

BARRIER PROPERTIES OF VINYLIDENE CHLORIDE/METHYL ACRYLATE COPOLYMER*

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ABSTRACT

A series of vinylidene dichloride (VDC) copolymers with methyl acrylate (MA) as comonomer (3–12 wt%), was prepared by free-radical suspension copolymerization. The permeability coefficients of the copolymers to oxygen and carbon dioxide were measured at 1.0 MPa and at 30°C, and those to water vapor were measured at 30°C and 100% relative humidity. All the VDC/MA copolymers studied are semicrystalline. As the MA content increases, the permeability coefficients of the copolymers to oxygen, carbon dioxide, and water vapor are progressively increased, caused by decrease in crystalline fraction and increase in free volume of VDC/MA copolymers.

INTRODUCTION

The gas and vapor permeability of polymers is an important property of functional polymer materials. The polymers with high gas and vapor permeability and high permselectivity have widely been used for gas or liquid separation systems based on membrane^[1], and others with low gas and vapor permeability have been used for barrier packaging films and containers to protect foods, tea, beverage, and medicine from deterioration, for decades^[2]. The desirable barrier polymer materials should have very low permeability to oxygen, carbon dioxide, aroma, and water vapor, high mechanical strength, and good compatibility with foods^[3]. Poly (vinylidene chloride) (PVDC) with high crystalline fraction has excellent gas and water barrier properties^[4]. However its melting temperature is only slightly lower than its decomposition temperature, causing poor processability. The most efficient way to improve its processability is to copolymerize VDC with other monomers such

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as acrylate and vinyl chloride. Unfortunately, there is almost no report of detailed study on the barrier property and the processability of the VDC copolymers^[4].

The main purpose of this work is to determine the effect of copolymer composition on the melting temperature and crystalline fraction of VDC/MA copolymer, to investigate their structure/barrier property relationship, and to develop promising VDC/MA barrier copolymer.

EXPERIMENTAL

VDC/MA copolymer containing 8% MA was kindly supplied by Quzhou Chemical Co. The other copolymers were synthesized in our laboratory by the process which is similar to that described in the previous paper^[5]. The average molecular weights of all the copolymers were ranged from 65000 to 80000. The purity of the permeation gases is above 99.9%.

The copolymer solutions in DMF were filtered through a 10- μm sintered glass filter before casting. Films were cast from solution on glass plates in a controlled dust-free environment. The freshly prepared cast films were then heated at 40–50°C, 100°C, and 150°C each for 24 h under vacuum. The polymer films were removed from the glass plates by stripping carefully, and then dried in vacuum oven at 100°C for one week. The resulted polymer films were about 25 μm in thickness.

The densities of the polymer films were determined at 25°C by the density gradient column method using a mixture of carbon tetrachloride and ethylene trichloride. Differential scanning calorimetry runs made on a Perkin-Elmer series 7 DSC instrument. Wide angle X-ray diffraction (WAXD) measurements for the VDC/MA copolymers were undertaken on a Philips X-ray diffractometer with $\text{CuK}\alpha$ radiation, $\lambda = 0.154 \text{ nm}$. Gas permeability coefficients of VDC copolymer films were measured at 1.0 MPa and 30°C, and water vapor permeability coefficients were measured at 30°C and 100% relative humidity.

RESULTS AND DISCUSSION

Table 1 listed the physical properties of VDC/MA copolymers. The average molecular weight (MW) or intrinsic viscosity of VDC/MA copolymers is decreased gradually with the increase in MA content. WAXD and DSC studies indicate that all the VDC/MA copolymers studied were semicrystalline polymers. Crystallinity of PVDC originates from the symmetry of molecular chain segment. MA chain segments with low symmetry and bulky side substituent ($-\text{COOCH}_3$) hinder crystal growing and result in crystal grating defect. Assuming that the crystalline phases

of the copolymers are composed of VDC chain segments, and the melting heats of the crystalline phases do not depend on the copolymer composition, the crystalline fractions can be estimated by equation (1):

$$\Phi_C = \Delta H / \Delta H^0 \quad (1)$$

where Φ_C is crystalline fraction, ΔH and ΔH^0 are the melting heat of VDC/MA copolymer and crystal PVDC respectively. ΔH^0 is 58.6 J/g^[4]. It can be noticed that the melting temperature, melting heats, and the crystalline fractions of VDC/MA copolymers are gradually decreased with the increase in MA content.

Barrier property of a polymer is mainly controlled by the chemical structure and morphology of the polymer. The permeability coefficients of VDC/MA copolymers to oxygen, carbon dioxide and water vapor are higher in comparison with those of PVDC as reported by Wessling^[4] due to the increase in free volume and to the decrease in crystalline fraction. The free volume and intra-segmental mobility are two dominant factors to determine the barrier property of polymer. As above-mentioned, the free volume is gradually increased with the increase in MA content. The pendant group ($-\text{COOCH}_3$) of VDC/MA copolymers is flexible, so that the intra-segmental mobility of VDC/MA copolymers becomes better as MA content increases. Fig. 1 is the plots of the permeability coefficients of the copolymer versus VDC/MA composition. The permeability coefficients of VDC/MA copolymers to oxygen and carbon dioxide are enhanced with the increase in MA content of the copolymers. In other words, the barrier properties of VDC/MA copolymers are lower than that of PVDC. The higher the MA content of VDC/MA copolymer is, the lower the barrier property will be. Therefore, the MA content is usually controlled at 7–8 wt% to improve the processability and to preserve the barrier property.

Table 1 The properties of VDC/MA copolymers

Polymer	MA content (%)	Av. mol. wt. ($\bar{M}_n \times 10^{-4}$)	Melting temp. ($^{\circ}\text{C}$)	Melting heat ΔH (J/g)	Crystalline fraction Φ_C (%)
PVDC	0	0.618 ^{a)}	187	51.0	87
P1	3.0	0.518 ^{a)}	173	44.8	76
P2	5.0	9.8	167	35.5	61
P3	7.0	7.1	162	29.1	49
P4	8.0	4.2	151	22.3	38
P5	10	3.7	147	13.0	22
P6	12	0.324 ^{a)}	134	3.5	6

^{a)} intrinsic viscosity in tetrahydrofuran

One can notice that in Fig. 1, the curvature of the curves are concave indicating the logarithm of the permeability coefficients of VDC/MA copolymers is accelerated increased with the increase in MA content of the copolymers. This can be explained by the fact that the rate of the increase in the free volume fraction is accelerated up with the increase in MA content of the copolymers. Free volume is one of the main factors that controls the permeability of polymers to gas and vapor. Lee^[8] put forward a correlation technique for gas permeability coefficients and polymer structure based on a free volume diffusive theory.

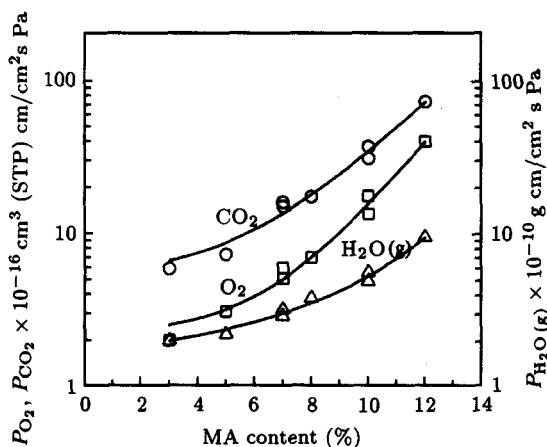


Fig. 1 Plots of the permeability coefficients versus the composition of VDC/MA copolymers

The permeation of water vapor through polymer films is a complex process that can be explained by "solvency-diffusion mechanism" as that of gases^[9]. The permeability coefficient (P) can be regarded as the product of diffusion coefficient (D) and solubility coefficient (S):

$$P = D \cdot S \quad (2)$$

S is mainly controlled by the inherent condensability of the penetrant, the polymer-penetrant interactions, and the amount of excess volume existing in polymer matrix (free volume), D is mainly controlled by the amount of excess volume existing in polymer matrix^[10]. There is no any special polymer-penetrant interaction for the system of VDC/MA copolymers and the penetrators such as oxygen, carbon dioxide, and water vapor. Hence, the permeability coefficients of VDC/MA copolymers to oxygen, carbon dioxide, and water vapor can all be described by Lee's free volume modelling.

In Fig. 2, the permeability coefficients of VDC/MA to oxygen, carbon dioxide,

and water vapor were plotted against amorphous fraction. VDC/MA copolymers are semicrystalline polymers, which consist of crystalline phase with no free volume and amorphous phase with free volume, the permeability of semicrystalline polymers can be two phases modelling staged^[11]. The molecular chain segment packing of crystalline phase is so efficient that no free volume exists here and the gas and vapor solution and diffusion do not take place. As result, the logarithms of permeability coefficients increase linearly with the decrease of the crystalline fractions of VDC/MA copolymers.

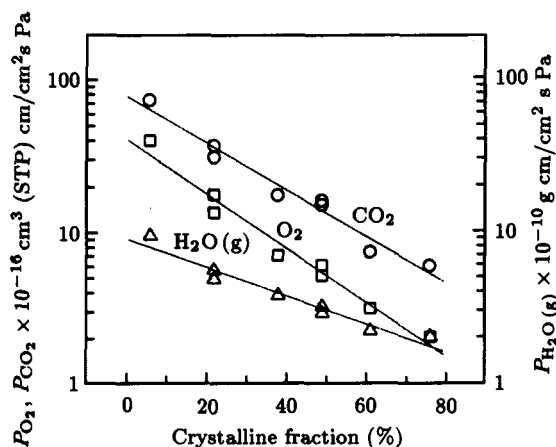


Fig. 2 Plots of the permeability coefficients of the VDC/MA copolymers versus crystalline fractions

In conclusion, the melting temperature and crystalline fraction of VDC/MA copolymers are decreased progressively with the increase in MA content. The barrier properties of VDC/MA copolymers become gradually worse as VDC composition decreases. A linear relationship exist between the logarithm of the permeability coefficients and the crystalline fractions of VDC/MA copolymers. The VDC/MA copolymers with 7 or 8% MA have good processability (moderate melting temperature) and favorable barrier property.

Keywords:

Barrier properties; Copolymer films; Vinylidene chloride; Methyl acrylate

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