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SOLUBILITY AND CROSSLINKING CHARACTERISTICS
OF ETHYLENE/VINYLACETATE COPOLYMERS

R. L. Feller and M. Curran*

In the publication of IIC-American Group Technical Papers from 1968 Through 1970, pp. 63-71, Gustav Berger described tests and projected applications of adhesives based on the recently developed copolymers of vinylacetate and ethylene. As part of a search for durable materials for use in conservation and in the fine arts, the National Gallery of Art Research Project has also been investigating these interesting copolymers. We shall describe solubility and cross-linking characteristics that we have observed.

Two types of these copolymers were offered by the duPont Company in 1961, but several companies now manufacture solid and emulsion forms in a variety of molecular weight and monomer ratio grades. The duPont Company offers a series of thirteen Elvax® polymers varying from 18 to 40% vinylacetate, as well as a series of Elvace® emulsions and of Elvax-D® dispersions in water. Mr. Berger reported the results of tests on adhesives in which Elvax® 40 and 150 were used. The Union Carbide Corporation, 270 Park Avenue, New York, New York 10017, markets a series of nine Co-Mer® copolymers varying in average molecular weight and also in vinylacetate content from 18 to 28%. The Airco Chemicals and Plastics Co. (150 East 42nd Street, New York, New York 10017) markets an "Aircoflex"® series of emulsions. Commercial literature indicates that the emulsions range in pH from 4.5 to 7.0.

The properties of these copolymers depend, of course, upon their molecular weight, as do all polymers, and, more particularly, upon the proportion of vinylacetate in the polymer. (A copolymer has a structure such as - VEVVEVVEVVE - in which different monomer units are joined together in a polymer chain - V for vinylacetate, E for ethylene. They are not a physical mixture of poly(vinylacetate) and polyethylene polymers.) A discussion of their copolymer structure and a summary of the physical properties of some of the emulsion polymers may be obtained from the data published by G. E. J. Reynolds of Vinyl Products, Ltd., Carshalton, England in J. Oil & Colour Chemists' Assoc., 53 (1970), pp. 399-410 (Table I). Copolymers high in vinylacetate are most commonly encountered in polymer emulsions, although the duPont Elvax-D® dispersions are formulated with types having lower percentages of vinylacetate.

Although poly(vinylacetate) requires nearly pure toluene to dissolve it and is not soluble in xylene at room temperature (Feller, Stolow and Jones, On Picture Varnishes and Their Solvents, Oberlin, 1959, pp. 34, 46), the E/VA copolymers are soluble in rather mild petroleum solvents: Elvax® 150 (28% VA) and Union Carbide's EVA 505 (33% VA) form clear solutions in methylcyclohexane until the temperature is lowered to about 9°C (48°F); the lower molecular weight Elvax 40 (40% VA) forms a clear solution in methylcyclohexane down to about 0°C. Films of emulsions based

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on copolymers containing from 10 to 17% vinylacetate, kindly supplied by Dr. Reynolds of Vinyl Products, Ltd., were easily removed in a 50/50 mixture (by volume) of methylcyclohexane/toluene.

TABLE I

Physical Properties of E/VA Copolymer Emulsions

(from G. E. J. Reynolds, J. Oil & Colour Chemists' Assoc., 1970)

Comonomer:	Ethylene					2-ethylhexyl- acrylate	
	4*	10	12.5	17.5	20	15	25
% Comonomer wt%	4*	10	12.5	17.5	20	15	25
mole%	11.4	25.4	30.5	39.4	43.4	7.6	13.5
Min. Film Form. Temp °C	9	2	0	—	—	10	5
Tensile Strength Kg/cm ²	80.7	40.7	36.7	5.6	4.9	59.7	28.2
Tensile Strength lb/in ²	1148	579	522	77	70	849	401
Elongation at Break	210	340	415	615	1220	200	300
Rigidity Modulus, Kg/cm ²	500	130	70	55	20	1140	90
Sward Rocker Hardness	27	16	10	4	2	24	12
Brittle point °C	10	0	-5	-10	-15	10	5
Heat Seal Temp. °C	120	105	95	75	60	120	110
Heat Seal Temp. °F	248	221	203	167	140	248	230

* 96% of the copolymer by weight is vinylacetate.

Near ultraviolet radiation does not cause poly(vinylacetate) to crosslink but will cause polyethylene to crosslink (unless inhibited*). The copolymers thus pose an interesting question and prompted our investigation of their behavior. We have found that a number of the copolymers undergo both crosslinking and chain breaking; the latter process increasing as the vinylacetate content increases. The particular copolymers tested are shown in Table II and the results summarized in Figure 1. After 800 hours of exposure on aluminum foil in an Atlas xenon arc fadeometer (using an ordinary glass rather than a quartz filter) the films were removed with ease as a gel in methylcyclohexane even though they had from 14 to 62% insoluble matter present at that point. In contrast, Elvacite® 2046 (a copolymer of isobutyl and n-butyl methacrylate) becomes 30% insoluble in about 80 hours; about 80% after 500 hours exposure. The copolymers tested in Table II are 8 to 10 times more resistant to loss of solubility under near ultraviolet radiation than the easily crosslinked butyl methacrylate polymers.

* Many of the Elvax® resins contain 500-1000 ppm of butylated hydroxytoluene (BHT) antioxidant.

TABLE II

Soluble Matter in Ethylene/Vinylacetate Copolymers After 800 Hrs.
Exposure on Aluminum Foil in Xenon Arc Fadeometer (Ordinary Glass Filter)

Polymer	Weight Per Cent Vinylacetate in Copolymer	Per Cent Soluble Matter Remaining After 800 Hours Exposure
Co-Mer [®] EVA 303 (UC)	18	38
Co-Mer [®] EVA 508 (UC)	28	59
Co-Mer [®] EVA 505* (UC)	28	92
Elvax [®] 150 (duP)	33	86

* lower molecular weight than EVA 508; (UC) Union Carbide, (duP) duPont

TABLE III

Influence of Wax on Tendency to Crosslink

Hours of Exposure on Aluminum Foil in Carbon-Arc Fadeometer
(Corex D Filter) Before Developing High Resistance to Removal
in Various Solvents (Rubbing with Cotton Swabs Dipped in Solvent)

Film	Methylcyclohexane	Toluene	Acetone
Poly(isoamylmethacrylate)(PIAM)	68	105	—
PIAM + 0.5% Beeswax	115	150	240
PIAM + 1% "	120	168	240
PIAM + 3% "	~ 140	260	480
PIAM + 6% "	250	340	—

Mr. Berger mentions that the addition of small quantities of wax will reduce the tendency of many polymers to form insoluble matter owing to crosslinking. In our investigations on protective coatings this possibility was tested in 1957 following a question raised by Mr. Mario Modestini. The results, summarized in Table III, inferred that, at sufficiently low concentrations to yield reasonably transparent varnish (1 to 3%), beeswax would not offer more than a two-fold improvement in the resistance-to-crosslinking, insufficient to warrant a broad endorsement of its use for this specific purpose alone. At higher concentrations of wax, however, the data indicate that the wax will indeed interfere significantly with the tendency to crosslink.*

Because the copolymers having a percentage of vinylacetate higher than 25% exhibit a negligible tendency to crosslink under near ultraviolet radiation, and are soluble in petroleum hydrocarbons of low solubility parameter, we consider that they merit consideration for use in conservation and have suggested that practical applications be explored. In the meantime, tests of the durability of the copolymers, both in solution and emulsion grades, continues; we are currently investigating their chain-breaking characteristics.

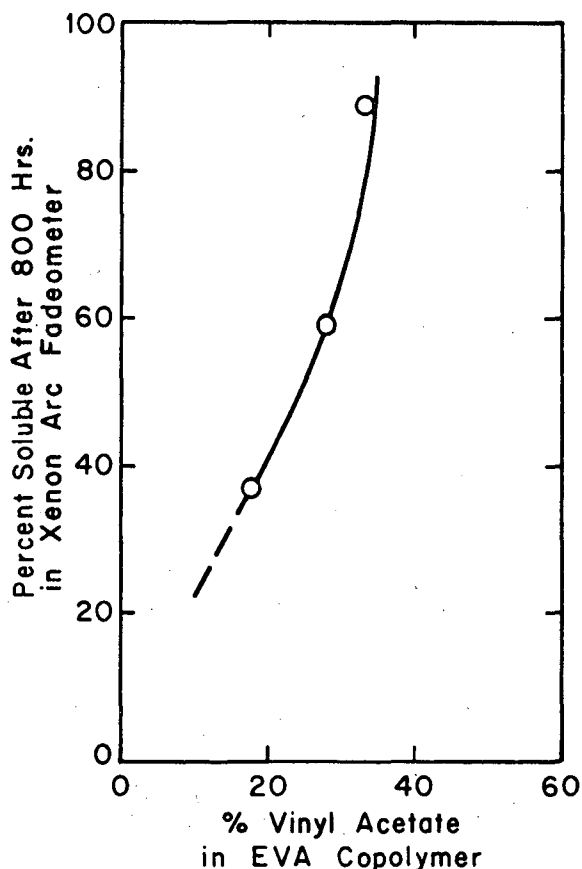


Figure 1

* The National Gallery of Art Research Project's current research program on the inhibition of oxidation has also shown that an antioxidant system based on Geigy's ultraviolet absorber Tinuvin 328 and the synergist, di-laurylthiodipropionate, at concentrations of about 1% each will markedly protect polymers and copolymers of n-butyl and isobutyl methacrylate from crosslinking by near ultraviolet radiation, but we wish to make further tests before making specific recommendations regarding the application of such a system.