

LETTERS TO THE EDITORS

The Preparation and Gas Permeability of Vinylidene Chloride Copolymer Films .

We have shown experimental vinylidene chloride-acrylonitrile copolymer films to be excellent gas barriers, although they are completely amorphous. In a study designed to gain a better understanding of the nature of permeability, the copolymers were prepared, films were cast from solutions, and gas permeabilities were measured, these data then being correlated with "structure" of the films. The importance of crystallinity has been reconsidered.

The copolymers were prepared by emulsion techniques. The recipes allowed preparation of copolymers representing equivalent degrees of conversion of monomer to polymer, but with varying monomer ratios and molecular weights. An example of the type of recipe employed is:

	Parts by weight
Water	214
Sulfated fatty acid ¹	5.0
<i>tert</i> -Dodecyl mercaptan	0.2
Potassium persulfate	1.0
Sodium <i>meta</i> -bisulfite	0.4
Vinylidene chloride	80
Acrylonitrile	20

Several anionic surfactants were evaluated as emulsifiers during the development of this recipe. All of them provided attractive polymerization rates when the system was activated with sodium *meta*-bisulfite. However, the choice of the particular sulfated fatty acid was largely based on its latex stability. In this respect, the emulsifier used was outstanding.

Monomer ratios were varied by increments of ten parts between 90 and 60% vinylidene chloride content. Polymerization rates increased with increasing acrylonitrile content. Variation in molecular weight was effected by changing the mercaptan modifier concentration. The recipe appeared to require the presence of mercaptan, since omitting this material resulted in extremely slow conversion of monomer to polymer. The rate was greatly enhanced by addition of as little as 0.02 part mercaptan.

All polymerizations were carried out in carbonated-beverage bottles that were rotated end-over-end in a water bath maintained at 50°C. Stable latexes were obtained. Polymer was isolated from the latexes by precipitation with isopropanol or hydrochloric acid. The granular products were filtered out, washed, and finally dried in a vacuum oven at 50 to 60°C. Nitrogen analyses of the copolymers were made and showed their acrylonitrile content to be higher than the charged ratio of the monomer. The exact behavior of the system followed closely that predicted from the reactivity ratios for the two monomers reported in the literature.²

The copolymers were found to be soluble in methyl ethyl ketone, cyclohexanone, 1,4-dioxane, or dimethylformamide. Intrinsic viscosities of the polymers were determined in one or more of these solvents, in attempts to measure relative molecular weights. However, the results were complicated by the fact that intrinsic viscosity of the copolymers increased with both higher molecular weight and acrylonitrile content. This point may be resolved by the fractionation of these polydisperse polymers and through the application of light scattering techniques for molecular weight determinations.

Pliable, fairly clear films were obtained by casting 10% solutions of the copolymers on cellophane stretched over glass or on ferrotype plates. Initial efforts resulted in films with a surface like orange peel. This effect was corrected by adjusting the viscosity of the casting solutions upward. For example, raising the solids content of methyl ethyl ketone solutions to at least 20% or adding a higher boiling solvent such as 1,4-dioxane to a more dilute system served to eliminate the orange-peel surface. Films were cast with the aid of either a 16- or 30-mil drawdown bar. They were initially dried for 4 hr. at 55-70°C. Then final traces of solvent were removed by placing the films in a vacuum oven for a minimum of 24 hr. at 50°C. The switch from cellophane to ferrotype plates was made to eliminate any possible effect of plasticizer that might migrate from the cellophane to the cast films.

Films prepared by this technique were examined for their gas barrier properties and possible crystallinity. Gas transmission studies were made by means of the manometric method embodied in the Dow cell and widely accepted in the plastic film field.³ Gas transmission measurements were carried out at 23°C. on specimens that had been conditioned in a desiccator for a minimum of 24 hr. Test gases were passed through a drying column. The gas pressures used were between 1 and 2 atm. Preliminary examinations of the films for crystallinity were made with polarized light microscopy. These tests were followed by x-ray diffraction studies of selected films.

Reference to Table I will show the excellent barrier properties of typical experimental films to permeation by nitrogen, oxygen, and carbon dioxide. It can be seen that the 80/20 copolymer is five times better as a barrier than the 60/40 copolymer. This general effect of polymer composition of gas barrier properties of the series was consistent over the entire range of copolymer compositions. The 80/20 copolymer film showed no signs of crystallinity either by polarized light microscopy or x-ray diffraction studies. Dilatometric study of the copolymer from which the 80/20 films were cast showed no evidence of crystallinity between 25 and 92°C. As expected, polymers containing less than 80% vinylidene chloride were also completely amorphous. Thus, the permeability of these films is not related to crystallinity.

TABLE I
Properties of Typical Vinylidene Chloride-Acrylonitrile Copolymers

	F-218	F-220
Monomer charging ratio, VC/A	80/20	60/40
Polymerization time, hr.	22	7
Conversion, monomer to polymer, %	49	41
Nitrogen content of polymer, %	6.1	11.2
Acrylonitrile in polymer, wt.-%	23.1	42.4
Intrinsic viscosity in cyclohexanone	0.95	1.87
Intrinsic viscosity in dimethylformamide	0.83	1.84
Permeability of film, cc. (STP)/100 sq. in./ 24 hr./atm./mil		
Nitrogen	0.084	0.422
Oxygen	0.710	3.42
Carbon dioxide	1.77	7.91

Considering experience with other vinylidene chloride-containing films, it is not surprising that these experimental copolymers should exhibit outstanding gas barrier properties. However, such a high degree of impermeability is generally associated with crystalline polymers. For example, the permeability of the amorphous film designated F-218 is of the same order of magnitude as that reported by Dulmage⁴ for crystalline Saran film:

	F-218	Saran
Nitrogen (cc./100 sq. in. 124 hr./atm./mil)	0.084	0.11
Oxygen	0.710	0.56
Carbon Dioxide	1.77	2.4

Various researches have emphasized the importance of crystallinity in highly impermeable films. For example, Van Amerongen⁵ in his studies of hydrogen permeation through guttapercha, Doty, Aiken, and Mark⁶ in their investigation of water vapor permeability of rubber, Morgan's studies⁷ of moisture vapor transmission through numerous polymers, Myers and co-workers' studies of the permeability of polyethylenes to gases and vapors⁸ and permeability of chlorotrifluoroethylene polymers,⁹ and Lasoski and Cobb's study¹⁰ of moisture vapor permeability of polyethylene terephthalate, Nylon 610, and several polyethylenes, have all emphasized the role of crystallinity. Morgan has noted that metal foils, which are highly crystalline materials, are nearly impermeable to water vapor.⁷

Such investigations have not singled out crystallinity as the only factor determining the barrier properties of film-forming materials. However, the importance of this factor in those barrier materials which are crystallizable can easily lead to the generalization that a material must be crystalline to be a good gas or vapor barrier. This is definitely not the case: completely amorphous glass is an excellent gas and vapor barrier. The completely amorphous copolymer films described in this report are also good gas barriers.

It is our belief that studies like the present one will serve to bring the crystallization picture into better perspective. There is ample evidence suggesting that a barrier material will become less permeable as its degree of crystallinity is

increased. This finding does not rule out the eventual possibility of a still better barrier that is completely amorphous. Indeed, if a gas barrier depends on crystallinity for its prime property, this may be at the expense of higher density, reduced low-temperature flexibility, and other effects that are also associated with a high degree of crystallinity.

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The Glass Transition Concentration

If a polymer has a glass transition temperature above room temperature, as solvent is removed from a polymer system, a critical concentration region should exist where the concentration of diluent is such that rotation of segments of the polymer molecules starts to be restricted. This should be reflected in the dynamic mechanical properties of the system. A plot of dynamic modulus and damping versus concentration at a fixed temperature should thus have a form analogous to the modulus or damping-temperature plot. This, in fact, proves to be the case.

In measuring the dynamic mechanical properties of solutions, we used the following technique. A fine cotton thread is coated with a polymer solution.² While the solvent is evaporating, the dynamic mechanical properties of the supported polymer solution are measured. A free-vibration flexural-pendulum device is used for measuring modulus and damping.² In a parallel experiment the rate of solvent evaporation from a polymer-solution-coated cotton thread is measured directly from weight loss. With these data modulus and damping versus concentration curves can be