

BARRIER PROPERTY AND STRUCTURE OF ACRYLONITRILE/ACRYLIC COPOLYMERS*

YANG Zhenghua (杨正华) and LI Yuesheng (李悦生)**

(Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022)

ABSTRACT

A series of acrylonitrile (AN) copolymers with methyl acrylate (MA) or ethyl acrylate (EA) as comonomer (5—23 wt%) was prepared by free-radical 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 also measured at 100% relative humidity and at 30° C. All the AN/acrylic copolymers are semicrystalline. As the acrylate content increase, the permeability coefficients of the copolymers to oxygen and carbon dioxide are increased progressively, but those to water vapor are decreased progressively. The gas permeability coefficients of the polymers were correlated with free-volume fractions or the ratio of free volume to cohesive energy.

INTRODUCTION

Barrier polymers used as food, tea, beverage and medicine packing materials, which have been developed over passed few decades, are a kind of important functional polymer materials. These polymers can be fabricated into plastics films and bottles used for replacing the expensive aluminum cans, and heavy and breakable glass bottles. The desirable barrier polymers should have very low permeability to oxygen, carbon dioxide, aroma, and water vapor, high mechanical strength, favorable processability and good compatibility with foods^[1]. Polyacrylonitrile (PAN) is an important barrier polymer^[2-4], which can be used for making ordinary food package or used as part of the multilayer laminates^[5]. PAN with high crystalline fraction, high polarity, small free-volume fraction and high cohesive energy density, has good compatibility with foods and very low permeability to oxygen, carbon dioxide and aroma. However, its melting temperature is only slightly lower than decomposing temperature, causing some difficulties to process it into available forms. By the way,

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** To whom all correspondence should be addressed

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it possesses much higher permeability to water vapor than desirable barrier polymers such as vinylidene chloride copolymers due to the hydrophilic nitrile groups^[5,6].

The main purpose of this work is to determine the effect of the structure of AN/MA and AN/EA copolymers on barrier property and to develop favorable AN-based barrier copolymers.

EXPERIMENTAL

Materials

Acrylonitrile, methyl acrylate and ethyl acrylate (reagent grade) were purified by distillation under ambient and reduced pressure respectively before use. 2,2'-Azoisobutyronitrile (AIBN) (reagent grade) was purified by repeated crystallization, and dimethyl sulfoxide (DMSO) (reagent grade) was purified by distillation before use. N,N-dimethylformamide (DMF) was reagent grade. Ethanol was technical grade. The purity of the permeation gases used was more than 99.9%.

Preparation of copolymers

The copolymerizations were conducted at about 50°C in a three-necked flask equipped with stirrer. The three-necked flask was filled with AN/MA or AN/EA mixtures, solvent (DMSO or mixtures of DMSO and water) and initiator (AIBN) in N₂ atmosphere. The copolymers formed were isolated with ethanol, then washed three times with ethanol. The composition of the copolymers was determined using FTIR spectroscopy. For the determination of the composition, the integral absorption intensities of the following characteristic bands were: 1770—1670 cm⁻¹ ($\nu_{C=O}$) and 2330—2310 cm⁻¹ ($\nu_{C\equiv N}$).

Preparation of polymer films

The copolymer solutions in DMF were filtered with a 10- μ m sintered glass filter before casting films. Films were cast from the solution on glass plates in a controlled dust-free environment. The freshly prepared cast films were then heated for 24 h at about 40—50°C and 24 h at about 100°C to speed drying. Relative humidity during drying was maintained at 20—30%. Polymer films were removed from the glass plates by stripping carefully, and then dried in vacuum oven at 150°C for three days. The resultant polymer films generally were about 25 μ m in thickness.

Apparatus and procedure

The density of the polymer film was determined at 25°C by the density gradient column method using a mixture of carbon tetrachloride and ethanol. Wide angle X-ray diffraction (WAXD) measurements for the polymer films were undertaken on a Philips X-ray diffractometer with CuK α radiation, $\lambda = 0.154$ nm. FTIR measurements for the polymer films were undertaken on a Digilab FTS-200 infrared

spectrograph. Gas and water vapor permeability coefficients were measured according to the same procedure as described in the previous paper^[7].

RESULTS AND DISCUSSION

Characterization of polymer films

Fig.1 is the WAXD curves of AN/MA copolymers. The diffraction angle of the highest crystal diffraction intensity in each sample appears at about 17.3°. WAXD curves of AN/EA copolymers are similar to that of AN/MA copolymers. As Fig.1 shows, the diffraction intensities of crystallinity are decreased progressively with the increase in acrylate content, indicating the crystalline fraction of the copolymer films is decreased progressively with the increase in acrylate content. The crystal diffraction intensity of AN/EA copolymer given is stronger than that of the corresponding AN/MA copolymers. Hence, the crystalline fraction of a definite AN/EA copolymer given is higher than that of AN/MA copolymer with the same AN content.

Some physical properties of the polymer films are listed in Table 1. According to the group contribution method reported by Bondi and Lee^[8,9], 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 which was calculated from the density of the polymer films at 25° C, and V_w is van der Waals volume calculated by the group contribution method reported by Bondi^[9]. The free-volume fraction (FFV) is the ratio of the estimated molar free volume to polymer molar volume measured at 25° C. The cohesive energy densities (CED) of the polymer films were estimated by the group contribution method reported by van Krevelen and coworker^[10]. From Table 1, one can observe that FFV of the copolymer films is increased progressively, CED decreases with increase in acrylate content, and V_f/CED is increased progressively. FFV of

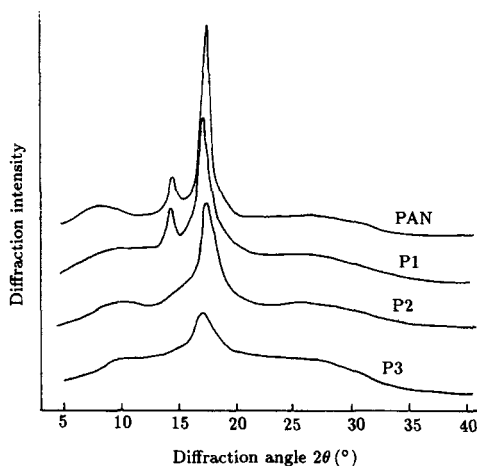


Fig.1 Wide angles X-ray diffraction (WAXD) curve of AN/MA copolymers

AN/EA copolymer films given is slightly smaller than that of corresponding AN/MA copolymer films, contrarily, CED of a definite AN/EA copolymer film is slightly larger than that of AN/MA copolymer (with the same AN content) film.

Table 1 Some physical properties of the polymers

Code	Acrylate content (wt%)	Intrinsic viscosity η_{in} (dl/g)	Density ρ (g/cm ³)	Cohesive energy density CED (J/cm ³)	Free volume V_f (cm ³ /mol)	Free-volume fraction FFV	V_f /CED $\times 10^{-5}$ (cm ³ /kJ)
PAN	0	3.25	1.165	745.2	3.56	0.079	0.105
P1	MA, 5	3.22	1.166	729.9	3.84	0.083	0.114
P2	MA, 10	3.20	1.171	716.5	4.03	0.086	0.120
P3	MA, 12	3.21	1.172	710.7	4.10	0.087	0.122
P4	MA, 17	1.98	1.172	693.6	4.52	0.093	0.135
P5	MA, 22	1.95	1.176	680.1	4.70	0.095	0.140
P6	EA, 5	3.37	1.166	729.2	3.80	0.082	0.112
P7	EA, 9	2.89	1.167	716.8	3.98	0.084	0.117
P8	EA, 13	2.85	1.164	703.1	4.24	0.087	0.125
P9	EA, 17	1.96	1.165	690.0	4.48	0.091	0.131
P10	EA, 22.5	2.10	1.168	673.5	4.72	0.093	0.138

Barrier properties of the polymers

Barrier properties of polymer are mainly controlled by its chemical and physical structure. There is a lot of structure parameters such as crystalline fraction, polarity, free volume, chain segment orientation and cohesive energy density, but they are not independent. For example, the polymers with high crystalline fraction have low free volume fraction, and the polymers with high polarity have high cohesive energy density. According to Jia and coworker^[11], the permeability of polymers may be controlled mainly by free-volume fraction, cohesive energy density and interaction between polymer matrix and penetrant molecule.

Fig.2 and 3 are the plots of the permeability coefficients versus the composition of AN/MA and AN/EA copolymers respectively. The permeability coefficients of PAN to oxygen and carbon dioxide are 9.7 and $2.4 \times 10^{-16} \text{ cm}^3(\text{STP})\text{cm}^2\cdot\text{s}\cdot\text{Pa}$ respectively at 30°C and 1.0 MPa , and that to water vapor is $2.54 \times 10^{-14} \text{ g}\cdot\text{cm}/\text{cm}^2\cdot\text{s}\cdot\text{Pa}$ at 30°C and 100% relative humidity. These values are much higher than the results reported by Allen et al.^[5] and slightly lower than the results reported by Koros and coworker^[12].

The permeability of AN/MA copolymers to oxygen and carbon dioxide is higher than those of PAN due to the increase in free-volume fraction and crystalline fraction, and the decrease in cohesive energy density. As shown in Fig.2, the logarithms of the permeability coefficients to oxygen and carbon dioxide increases linearly with

the percentage of MA or EA in the copolymers. In other words, the barrier property

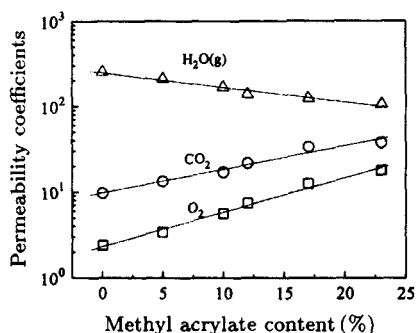


Fig. 2 Plots of the gas and water vapor permeability coefficients versus the composition of AN/MA.

(Units: $\text{H}_2\text{O(g)}$, $10^{-16} \text{ g}\cdot\text{cm}/\text{cm}^2\cdot\text{s}\cdot\text{Pa}$; O_2 and CO_2 , $10^{-16} \text{ cm}^3(\text{STP})/\text{cm}^2\cdot\text{s}\cdot\text{Pa}$.)

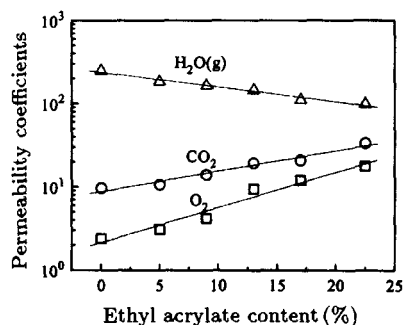


Fig. 3 Plots of the gas and water vapor permeability coefficients versus the composition of the AN/EA copolymers.

(Units: $\text{H}_2\text{O(g)}$, $10^{-16} \text{ g}\cdot\text{cm}/\text{cm}^2\cdot\text{s}\cdot\text{Pa}$; O_2 and CO_2 , $10^{-16} \text{ cm}^3(\text{STP})/\text{cm}^2\cdot\text{s}\cdot\text{Pa}$.)

to oxygen and carbon dioxide becomes worse progressively with the percentage of MA or EA in the copolymers. However, the permeability of AN/MA copolymers to water vapor is low as compared with that of PAN. This can be explained by the "solution-diffusion mechanism"^[13]. The permeability coefficient (P) can be regarded as a product of diffusion coefficient (D), and a solubility coefficients (S):

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

S is mainly controlled by the inherent condensability of the penetrant gas, the polymer-penetrant gas interactions and the amount of excess volume existing in polymer matrix, D is mainly controlled by the amount of excess volume (free volume) existing in polymer matrix. The decrease in $D_{\text{H}_2\text{O}}$ or in $S_{\text{H}_2\text{O}}$ results in a decrease in $P_{\text{H}_2\text{O}}$. PAN is one of the polymers possessing a lot of hydrophilic nitrile groups which strongly interact on with water molecules. Thus, the solubility coefficient of PAN to water vapor is much larger than the other polymers that contain no highly hydrophilic substituents. Thus, PAN shows low barrier property to water vapor. The solubility coefficients of AN/MA copolymers to water vapor are decreased progressively with the decrease in AN content. These facts cause the decrease of the permeability of AN/MA copolymers to water vapor. In other words, the barrier property of AN/MA copolymers to water vapor increases with the increase in MA content.

As Fig. 3 shows, the effect of copolymeric composition upon barrier properties of AN/EA copolymers is similar to the case of AN/MA copolymer. The permeability

coefficients of the AN/EA copolymers to oxygen, carbon dioxide and water vapor are slightly lower than those of the corresponding AN/MA copolymers.

CONCLUSION

All AN copolymers with 5—23 wt% MA or EA are semicrystalline. The crystalline fraction of AN copolymers is decreased gradually with the increase in acrylic content. The packing properties of the copolymer films is decreased progressively, and the interactions of the copolymer chain is also decreased with the increase in acrylic content. Although barrier properties of AN/MA copolymers to oxygen and carbon dioxides decreases progressively with the increase in MA or EA content, whereas those to water vapor increases gradually. The barrier property of AN/EA copolymers are better than that of AN/MA copolymers with the same AN content.

Keywords:

Barrier property; Copolymer film; Acrylonitrile; Methyl acrylate; Ethyl acrylate

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