

Physical Properties of Some Vinyl Tetrahydroabietate and Vinyl Maleopimarate Acid Anhydride Copolymers

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Synopsis

The stress-strain and torsional characteristics of some experimental copolymers of vinyl tetrahydroabietate and vinyl maleopimarate acid anhydride with vinyl chloride and vinyl acetate have been determined. Similar studies were also undertaken on peroxide-cured compositions of a vinyl chloride-vinyl tetrahydroabietate copolymer. Elastic moduli for the uncured copolymers range from 80,200 to 338,000 psi. Cured compositions of vinyl chloride-vinyl tetrahydroabietate copolymer exhibited both lower and higher moduli than that of the uncured copolymer. Some of the cured compositions appear to have an improved impact resistance over that of the uncured polymers.

Introduction

Marvel et al.^{1,2} have reported on the homopolymerization and copolymerization of vinyl tetrahydroabietate and vinyl maleopimarate acid anhydride monomers prepared by Liepins and Marvel¹ and by Lewis et al.^{3,4} The present paper reports on some of the physical characteristics of copolymers of these vinyl esters with vinyl chloride and with vinyl acetate. (Polymers were provided and prepared by C. S. Marvel and his co-workers, University of Arizona, Tucson, Arizona, from monomers prepared by J. B. Lewis and G. W. Hedrick, Naval Stores Laboratory, U.S. Department of Agriculture, Olustee, Florida.) The monomer ratios and inherent viscosities of these four copolymers are given in Table I.

Results and Discussion

Test specimens were cut from films 0.014-0.025 in. thick, which had been cast from tetrahydrofuran (THF) solutions of the respective copolymers. This preparative procedure was used because of the inability to mill the VCI-VTA copolymer at 350°F, the maximum temperature attainable on the mill, and the undesirability of comparing characteristics of specimens prepared by different procedures.

Casting solutions were prepared in THF, which incorporated 100 parts of experimental polymer, 4 parts of Advastab T-360 stabilizer, and 0.5 part of stearic acid. The stabilizer was omitted from those VCI-VTA solutions of

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the copolymer which incorporated dicumyl peroxide, Hercules DiCup T, for curing studies. There were no changes in the casting and desolventizing techniques reported previously.⁵

The VCl-VTA, VCl-VMPA, and VA-VMPA copolymers gave transparent, colorless, or yellow-tinged semiflexible films. The VA-VTA copolymer, contrary to published information,¹ could not be completely dissolved in either THF or CHCl_3 . Neither could sheets be prepared by

TABLE I
Monomer Proportions and Inherent Viscosities of Copolymers^a

Copolymer ^b	Incorporated monomer, ratio	η_{inh}^c 30°C
VCl-VTA	92:8	0.74
VA-VTA	60:40	1.10
VCl-VMPA	80:20	0.688
VA-VMPA	80:20	1.026

^a Data courtesy of C. S. Marvel and his co-workers.

^b VTA = vinyltetrahydroabietate, VMPA = vinyl maleopimarate acid anhydride, VCl = vinyl chloride, VA = vinyl acetate.

^c Determined from solutions containing 0.100–0.250 g per 100 ml of THF.

milling, because of the very brittle and friable character of the sheeted material at or near room temperature, which precluded the preparation of sheeting in a satisfactory physical condition. The solubility discrepancy and the strong acetic acid odor emanating from the polymer suggest that it had undergone some degradative changes. No mechanical or physical tests were made with this copolymer.

TABLE II
Some Physical Characteristics of Copolymers

Copolymer	Elast. mod. (tension), psi	Yield pt., ^a psi	Tens. streng., ^a psi	Elong., %	T_f , °C	T_d , °C
VCl-VTA	298,000	5660	5270	3.5	21	37
VA-VMPA	80,200	1190	980	180	–2	5
VCl-VMPA	338,000	—	6542	2.5	39	50

^a Based upon original cross-sectional area.

The VCl-VTA copolymer was subjected to peroxide curing at 75 and 125°C with 3.85 and 7.41% levels (4 parts and 8 parts, respectively, per 100 parts polymer) of DiCup T for various periods of time. The films containing DiCup T were slightly darkened when cured for 1 hr at 75°C and were severely darkened after 30 min at 125°C. All cured compositions were completely soluble in THF.

The physical characteristics of the polymers, reported in Table II and III, were determined in accordance with ASTM Tests 638-52T and 1043-61T. Among the uncured polymers (Table II) the VCl-VMPA copolymer exhibits the highest modulus and tensile strength and the VA-VMPA copolymer the lowest modulus and tensile strength and greatest elongation.

The data of Table III show that the VCl-VTA copolymer is receptive to peroxide curing, as reported by Liepins and Marvel.¹ All tests specimens incorporating the peroxide exhibit a transitory drop in modulus, yield point, and tensile strength in the early stages of the curing cycle. However, an almost complete recovery in these properties was made by those specimens incorporating 3.8% DiCup T, during the course of the curing cycle; so much so, that eventually the cured polymer surpassed the original material in some of these characteristics. An even more pronounced recovery was recorded by the composition containing 7.41% DiCup T, which had been

TABLE III
Effect of Cure on Some Physical Characteristics of VCl-VTA Copolymer

Di-Cup T ^a	Cure, hr. and °C.	Elast. mod. (tension), psi	Yield pt., ^b psi	Tens. streng., ^b psi	Elong., %	T_f , °C	T_d , °C
0	none	298,000	5660	5270	3.5	21	37
4.0	1, 75	272,000	5300	4030	6.2	—	—
4.0	2, 75	288,000	6170	5240	5.2	—	—
8.0	0.5, 75	123,000	2360	2520	150	-1	13
8.0	1.0, 75	228,000	4390	2910	110	—	—
8.0	1.5, 75	216,000	3530	4100	110	2	16
8.0	{ 1, 75 1, 125	354,000	6420	6200	2.4	—	—

^a Parts per 100 parts polymer.

^b Based on original cross-sectional area.

cured for successive 1 hr periods at 75 and 125°C. On the other hand, the composition containing 7.41% DiCup T but cured at 75°C did not recover to this degree, and the performance never exceeded that of the uncured composition in these specific areas; it did, however, outperform both the uncured and other cured compositions in the area of elongation by a wide margin and was qualitatively more resistant to fracturing by impact. The better impact resistance of this composition can probably be attributed to its superior elongation and more favorable T_f and T_d characteristics.

Although these performance differences between the various cured compositions would be expected to be reflections of cure (i.e., degree of crosslinking), the possibility that they may also reflect to some degree a plasticizer-like contribution of residual DiCup T cannot be dismissed.

Use of a company or product name by the Department does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

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