solvent between the watch glass and the film surface. Periodic examination was conducted until the film showed evidence of softening or deterioration.

Hardness tests of films were made by the Sward rocker technique, and their color was obtained by comparison with standard Gardner color tubes. Flexibility and adhesion of baked films were determined by a) conical mandrel, b) reverse impact using a Gardner variable impact tester with 5/8-in. diam hammer, and c) can end-forming test using an R and K No. 2A press with a No. 307 sanitary can-end die. For these tests, polymers were cast on tin plate unless otherwise specified and baked to give films 0.2–0.3 mils thick. After being subjected to the three tests, films were examined for cracks, lack of adhesion, or other indications of film failure.

Discussion and Results

Chemical Resistance and Flexibility of Styrenated Homopolymers and Copolymers. Film properties of 12 polymers evaluated are shown in Table II and III. A baking cycle of 400F/10 min was used since it gave a satisfactory cure and was similar to baking schedules for metal coatings in commercial operations. Polymers A,B,C and D represent a group of styrenated conjugated fatty vinyl ether homopolymers containing grafted styrene at several levels (4). Increasing the styrene level of low-mol-wt polymers from 15–52% gave films with improved alkali resistance, but other properties were not significantly different. Styrenation of the medium-mol-wt linseed polymer (D) gave a product with excellent acetone and xylene resistance compared to the styrenated low-mol-wt homopolymers. With the low-mol-wt polymers A–C, films baked without drier were much harder than those with drier based on the Rocker test. Polymer D also showed this trend, but the difference in hardness was small. Previous work on the hardness of styrenated homopolymer films supported the Rocker hardness data, but pencil hardness tests did not reveal the marked difference in hardness between films with and without drier (4). Styrenated copolymer E showed no dif-

TABLE I

Fatty Vinyl Ether Polymers and Their Styrenated Products

Polymer	Polymer composition[a]	Mol wt[b]	Solution tested[c]
A	CS 15% styrene	Low	47 Dipentene
B	CL 29% styrene	Low	40 Dipentene
C	CL 52% styrene	Low	52 Dipentene
D	CL 38% styrene	Med	48 Dipentene
E	CP(3) CL(1) 35% styrene	Low	53 Dipentene
F	CP(3) IB(3) CL(1)	Med	59 Toluene
G	CP(3) IB(2) CL(1)	Med	54 Toluene
H	CP(3) IB(1) CL(1) 10.9% styrene	Med	40 Dipentene
J	CP(2) IB(1) CL(1) 10.3% styrene	Med	48 Dipentene
K	CP(3) IB(3) CS(1)	Med	69 Toluene
L	CP(3.2) IB(2) CS(1)	Med	62 Toluene
M	CP(3.2) IB(2) CS(1) 14.2% styrene	Med	58 Dipentene

[a] CS = conjugated soybean vinyl ether; CL = conjugated linseed vinyl ether; CP = cyclopentadiene; IB = isobutyl vinyl ether. Number in parentheses shows moles of monomer in polymer. Styrene shown as wt percentage of total.

[b] Approx number-average mol wt: Low = 1,500–2,000; Med = 3,000–5,000.

[c] Wt percentage nonvolatiles in indicated solvent.

---

[1] Presented at the AOCS Meeting in Minneapolis, 1963.

[2] The evaluation studies were conducted at Battelle Memorial Institute under contract with the U. S. Department of Agriculture and authorized by the Research and Marketing Act. The contract was supervised by the No. Reg. Res. Lab.

[3] A laboratory of the No. Utiliz. Res. & Dev. Div., ARS, USDA.

TABLE II

Hardness and Chemical Resistance of Vinyl Ether Polymers and Styrenated Products. Baked at 400F for 10 min

Polymer	Drier	Sward hardness	Chemical resistance[a]		
			NaOH	Xylene	Acetone
A	—	60	5	2	2
	+	28	24	2	2
B	—	50	24	1	1
	+	16	96	3	1.5
C	—	46	48	3	1.5
	+	22	120	3	1.5
D[b]	—	44	48	>200	>200
D[c]	+	40	144	>200	>200
E	—	34	120	3	1.5
	+	33	120	3	1.5
F	—	20	384	2	2
	+	15	840	2	2
G	—	19	624	2	2
	+	18	840	2	2
H	—	41	384	2	2
	+	44	192	2	2
J	—	31	384	2	2
	+	20	384	2	2
K	—	16	24	48	>200
	+	20	24	>200	>200
L	—	16	24	>200	>200
	+	24	48	>200	>200
M	—	30	48	>200	>200
M[b]	+	30	48	>200	>200

[a] Time to failure in hours.
[b] Baked at 400F for 15 min.
[c] Baked at 400F for 30 min.

TABLE III

Flexibility and Adhesion Tests on Vinyl Ether Polymers and Styrenated Products Baked at 400F for 10 Min

Polymer	Drier	Flexibility tests[a]			
		Conical mandrel	Reverse impact		Can-end forming
			25 in/lb	50 in/lb	
A	—	P	P	P	P
	+	P	P	P	F4
B	—	P	Fl	Fl	P
	+	P	P	P	F4
B[b]	+	P	P	P	P
C	—	P	F3	F3	F2,4
	+	P	F3	F3	F3,4
D[c]	—	P	F2	F2	P
D[d]	+	P	P	P	P
E	—	Fl	Fl	Fl	F2,4
	+	Fl	Fl	Fl	F2,4
A and urethane	+	P	P	P	F4
B and urethane	+	P	P	P	F4
D and urethane	+	P	P	P	P

[a] P = passed; Fl = small cracks; F2 = moderate cracks; F3 = severe cracks; F4 = poor adhesion.
[b] Baked at 400F/20 min.
[c] Baked at 400F/15 min.
[d] Baked at 400F/30 min.

ferences in hardness or chemical resistance between films with and without drier.

Flexibility tests on films of the styrenated homopolymers and copolymer E are shown in Table III. The baking cycle of 400F/10 min was also chosen for these products to illustrate differences between the polymers. However with some polymers, other baking cycles gave films with improved properties particularly with regard to flexibility over those shown in the Table. Thus not all of the film data is reported, but mention is made of those polymers giving particularly promising films under other baking cycles.

The effect on flexibility of increasing styrene from 30–50% with conjugated linseed homopolymer (low-mol-wt) is shown by B and C. While these films passed the conical mandrel test, polymer C failed both reverse impact and can end-forming test. Polymer B passed all flexibility tests when baked at 400F for 20 min with drier. Polymer D films without drier appeared intermediate between B and C in reverse impact tests but passed the can end-forming operation. Films of D with drier passed all flexibility tests when baked at 400F/30 min. Polymer E showed that flexibility of films was markedly reduced in styrenated copolymers containing cyclopentadiene (compare B and E).

Polymers A,B,D and E were compatible at the 1:1 wt ratio with the urethane polymer but were incompatible with the other resins tried. Polymer C was compatible with silicone DC-840 at the same wt ratio. Films from mixtures of A or B with urethane polymer did not show improved flexibility but did show improved alkali resistance over the untreated polymer films.

Chemical Resistance and Flexibility of Terpolymers and Styrenated Terpolymers. Polymers F through M represent a group of fatty vinyl ether terpolymers and styrenated terpolymers carefully selected as to type and composition from previous data obtained on polymers for metal coatings. The best combination of properties consistent with cost occurred in terpolymers containing cyclopentadiene, isobutyl vinyl ether and fatty vinyl ethers. Table II lists hardness and chemical resistance of films prepared from seven terpolymers. The most striking difference in this series occurred in the chemical resistance of soybean and linseed terpolymer films. Linseed polymers F through J had excellent alkali resistance ranging up to 840 hr, whereas both acetone and xylene resistance were moderate. Soybean products K through M showed a reverse trend in properties, excellent acetone and xylene resistance (>200 hr), and moderate alkali resistance from 24–48 hr.

With both soybean and linseed terpolymers, styrenation improved hardness. However, the best alkali resistance was achieved on films from unstyrenated linseed products F and G.

Acetone and xylene resistance of soybean terpolymers (K–M) were outstanding. Acetone resistance of the linseed products was also considered adequate since resistance of 2 hr in a spot test generally indicates that the film will pass the 100-cycle wet acetone rub test.

Polymers F through M were not compatible at the 1:1 wt ratio with the five commercial resins previously mentioned. This group of polymers, however, exhibited excellent flexibility and adhesion as evidenced by conical mandrel, reverse impact and can end-forming tests. All polymer films baked at 350 and 400F/10 min, both with and without driers, passed flexibility and adhesion tests. No cracks nor loss of adhesion was observed. These materials appeared to have the flexibility required for can coatings, and the selection of a polymer for a particular application would depend on the chemical resistance desired. While the chemical tests performed were limited, they serve to show that marked differences in chemical resistance can be obtained in these polymer films depending on their composition, baking cycle, and substrate to which they are applied.

End-Use Evaluation. Terpolymers exemplified by F through M appeared to have the most potential for commercial use as can coatings. Of these, the soybean terpolymer exemplified by L was selected for further evaluation since it appeared to be a good compromise giving desirable film properties at low cost. A polymer similar to L was baked for 10–12 min at 400F after drawdowns were made on electrolytic tin plate at 11,14 and 21 mg/4 sq in. The baked films from L were equivalent to those of a commercial oleoresinous can coating in their performance in typical can-end fabrication tests and in their resistance to water in pasteurization tests. This polymer possessed a rich gold color considered highly desirable for interior can liners. However, in a more severe fabrication test with a 28-mm screw cap, L was inferior to the commercial resin. Both L and the commercial resin were prepared as "R" and "C" enamels. "C" enamels contain zinc oxide to prevent sulfide staining and are used in cans packed with corn, peas, green beans, etc., while "R" enamels contain no zinc oxide and are formulated for use with acid-type foods, e.g., cherries, pumpkin and tomatoes. Pack tests of the "R" enamels (18 mg/4 sq in.) in water and cherries showed the commercial resin to be slightly superior. Both corn and dog food packs were prepared with "C" enamels coated at 21 mg/4 sq in. The commercial resin was again slightly better. Polymer films and the commercial resin were also baked for 10 min at 350F,375F,400F and 415F. Since both coatings exhibited equal preprocessing fabrication and water-pasteurization resistance at all bakes, a wide latitude of curing schedules is indicated.

ACKNOWLEDGMENT

Preparation of the vinyl ether polymers used in this study by Wilma J. Schneider and E. J. Dufek. Certain evaluation studies by Pittsburgh Plate Glass Co.

REFERENCES

1. Dent, R. H., B. G. Brand, H. M. Teeter and J. C. Cowan, JAOCS *40*, 713–16 (1963).
2. Dufek, E. J., R. A. Awl, L. E. Gast, J. C. Cowan and H. M. Teeter, *Ibid. 37*, 37–40 (1960).
3. Dufek, E. J., L. E. Gast and H. M. Teeter, *Ibid. 39*, 238–41 (1962).
4. Gast, L. E., Wilma J. Schneider, H. M. Teeter, G. E. McManis and J. C. Cowan, *Ibid. 40*, 88–91 (1963).

[Received February 5, 1964—Accepted May 6, 1964]

Mustard Seed Processing: Essential Oil Composition[1]

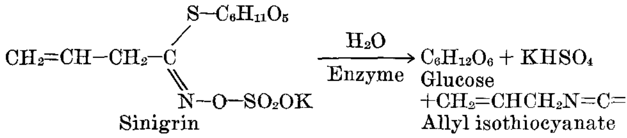
L. D. KIRK, L. T. BLACK and G. C. MUSTAKAS, Northern Regional Research Laboratory,[2] Peoria, Illinois

Abstract

Recent investigations into the processing of oriental mustard seed for production of livestock feed and of lipid-containing erucic acid have stimulated interest in the composition of the by-product essential oil. The development of a method for analysis of this oil by gas-liquid chromatography has led to the demonstration of an equilibrium reaction between the two main constituents. A similarity in composition and response to heat is shown between the natural essential oil and oils prepared synthetically. These observed similarities should lead to a better understanding of the enzymatic reaction responsible for release of this oil from the seed.

Introduction

ORIENTAL MUSTARD SEED, like other members of the Cruciferae family, contains thioglucosides, such as sinigrin, which are hydrolyzed to isothiocyanates (essential oils) by the action of enzymes naturally present in the seed. The following equation shows the main conversion products of sinigrin based on the thioglucoside structure of Ettlinger and Lundeen (3):



$$CH_2{=}CH{-}CH_2{-}C(S{-}C_6H_{11}O_5){=}N{-}O{-}SO_2OK \xrightarrow[\text{Enzyme}]{H_2O} C_6H_{12}O_6 + KHSO_4 + CH_2{=}CHCH_2N{=}C{=}S$$

Sinigrin; Glucose; Allyl isothiocyanate

The composition of the essential oil derived from thioglucosides in oriental mustard seed (*Brassica juncea*) remains controversial. In their review article Vaughan and Hemingway (13) state that the oil is generally considered to be a mixture of allyl and crotonyl isothiocyanates. However, they also report the work of others who have concluded that allyl isothiocyanate is the only isothiocyanate present. Jensen et al. (6) of Denmark report allyl isothiocyanate as the sole volatile constituent of this seed.

Other compounds have been reported associated with allyl isothiocyanate derived from plant sources. Traces of allyl thiocyanate were reported by Schmidt (10) in allyl isothiocyanate recovered from an enzyme hydrolysis of sinigrin at 0C. This occurrence of organic thiocyanates seem to have been neglected until observed by Gmelin and Virtanen (4) in 1959. They reported allyl thiocyanate derived from sinigrin in *Thlaspi arnense* and benzyl thiocyanate derived from glucotrapaeolin in two *Lepidium* species. They suggested a dual enzyme system in some seeds to release either the isothiocyanate or the thiocyanate form from the thioglucoside.

In addition to the thiocyanate, allyl cyanide and carbon disulfide have also been reported with allyl isothiocyanate. Carbon disulfide is believed formed by chemical hydrolysis of the isothiocyanate (2).

Oriental mustard is being considered as a possible new crop in this country, and a process has been developed for removing the essential oil which otherwise contributes pungency to the meal (7,8). This oil, which has value for the pharmaceutical, flavoring, pesticide and plastics industries, can be recovered in a yield of 12 lb/ton of seed processed. If substantial quantities become available for marketing, more exact information regarding composition is needed.

Experimental

Materials and Equipment. Montana-grown oriental mustard seed, containing 4.5%moisture, 26% protein, 37% lipid and 0.7% isothiocyanate, was used throughout these studies. The commercial sample of allyl isothiocyanate was "practical grade" purchased from Distillation Products Industries (16).

Equipment for recovering essential oil from the seed was that described by Mustakas et al. (8) and consisted of a steam-jacketed stainless-steel vessel capable of processing 4,000 g seed and fitted with a steam-sparging coil, meshing-rod agitation system, condenser and spray nozzle. A Beckman Model GC-2A was used for gas-liquid chromatography (GLC) determinations. The column was 6-ft, 0.25-in. stainless steel packed with acid-washed celite 545 mesh size 80–100, coated with 20% Apiezon M. A Spinco MS amino acid analyzer was used for determination of the sulfur-containing amino acids, methionine and cystine. Synthetic oils were prepared in a 1,000-ml flask equipped with magnetic stirrer, condenser, receiver flask and vacuum pump.

Recovery of Natural Essential Oil. The seed was tempered by addition of water to 7% moisture and rolling in a sealed drum for 2 hr. Flakes of 0.005-in. average thickness were prepared either by cracking on corrugated rolls set at 0.002-in. clearance followed by rolling through smooth rolls or by a double pass through smooth rolls. About 4,000 g of the prepared

---

[1] Presented at AOCS Meeting in Atlanta, 1963.

[2] A laboratory of the No. Utiliz. Res. & Dev. Div., ARS, USDA.