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Effect of molecular weight and annealing temperature on the oxygen barrier properties of oriented PET film

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SUMMARY

The influence of molecular weight and annealing, or heat setting, temperature on the crystallinity and subsequent resistance to oxygen permeability was evaluated for biaxially oriented films of poly(ethylene terephthalate). Within the range investigated, molecular weight affected the amount of crystallinity developed at a given temperature, yet had little influence on oxygen permeability. Annealing temperature more directly influenced permeability than did the absolute amount of crystallinity.

INTRODUCTION

Resistance to gas transport is an important property for many polymer film applications in the packaging industry. A good barrier polymer must have the following attributes (1): polarity such as found in the nitrile, halogen, acrylic or ester groups; high chain stiffness; inertness; close chain packing via symmetry; crystallinity and/or orientation; intermolecular bonding or attraction; and a high glass transition temperature. Poly(ethylene terephthalate), PET, is a thermoplastic polyester which incorporates, to a reasonable extent, all of these attributes, when it is processed in a manner which imparts orientation and crystallinity to its molecular structure (2). It has emerged as a container material of major importance, and its oxygen/nitrogen gas barrier properties have been widely investigated (3-7). Although it is generally recognized that increasing polymer crystallinity reduces gas permeability, the effects of heat setting temperature and molecular weight on the crystallinity, and subsequent resistance to permeability, have not been fully investigated.

EXPERIMENTAL

The films evaluated in this study were cut from the label panel sidewalls of 2-liter PET carbonated beverage bottles. Intrinsic viscosities (IV) of the samples were 0.72, 0.80 and 1.04, corresponding to number average molecular weights of ca. 24,000, 28,000 and 42,000, respectively (8). This covers the usual range of molecular weights used in the beverage bottle industry. The total area stretch ratio of each sample was 11.3, calculated from distention of a grid pattern scribed on the bottle preform prior to blow molding.

Samples were annealed under constraint (heat set) by being clamped in an annealing jig consisting of two four-inch-square aluminum plates which had a 3-inch diameter "window area" bored in each. The clamped samples were then placed between preheated press platens for 15 minutes at each annealing temperature. Platen separation was one inch.

Sample crystallinity was determined from density measurements taken on discs punched from the "window area" with a paper punch. The discs were immersed in a potassium iodide solution gradient column and Bunn's data (9) for PET unit cell density was used in the calculations.

Permeability data was gathered on a MoCon OxTran 10/50 instrument yielding values for oxygen permeability of the heat set and control samples. Measurements were made at 30°C, expressed as cubic centimeters of gas transmitted through 100 sq. in. of barrier per day at a pressure differential of one atmosphere and a thickness of one mil (cc-mil/100 sq. in.-day-atm.). These units are in common use and enjoy reasonably wide recognition (10).

RESULTS AND DISCUSSION

Figure 1 shows the effect of annealing (heat setting) temperature and molecular weight on the oxygen permeability of bottle sidewalls (units specified above). The three IVs are shown. Although there is scatter in the data, the trend is clear. Oxygen permeability decreases with increasing annealing temperature in an essentially linear fashion. For a given heat setting temperature, the highest molecular weight sidewall is poorest as an oxygen barrier, whereas the other two samples exhibit negligible differences in permeability between them. In the molecular weight range examined herein, one expects less facile rearrangement of morphology and slower crystallization rates, at a given temperature, for the higher molecular weight material. This chain entanglement-related effect would explain the weaker response to annealing.

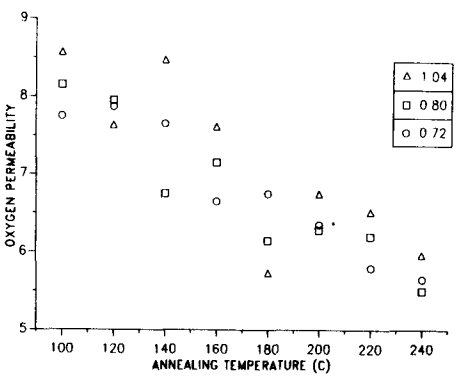

FIGURE 1: EFFECT OF ANNEALING TEMPERATURE ON THE OXYGEN PERMEABILITY OF ORIENTED PET FILM---POLYMER IV AS SHOWN

The effect of annealing temperature on crystallinity is shown in Figure 2 for each molecular weight (IV). As expected, the lower molecular weight (0.72 IV) sidewall samples generally crystallize to a greater extent at any given temperature. The curves are sigmoidal in shape, suggesting an annealing temperature range (120-160°C) wherein morphological reorganization is less efficient. On either side of this range, crystallinity increases an average of 2 percent for every 10 degree increase in annealing temperature.

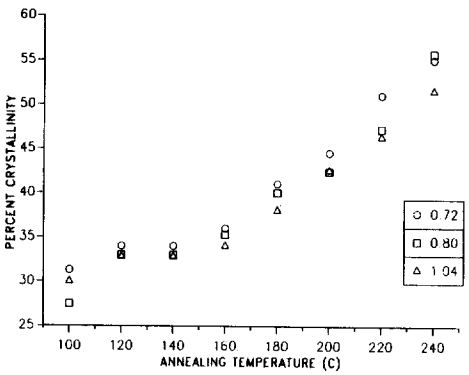

FIGURE 2: EFFECT OF ANNEALING TEMPERATURE ON THE CRYSTALLINITY OF ORIENTED PET FILM ---POLYMER IV AS SHOWN

Figure 3 combines the first two Figures to show the effect of crystallinity on oxygen permeability. There is a clear trend toward lower permeability with increasing crystallinity, but it may not be monotonic in nature. In the vicinity of 35 to 40 percent crystallinity, there appears to be a minimum in oxygen permeability for this system. This apparent discontinuity may be due to reorganization of unstable crystal forms, and/or a difference in the crystallization kinetics in this region.

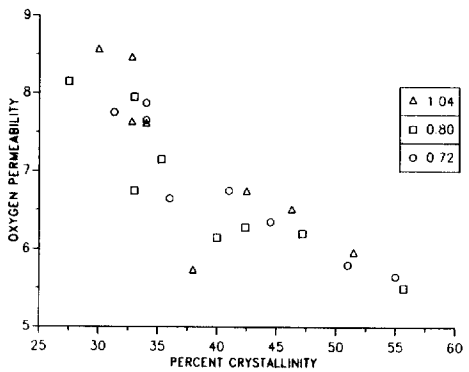

FIGURE 3: EFFECT OF CRYSTALLINITY ON OXYGEN PERMEABILITY OF ORIENTED PET FILM---POLYMER IV AS SHOWN

Figure 4 depicts the average values of the Figure 1 data, in order to show the permeability vs annealing temperature relationship independently of molecular weight effects. Units are the same as Figure 1. The linear regression curve fits the data well (correlation coefficient = -0.997), with the exception of the value at 180°.

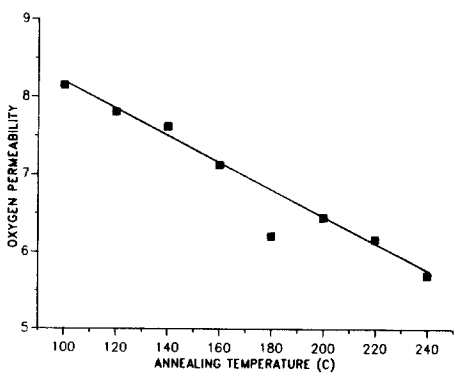

FIGURE 4: EFFECT OF ANNEALING TEMPERATURE ON THE OXYGEN PERMEABILITY OF ORIENTED PET FILM (AVERAGE VALUES)

This value at 180° corresponds to the low permeability value observed at 35-40 percent crystallinity.

Figure 5 is a plot of the percent crystallinity averaged over all IVs, plotted against annealing temperature. The sigmoidal shape of Figure 2 is again apparent, and there is no deviation at 180°. This suggests that the drop in permeability shown in Figure 4, at 180°, is related to something other than the total amount of crystallinity in the sample.

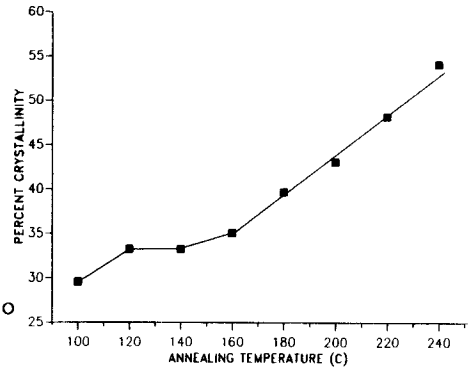

FIGURE 5: EFFECT OF ANNEALING TEMPERATURE ON THE CRYSTALLINITY OF ORIENTED PET FILM (AVERAGE VALUES)

Finally, Figure 6 is a plot of the average oxygen permeability versus percent crystallinity, for all IVs. Neglecting values at 36 38 and 40 percent, the linear regression curve fits reasonably well (correlation coefficient = -0.969). The low permeability values correspond to the low values previously seen at the 180° annealing temperature. This indicates that the morphology obtained at this annealing temperature results in greater resistance to oxygen permeation than that expected from crystallinity alone.

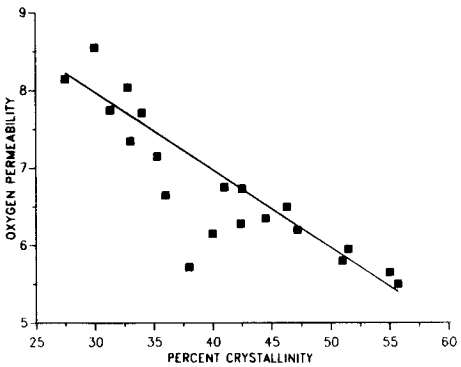

FIGURE 6: EFFECT OF CRYSTALLINITY ON OXYGEN PERMEABILITY OF ORIENTED PET FILM---ALL IVs REPRESENTED

CONCLUSIONS

According to Peterlin (11), annealing lets the crystals grow in thickness, removes crystal defects, sharpens the boundaries between crystalline and amorphous components, and relaxes taut tie molecules. These factors partially explain the observed behavior, since permeability occurs via the combination of solubility and diffusion, and these can take place only in the amorphous regions. This is why oxygen permeability through oriented PET film generally decreases with increasing film crystallinity. In the present case,

however, there is an annealing temperature range in the vicinity of 180°C wherein permeability decreases disproportionately to the amount of crystallinity, suggesting a morphology differing from that encountered outside this range. It is known that the maximum crystallization rate for PET occurs at ca. 180° (12), but the nature of the morphology created therein has not yet been elucidated. It is possible that the high nucleation and crystal growth rate at that temperature minimizes void formation and increases film density. Consequently, the crystallites could act as crosslinking agents gripping the polymer chains and restricting the segmental motions involved in the diffusion process. As pointed out in an early work by Szwarc et al. (13), this would reduce the probability of hole formation and lead to a decreased entropy of activation for diffusion.

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