

BARRIER PROPERTIES OF VINYLIDENE CHLORIDE COPOLYMERS

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ABSTRACT

The permeability coefficients of a series of copolymers of vinylidene chloride (VDC) with methyl acrylate (MA), butyl acrylate (BA) or vinyl chloride (VC) (as comonomer) to oxygen and carbon dioxide have been measured at 1.0 MPa and 30°C, while those to water vapor have been measured at 30°C and 100% relative humidity. All the copolymers are semicrystalline. VDC/MA copolymers have lower melting temperature compared with VDC/BA copolymers, while that melting temperature of VDC/VC copolymer is higher than that of VDC/acrylate copolymers with the same VDC content. The barrier property of the copolymers is predominantly controlled by crystallite, free volume fraction, and cohesive energy. The permeability coefficients of VDC/MA copolymers to oxygen, carbon dioxide, and water vapor were successfully correlated with the ratio of free volume to cohesive energy.

INTRODUCTION

The polymers with low gas and vapor permeability have been used as barrier packaging films and containers to conserve foods, tea, beverage, and medicine^[1]. The desirable barrier polymer materials must have very low permeability to oxygen, carbon dioxide, aroma, and water vapor; high mechanical strength and compatibility with foods^[2]. Polyvinylidene chloride (PVDC) with high crystallinity has excellent gas and water vapor barrier properties^[3]. However, the melting temperature (203°C) of PVDC is only slightly lower than its decomposing temperature (210°C), causing rather difficult to process it into available forms. The most efficient method to improve its polymer processability is to copolymerize VDC with a few percent of

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other monomers such as acrylate and vinyl chloride. High comonomer content will lower the barrier property. Unfortunately, there is only few reports of detailed study on the barrier property and the processability of VDC copolymers^[3].

The aim of the present work is to study the effect of the molecular structure on the melting temperature and barrier property of copolymers of VDC with MA, BA, or VC. The main factors affecting barrier property of the copolymers were discussed.

EXPERIMENTAL

Materials

VDC/MA copolymer containing 8% MA and VDC/VC copolymers with 15% or 22% VC were kindly supplied by Quzhou Chemical Co.. The other copolymers were synthesized in our laboratory^[4,5]. Average molecular weights of all the copolymers were in the range of 65,000—80,000. The purity of the permeation gases was above 99.9%.

Preparation of polymer films

The copolymer solutions in DMF were filtered through a ten- μm sintered glass filter before casting. Films were cast from solution on glass plates in a controlled dust-free environment. The freshly cast films were then heated for 24 hours at about 40—50°C and 24 hours at about 100°C to speed drying. During drying the relative humidity was maintained at 20—30%. 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.

Apparatus and measurement

The density of the polymer film was determined at 25°C by the density gradient tube method using a mixture of carbon tetrachloride and ethylene trichloride. Differential scanning calorimetry were conducted on a Perkin-Elmer series 7 DSC instrument. Gas permeability coefficients of VDC copolymer films were measured at 1.0MPa and 30°C and water vapor permeability coefficients measured at 30°C and 100% relative humidity.

RESULTS AND DISCUSSION

Characterization of copolymers

The melting temperature and crystalline fraction (determined by melting heat) of VDC copolymers are mainly governed by the structure of macromolecule. The crystallinity of PVDC is originated from the symmetry of molecular chain segment.

MA, BA or VC chain segment having low symmetry, as well as its bulky side substituents ($-\text{COOCH}_3$ or $-\text{COOC}_4\text{H}_9$) hinder the crystal growing and result in crystal grating defect. Hence, the crystalline fractions and the melting temperature of VDC copolymers are lower than those of PVDC. The VDC/acrylate copolymers have also low melting temperature and crystalline fractions as compared with its corresponding VDC/VC copolymers.

Some physical properties of VDC copolymer films are listed in Table 1. According to the group contribution method reported by Bondi and Lee^[6,7], the free volume of the polymer films is calculated by Eq. (1).

$$V_f = V_t - 1.3V_W \quad (1)$$

where V_f is the molar free volume of the polymer films, V_t is the molar volume of the polymer films calculated from the density of the copolymer films at 25°C, V_W is van der Waals volume calculated by the group contribution method reported by Bondi^[7]. The free-volume fraction (FVF) is the ratio of the estimated molar free volume to polymer molar volume measured at 25°C. The cohesive energy densities of the polymer films were estimated by the group contribution method reported by van Krevelen^[8].

Table 1 Some physical properties of VDC copolymers

Sample code	Composition (%)	Melting temp. (°C)	Density ρ (g/cm ³)	Free volume V_f (cm ³ /mol)	Cohesive energy E_{coh} (kJ/mol)	FVF	V_f/E_{coh} (cm ³ /kJ)
P1	MA, 7.0	159	1.786	3.15	26.1	0.0582	0.124
P2	MA, 8.0	148	1.698	3.72	26.2	0.0690	0.142
P3 ^a	MA, 8.0	—	1.712	3.36	26.2	0.0646	0.142
P4	BA, 7.0	162	1.773	3.20	26.8	0.0550	0.120
P5	VC, 12	168	1.787	2.87	24.5	0.0573	0.117
P6	VC, 15	156	1.760	3.23	24.1	0.0648	0.133
P7 ^a	VC, 15	—	1.765	3.11	24.1	0.0626	0.129
P8	VC, 22	139	1.728	3.82	23.9	0.0764	0.159

a: Film samples were supplied by Quzhou Chemical Co.

Barrier properties of the polymers

Barrier property of polymer is mainly determined by the chemical structure and morphology of the polymer. The permeability coefficients of all the VDC copolymers to oxygen, carbon dioxide and water vapor are much higher than those of PVDC reported in the literature^[9]. The free volume and cohesive energy are two dominant

factors that determine the permeability of polymers^[10].

Table 2 lists the permeability coefficients of VDC copolymers to oxygen, carbon dioxide, and water vapor. P1 with smaller free-volume fraction and lower cohesive energy has smaller permeability coefficients to oxygen, carbon dioxide, and water vapor than P2 or P3 with higher free-volume fraction and similar cohesive energy. This indicates that the permeability of the VDC/MA copolymers is mainly controlled by free volume difference as compared with trivial variance in cohesive energy. Although the composition of P2 is the same as that of P3, P3 has lower free volume as compared with P2 due to their difference in preparation method. Hence, gas and water vapor permeability coefficients of P3 are smaller than those of P2. Despite the VDC content of P4 (VDC/BA copolymer) is the same as that of P1, P4 has slight higher permeability coefficients to oxygen, carbon dioxide, and water vapor than P1 due to the difference in the chemical structure between MA and BA.

Table 2 The permeability coefficients^{a)} of the VDC copolymers

Sample code	Composition (%)	P_{O_2}	P_{CO_2}	$P_{H_2O(g)}$
P1	Ma, 7.0	5.12	14.6	2.93
P2	Ma, 8.0	6.98	17.8	3.83
P3	Ma, 8.0	5.63	17.2	3.08
P4	BA, 7.0	5.48	16.1	3.08
P5	VC, 12	3.83	12.6	2.40
P6	VC, 15	7.50	19.7	3.92
P7	VC, 15	6.75	18.7	3.45
P8	VC, 22	18.2	31.6	5.93

a) P_{O_2} and P_{CO_2} : $10^{-16} \text{ cm}^3 \text{ (STP) cm/cm}^2 \cdot \text{S} \cdot \text{Pa}$, $P_{H_2O} \text{ (g)}$: $10^{-10} \text{ g} \cdot \text{cm/cm}^2 \cdot \text{S} \cdot \text{Pa}$

The free-volume fractions of the copolymers are increased progressively with increasing VC content in VDC/VC copolymer, while the cohesive energies of the copolymers are decreased gradually. These facts result in that the permeability coefficients of the VDC/VC copolymers to oxygen, carbon dioxide, and water vapor are magnified progressively as VC content in the copolymers increases. The main research goal of VDC copolymerization is to decrease the melting temperature of the copolymer and to improve its processability. When the melting temperature of VDC/VC copolymers is close to that of VDC/MA, the barrier properties of the former are lower than that of the latter one. For example, P6 (melting temperature 158°C) has better permeability coefficients to oxygen, carbon dioxide, and water vapor, than that of P1 (melting temperature 158°C).

Correlation of permeability coefficients with FVF or V_f/E_{coh}

As it is mentioned above, the free volume and cohesive energy are two main factors controlling the barrier property of polymers. JIA et al. put forward a method for predicting the permeability of polymers by means of free volume and cohesive energy (E_{coh})^[11]. Fig. 1 shows a plot of the permeability coefficients of the polymers to oxygen and carbon dioxide against free volume and cohesive energy in the form of Eq. (2).

$$\log P = A + B \left(\frac{V_f}{E_{coh}} \right) \quad (2)$$

where A and B are the parameters depending upon the type of penetrating gas. The correlation of gas permeability coefficients of VDC copolymer containing acrylate or VC is rather successful.

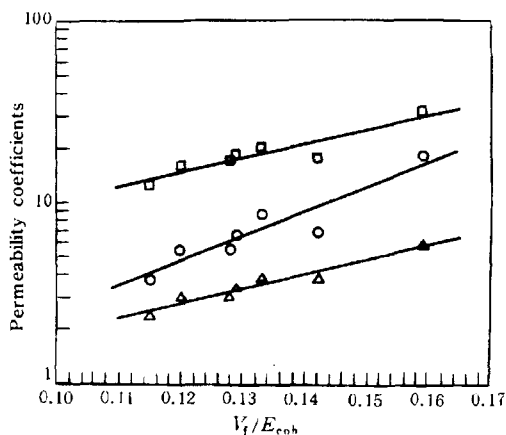


Fig. 1 Permeability coefficients of the VDC copolymers vs. the ratio of free volume to cohesive energy

$\circ$ oxygen, $10^{-16} \text{ cm}^3 \text{ (STP) cm/cm}^2 \cdot \text{S} \cdot \text{Pa}$, $\square$ carbon dioxide, $10^{-16} \text{ cm}^3 \text{ (STP) cm/cm}^2 \cdot \text{S} \cdot \text{Pa}$, $\triangle$ water vapor, $10^{-10} \text{ g} \cdot \text{cm/cm}^2 \cdot \text{S} \cdot \text{Pa}$

CONCLUSION

The melting temperature and crystalline fraction of VDC/MA copolymers are decreased progressively with the increase in MA composition in polymerization temperature. The barrier properties of VDC/MA copolymers become worse gradually with the decrease in VDC content. A linear relationship exists between the logarithm of permeability coefficients and the free volume fractions of VDC/MA copolymers. The VDC/MA copolymers with 7 or 8% MA have both good processability (moderate melting temperature) and favorable barrier property.

Keywords:

VDC copolymers modified; Barrier films; Permeability

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