Effect of the Thermal Treatment of Ionomer Films on Permeability and Permselectivity

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ABSTRACT: Ionomers have been studied in detail and have gained widespread commercial use. Interested in altering the ratio of CO_2/O_2 permeability (i.e., permselectivity) of films for use in packaging respiring produce, we pressed sodium-neutralized poly(ethylene methacrylic acid) ionomers into films at 120–160°C and investigated their thermal, morphological, and permeability properties. The heat treatment of the ionomers at 160°C increased the gas permeability for O_2 more than for CO_2 and reduced the CO_2/O_2 permselectivity ratio from 4.1 to 1.6. The reasons for these changes in the permeability characteristics of the ionomers are not understood but could be related to a reduction in the polyethylene (PE) crystallinity and the destruction of the aggregates into smaller, dispersed clusters. These results were supported by differential scanning calorimetry data and scanning electron micrographs. This suggests that the heat treatment of ethylene–methacyrlic ionomers may improve their potential for applications as selective barriers for modified-atmosphere packaging of respiring produce. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2811–2815, 2002

Key words: ionomers; annealing; gas permeation; differential scanning calorimetry (DSC)

INTRODUCTION

Rees and Vaughan[1,2] synthesized polymers containing metal ions that they termed *ionomers*. They found that the ionic forces that developed between ionized carboxylic acid groups pendant from the α-olefin chains and free group I or II metallic cations had a profound effect on the crystalline morphology. Ionomer films lack the haze caused by light scattering crystallites and are very clear. The ionic species may be randomly distributed along the polymer chain,[3] within the main chain (ionenes), or at the ends of the chains (halatotelechelic polymers).[4] Among widely studied ionomers are poly(ethylene methacrylic acid) (EMAA) copolymers, which are crystallizable, random ionomers. EMAA has a low molar percentage of methacrylic acid and is often neutralized with sodium or zinc ions. Ethylene ionomers have wide industrial applications and are commonly used for packaging, extrusion coating, and molding.[4]

Several groups have explored the properties and morphological characteristics of ionomers.[5,6] Models have been proposed to describe the morphology of ethylene ionomers, but it is generally agreed that the morphological structure of ionomers is not fully understood. For example, the structure of ionic aggregates and its effect on the melting behavior have not been resolved. Sakamoto et al.[7] suggested that the size of the ionic domains was 100 Å, whereas Eisenberg and coworkers[8,9] suggested that the clusters were 50–100 Å. Although some authors believe that the ionic clusters are composed of carboxylic and salt ions, others have suggested that ionic aggregates consist only of carboxylic groups.[10]

Kutsumizu et al.[5] recently observed a thermal anomaly at 52°C in the melt profile of ionomers. Ethylene ionomers typically exhibit one melting peak when reheated immediately after cooling from the melt. However, after storage for a few days at room temperature, another endothermic peak appears around 52°C. This new peak has been attributed to the melting of imperfect polyethylene (PE) crystallites, whereas others have proposed a model of a glass–rubber transition of ionic aggregates that melt around 52°C.[11] Another explanation is that an ordered state inside the ionic aggregates is reached during aging at room temperature and is transformed into a disordered state at 52°C.

This makes it clear that the thermal history can have an effect on ionomer morphology. However, little work has been published on the effects of thermal history on permeability. We are interested in modifying the CO_2/O_2 permeability and permselectivity of films that could be used in the packaging of respiring produce. In our view, the ratio of CO_2/O_2 permeability (i.e., permselectivity) is a limiting factor in extending the shelf life of packaged respiring fruits and vegetables.[12] Following the suggestions of Del Nobile et al.[13] and Mensitieri et al.[14] that annealing conditions

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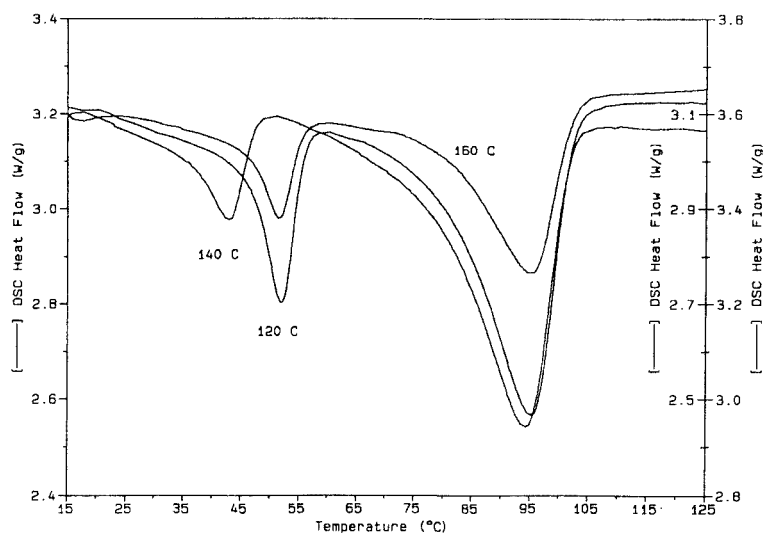
Figure 1 DSC thermograms of ethylene-*co*-methacrylic acid (8%) fully neutralized with sodium and annealed at 120, 140, and 160°C. The higher temperature peak corresponds to the melting of PE, and the lower temperature peak corresponds to the melting of ionic clusters. Films formed at 160°C had smaller PE and ionic-cluster peaks, whereas films formed at 140 and 120°C were similar and had higher PE and ionic-cluster peaks than films formed at 160°C.

[below the melting temperature (T_m)] could affect the permeability of ionomers, we set out to determine if thermal treatments of ionomers would favorably affect permselectivity.

MATERIALS AND METHODS

EMAA (sodium ion) was acquired from Scientific Polymer Products, Inc. (Ontario, NY; catalog no. 465). The ionomer was reported by the supplier to be 7–8% methacrylic with a melt index of 10.0, a density of 0.945, and a T_m value of 95°C.

Ionomer resin (0.2 g) was placed between two smooth-surface Mylar sheets, and the sheets were inserted between the plates of a preheated hot-press machine (model 341-20, Loomis Engineering, Caldwell, NJ). The temperature of the plates was stabilized at 120°C, as determined with a calibrated surface thermocouple. The sheets were heated between the plates for 20 min, and this was followed by the application of a total pressure of 1.36×10^4 kg for 40 min. The Mylar sheets were then removed and immediately cooled in an ice bath. The same procedure was repeated at 130, 140, 150, and 160°C. However, when the temperature was 150 or 160°C, the Mylar sheets were pressed for 30 or 20 min, respectively. The resulting films were 63–76 μm thick.

The O_2 and CO_2 permeation rates of three independent films formed at each temperature were determined at ambient temperatures of 22 ± 2°C (three or more independent films were tested at each temperature, each measured in triplicate, for a total of nine data points) with a universal permeation test apparatus.[15] The melting behavior was investigated with dif-

ferential scanning calorimetry (DSC; DSC 2920, TA Instruments, New Castle, DE). The temperature and heat flow were calibrated with mercury, distilled water, and indium standards [onset temperature (T_o) = 156.8°C and heat of fusion = 28.5 J/g]. The EMAA ionomer (0.8–1.2 mg) was hermetically sealed in aluminum pans. The pans were allowed to equilibrate in the DSC chamber for 20 min before the scanning from 0 to 120°C at a heating rate of 10°C/min. The heat of fusion, T_o, and peak temperature (T_p) were recorded by computer for films formed at 120, 150, and 160°C. T_m was determined as T_p in an endothermic peak.

Ionomer films formed at 120 and 160°C were further analyzed with scanning electron microscopy (SEM). Film specimens were coated with Au/Pd-sputtered coatings (ca. 15 nm) before examination.

TABLE I
Melt Parameters (± Standard Deviation) of Ionomer Films Formed at Different Temperatures as Determined by DSC

Melt parameter	120°C	140°C	160°C
Peak melting at 52°C ($n = 3$ at each temperature)			
Heat of fusion (J/gm)	30.2 ± 3.3	27.3 ± 4.1	11.7 ± 1.6
T_o (°C)	37.6 ± 2.1	30.1 ± 5.7	29.0 ± 1.4
T_p (°C)	52.0 ± 1.5	42.9 ± 6.2	52.2 ± 1.2
Peak melting at 95°C ($n = 3$ at each temperature)			
Heat of Fusion (J/gm)	70.4 ± 2.9	71.1 ± 2.2	33.7 ± 1.3
T_o (°C)	78.2 ± 1.2	75.5 ± 1.6	77.8
T_p (°C)	95.1 ± 0.8	94.3 ± 0.9	95.7 ± 1.1
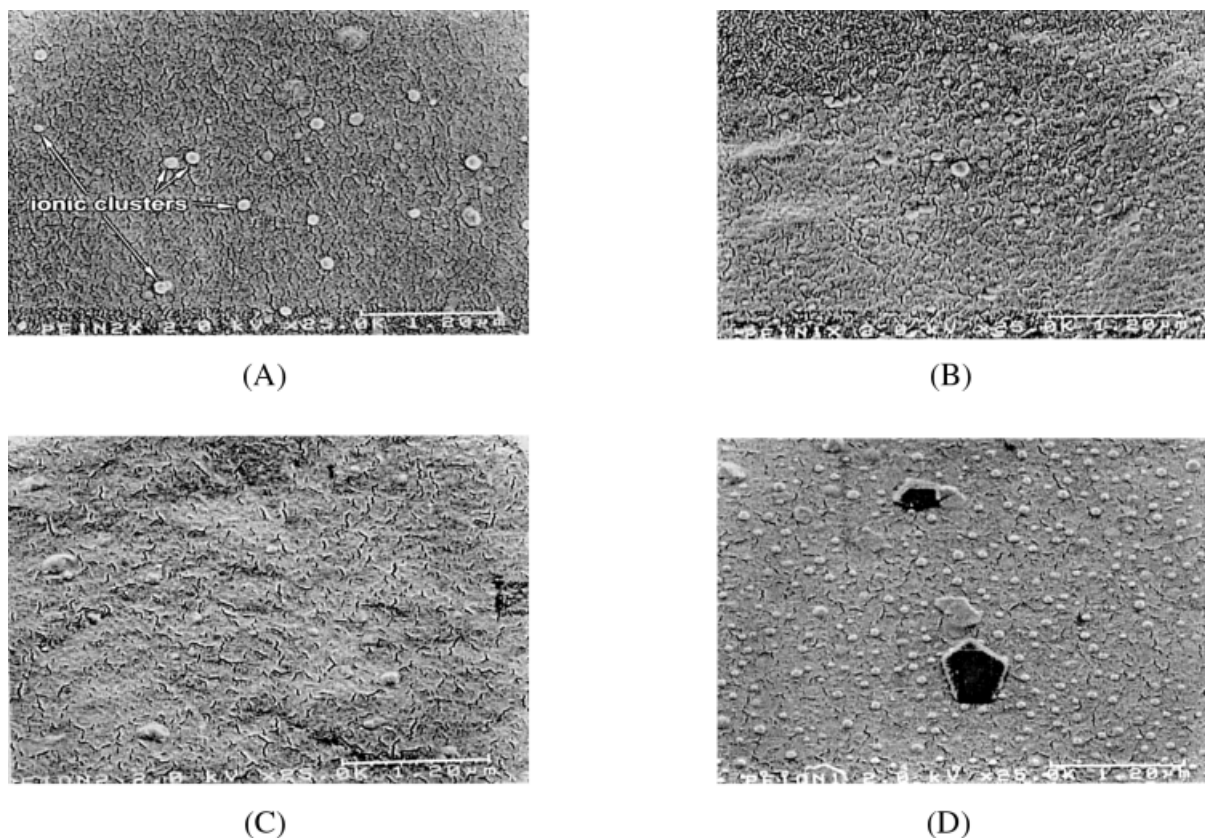
Figure 2 SEM micrographs of ionomer films formed at (A,C) 160 and (B,D) 120°C. A and B are cross-section scans; C and D are surface scans.

RESULTS

As expected, DSC curves gave two fundamental endothermic peaks at 52 and 95°C (Fig. 1). The lower melting point peak was attributed to the ionic aggregation in the polymer matrix, whereas the higher temperature peak resulted from the melting of PE crystals. The heat of fusion near T_m suggests that the ionomer was not fully neutralized. The effect of the temperature treatment above T_m was minimal on ionic domains and PE crystal structures up to 140°C (Table I). The ionic domain heat of fusion for the films formed at 140°C was slightly lower (27.3 J/g) than the heat of fusion for those formed at 120°C (30.2 J/g; Table I). However, the ionomer formed at 160°C had a markedly lower heat of fusion (10.5 J/g) than ionomers annealed at 120 and 140°C. A similar pattern was observed for PE crystal heats of fusion (Table I). The PE crystal heat of fusion for the ionomers annealed at 140°C was similar to the heat of fusion for those annealed at 120°C: 71.1 and 70.4 J/g, respectively. The heat of fusion of the PE crystals for the ionomer annealed at 160°C was approximately half that found for the lower temperatures (33.7 J/g).

These data suggest that ionic aggregates of ionomers formed at 160°C require less energy (10.5 J/g) to melt than the aggregates from ionomers formed at 120

and 140°C. This lower heat of fusion for the transition around 52°C implies a lower degree of local order in the region that includes ionic aggregates (ionic domains). In addition, forming at 160°C reduces the crystallinity of the ionomer, as indicated by the lower heat of fusion (33.7 J/g) in comparison with the heats of fusion for ionomers formed at 120 (70.4 J/g) and 140°C (71.1 J/g; see Table I).

Ionic clusters are known to undergo a phase transition as a result of heat treatment, exhibiting a glass-transition temperature that is different from that of the parent polymer.[5] Below the glass-transition temperature of the ionic clusters (T_i), their ordered structure is intact. Above T_i, the order is lost, and the clusters are in a disordered state. Kutsumizu et al.[5] proposed that the disordered state of the ionic aggregates above T_i is due mainly to the thermally agitated mobility of the chain segments attached to them. Therefore, it can be hypothesized that annealing at 160°C breaks the ionic clusters into ionic aggregates, which are dispersed over the PE matrix. Such conditions limit the clustering mechanism so that ionic aggregates are prevented from growing into ionic clusters when ionomers are quenched from the melt. Because ionic aggregates interfere with the crystallization of PE chains, PE crystallinity is lower for ionomers annealed at 160°C, and

this explains the lower heat of fusion. Annealing temperatures above 160°C were not successful because of the softening of the Mylar sheets.

SEM images reveal morphological differences between ionomer films formed at 120°C and those formed at 160°C. The cross sections of the ionomer films show that the aggregates are more numerous in the film treated at 120°C than in the film treated at 160°C [Fig. 2(A,B)]. The difference is even more profound when the surfaces are compared [Fig. 2(C,D)].

Films annealed at 160°C had significantly different CO_2 and O_2 permeability coefficients than those annealed at lower temperatures (Table II). The O_2 permeability coefficient was affected to a greater degree by the annealing conditions than the CO_2 coefficient. The O_2 permeability coefficient increased from 3.4×10^{-10} mL cm/cm² s cmHg for those ionomers formed at temperatures between 120 and 150°C to an average permeability coefficient of 2.46×10^{-9} mL cm/cm² s cmHg for films formed at 160°C. The CO_2 permeability coefficient increased from 1.39×10^{-9} mL cm/cm² s cmHg for ionomers annealed at 120–150°C to an average of 2.98×10^{-9} mL cm/cm² s cmHg for ionomers annealed at 160°C. It is not clear why the O_2 permeability coefficient was more affected by the higher formation temperature than the CO_2 permeability coefficient. However, when testing the O_2 and CO_2 permeability of ethylene ionomers, Mensitieri et al.[14] observed a similar pattern and alluded to a decrease in the tortuosity factor (diffusive path length) and immobilization factors (blocking effect), which could lead to an increase in gas permeability. Because diffusion is affected by the size of the permeating molecules, O_2 could permeate faster than CO_2; therefore, the relative increase in O_2 permeability was higher. The calculated solubility and diffusion coefficients (Table II) reveal that annealing at 160°C also caused a significant increase in O_2 solubility (from 2.37×10^{-6} to 1.65×10^{-5} mL of O_2/mL cmHg), which was largely responsible for the overall increase in the O_2 permeability. The O_2 diffusion coefficient of the annealed ionomer increased slightly from 1.42×10^{-4} (120°C) to 1.49×10^{-4} cm²/s (160°C). A similar pattern could be observed for CO_2 permeability. The CO_2 solubility coefficient increased from 1.11×10^{-5} to 1.96×10^{-5} mL of CO_2/mL cmHg, whereas the increase in the diffusion coefficient was minimal (from 1.25×10^{-4} to 1.52×10^{-4} cm²/s). We do not have an explanation for the observed increase in O_2 solubility relative to CO_2 solubility in ethylene ionomers annealed at 160°C, although it was consistently reproducible. It may be that annealing at 160°C followed by rapid cooling results in a lower PE crystallinity and a change in the local order inside the ionic domains. This may allow for easier solubilization and transport of permeant molecules. This lower crystallinity may

TABLE II
Gas Permeability, Diffusion (D), and Solubility Coefficients (S), and Permselectivity (PCO₂/PO₂) of Ionomer Annealed at Different Temperatures (n = 5, ± Standard Deviation)

Forming temperature (°C)	mL cm/cm² s cmHg		D_{O2} (cm²/s)	S_{O2} (mL$_{O2}$/ mL cmHg)	D_{CO2} (cm²/s)	S_{CO2} (mL$_{CO2}$/ mL cmHg)	PCO₂/ PO₂
	PO₂	PCO₂					
120	$3.37 \times 10^{-10} \pm 0.0$	$1.39 \times 10^{-9} \pm 0.0$	1.42×10^{-4}	2.37×10^{-6}	1.25×10^{-4}	1.11×10^{-5}	4.1
130	$3.37 \times 10^{-10} \pm 0.0$	$1.39 \times 10^{-9} \pm 0.0$	1.42×10^{-4}	2.37×10^{-6}	1.25×10^{-4}	1.11×10^{-5}	4.1
140	$3.37 \times 10^{-10} \pm 0.0$	$1.39 \times 10^{-9} \pm 0.0$	1.42×10^{-4}	2.37×10^{-6}	1.25×10^{-4}	1.11×10^{-5}	4.1
150	$3.37 \times 10^{-10} \pm 0.0$	$1.39 \times 10^{-9} \pm 0.0$	1.42×10^{-4}	2.37×10^{-6}	1.25×10^{-4}	1.11×10^{-5}	4.1
160	$2.455 \times 10^{-9} \pm 1.82 \times 10^{-9}$	$2.976 \times 10^{-9} \pm 9.48 \times 10^{-10}$	1.49×10^{-4}	1.65×10^{-5}	1.52×10^{-4}	1.96×10^{-5}	1.6

affect the solubility of O_2 to a greater extent than CO_2, resulting in a larger increase in O_2 permeability.

The changes in gas permeability resulting from the different processing temperatures, especially for O_2 permeability coefficients, resulted in a decrease in the CO_2/O_2 permselectivity of the ionomer from 4.1 (formation temperature = 120–150°C) to 1.6 (formation temperature = 160°C). Whatever the mechanism, this decrease in permselectivity could substantially improve the usefulness of ionomers for extending the shelf life of packaged respiring produce.[12]

Gas permeability is restricted by the PE crystal structure and by the ionic clusters, which act as crosslinks in the ionomer. Our data suggest that there is a temperature for ethylene ionomers at which the morphology of the ionomers can be altered. The heat treatment of the ionomers at 160°C increased gas permeability (especially for O_2) and reduced the CO_2/O_2 permselectivity. Such changes in the permeability characteristics of ionomers can be explained by a reduction in the PE crystallinity and the destruction of the ionic clusters into smaller, dispersed aggregates. This result is also supported by the DSC study discussed previously.

CONCLUSIONS

Because of the chemical and morphological nature of the ethylene ionomers, thermal treatments can alter ionic and crystal domains, which, in turn, affect the gas permeability. Changing the gas permeability and permselectivity could be useful for modifying polymeric materials. This work has shown that the heat treatment of ethylene–methacrylic ionomers has promising applications for changing gas permeability and especially CO_2/O_2 permselectivity.

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