Polymer Vol. 36 No. 22, pp. 4345-4346, 1995

0032-3861/95/$10.00+0.00

Discussion about the use of relative values of permeabilities between two gases for high molecular weight polymers

Fan Guisheng
Department of Food Engineering, Inner Mongolia Agriculture and Animal Husbandry College, Xin Jian Dong Jian 5, 010018 Huhhot, P. R. China

and L. Incarnato, L. Di Maio and D. Acierno*
Department of Chemical and Food Engineering, University of Salerno, Via Ponte Don Melillo, 84084 Fisciano (SA), Italy

Permeability measurements were performed on several polymeric films used for packaging applications. The results were analysed in terms of the ratio of the permeabilities between two gases. Moreover, recent experimental results and data reported in the literature have been compared with a simple relationship reported by van Krevelen for predicting the transport properties of high molecular weight polymers. Finally, a suggestion is made for improving the accuracy of the prediction of the permeabilities for high molecular weight polymers.

(Keywords: permeability; films; high molecular weight polymer)

Introduction

Transport properties play an important role in many technological applications of polymers. Barrier plastics are widely used in food, beverage and other protective packaging applications, consequently the prediction of gas transport properties of polymeric films is of great importance. Several calculation methods[1-3] have been developed for predicting the permeability of polymers, and the accuracy of these methods depends mainly on the accuracy of the relationship and data reported in the literature.

Van Krevelen[1] has reviewed the existing prediction theories and their applications. In particular, supported by the data of Stannet and Szwarc[4], Rogers *et al.*[5] and Frish[6], Van Krevelen claims that the permeability ratio between two gases through a series of thin polymeric films is constant. Van Krevelen[1] reports that, taking nitrogen as the standard gas, it is possible to calculate the permeabilities of the other gases by a simple factor. The accuracy of the relative value, therefore, directly determines the accuracy of the permeability estimation with respect to a single gas for a polymer.

In this work we have determined the ratios of permeability between CO_2 and N_2 and between O_2 and N_2 through a series of polymers. We have taken nitrogen as the standard gas to compare our results and some data reported in the literature[7] with those given by van Krevelen[1].

Our experimental data show that the relative values of permeability, i.e. the ratios of permeability between two gases, in some cases represent a very dispersive property depending on the materials and gases analysed. Such results suggest that great care is needed in using the proposed unique relative value for all polymers to estimate the permeabilities of a polymer for different gases.

* To whom correspondence should be addressed

Experimental

Permeability tests were carried out by means of a quasi-isostatic apparatus (Lyssy, model GPM 200). The simulative penetrant used was a gas mixture which is equally formulated with carbon dioxide (CO_2), oxygen (O_2) and nitrogen (N_2) (1:1:1).

In order to check the relationship between the permeabilities for two gases through a series of polymers, permeability measurements on different polymeric films were performed at 30°C. We analysed materials commonly used in packaging applications: low density polyethylene (LDPE) film, high density polyethylene (HDPE) film, linear low density polyethylene (LLDPE) film, polypropylene (PP) film, polystyrene (PS) thin sheet, nylon film and polyester film. The films analysed were conditioned in a dry ambient atmosphere prior to any measurement.

Results and discussion

In *Table 1* the average values of permeabilities of the analysed film are reported.

In order to make a comparison of the relative values of permeabilities between two gases from our experiments with literature data, we have taken N_2 as the standard gas. The relative values of permeabilities of other gases calculated from our experiments are shown in *Table 2*.

Van Krevelen[1] suggests that the relative values of permeabilities between two gases through a series of polymers is constant, and consequently reports the relative values of permeability to be 24 for CO_2 to N_2, and 3.8 for O_2 to N_2, for all polymers. Comparing these two relative values with those obtained from our experiments in *Table 2* and with other experimental

Table 1 Values of permeabilities [ml cm/(s cm^2 Pa)] from our experiments

Material	N_2	O_2	CO_2
PS	5.32×10^{-14}	1.37×10^{-13}	5.52×10^{-13}
LLDPE	6.58×10^{-14}	2.01×10^{-13}	7.30×10^{-13}
LDPE	9.36×10^{-14}	2.88×10^{-13}	1.00×10^{-12}
PP	4.00×10^{-14}	1.71×10^{-13}	5.44×10^{-13}
Nylon 6	7.88×10^{-16}	2.70×10^{-15}	1.45×10^{-14}
PET^a	1.65×10^{-15}	5.92×10^{-15}	2.93×10^{-14}
HDPE	2.30×10^{-14}	7.46×10^{-14}	2.74×10^{-13}

^{a} Poly(ethylene terephthalate)

Table 2 Relative values of permeabilities

Material	N_2	O_2	CO_2
Polystyrene sheet	1	2.6	10.4
LLDPE film	1	3.1	11.1
LDPE film	1	3.1	10.7
PP film	1	4.3	13.6
Nylon 6 film	1	3.4	18.4
PET film	1	3.6	17.8
HDPE film	1	3.2	11.9

data reported in the literature[7], the relative value of 24 for many polymers is very different from the experimental results. For the materials analysed in this work, such values range from 10.4 to 18.4. From such results it appears that for the relative value of permeability of CO_2 to N_2 the simple relationship given by Van Krevelen is far from representing the real value for all polymers. This implies that it would cause a great error for many polymers if the prediction of permeability for CO_2 were based on the unique relative value reported by Van Krevelen. Concerning the relative value of 3.8 for O_2 to N_2 reported by Van Krevelen, it falls in the range of the corresponding values reported in *Table 2*, showing that in this case a good agreement exists between our experimental results and data reported in the literature[7] and those reported by Van Krevelen.

Concluding remarks

The results obtained in this work and the data reported in the literature[7] have shown that Van Krevelen's statement[1] that a simple relationship exists between the permeabilities for two gases through a series of polymers is not applicable to all polymers.

In particular, according to the experimental results the relative value of permeability of CO_2 to N_2 is not a constant but is strictly correlated to the polymeric materials and the gases analysed. Our experiments suggest that for such materials as PP, LDPE, HDPE and PS, such a ratio is closer to 12, while for nylon and PET a suitable value is 18.

On the other hand, the relative value of permeability of O_2 to N_2 reported in the literature[1] is close to that obtained in our experimental results and data reported in the literature[7]. Such results indicate that a simple relationship between the permeabilities of O_2 and N_2 through a series of polymers can be defined with more accuracy.

We consider that the statement that the relative value of permeability for a pair of gases over a series of polymers is relatively constant is not always true for all pairs of gases, or at least, it is too general to describe the relationship of the permeabilities between CO_2 and N_2. It would cause a great error if the unique recommended relative value through a series of polymers were used to estimate the permeability of CO_2 for a given polymer. Hence it loses its practical sense. Regarding the permeability relationship between O_2 and N_2, the above conclusion is fairly true. By using a unique recommended constant which represents the relative value of permeabilities between O_2 and N_2 over a series of polymers, one can gain a reasonably accurate estimate of the permeability for O_2. Our research suggests that it is better to choose a relative value of permeabilities in the range from 10 to 30, in accordance with the barrier nature of the polymer, when predicting the permeability for CO_2. The greater the barrier nature, the higher the value that should be taken.

Acknowledgement

This research was financially supported by the National Research Council of Italy, Special Project RAISA, sub project no. 4. Paper no. 2334.

References

1 Van Krevelen, D. W. 'Polymer Properties', Elsevier, Amsterdam, 1990, p. 555
2 Salame, M. *Polym. Eng. Sci.* 1986, **26**, 1543
3 Bircerano, J. 'Prediction of Polymer Properties', Marcel Dekker, New York, 1993, p. 318
4 Stannet, V. and Szwarc, M. *J. Polym. Sci.* 1955, **16**, 89
5 Rogers, C. E., Meyer, J. A., Stannett, V. and Szwarc, M. *Tappi* 1956, **39**, 741
6 Frish, H.L. *Polym. Lett.* 1963, **1**, 581
7 Comyn, J. (Ed.) 'Polymer Permeability', Elsevier, London, 1985