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Influence of structure and chemical composition on oxygen permeability of crosslinked epoxy–amine coatings

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Abstract

The oxygen barrier properties of a series of coatings based on diglycidyl ethers of bisphenol and butanediol reacted with a wide range of amines in different stoichiometric ratios have been investigated. The oxygen permeability was analysed with respect to the molecular structure in general and the concentration of polar functional groups in particular. The results showed that formulations based on aliphatic amines gave good barrier performance, that coatings prepared from aromatic and cyclo-aliphatic amines yielded intermediate barrier properties, and that polyether amine formulations produced very poor barriers. It was also observed that pendant methyl groups had a strong detrimental effect on barrier properties and that using an excess of amine monomer significantly improved the barrier performance. Attempts at predicting the oxygen permeability from physical and chemical characteristics of the coatings showed that the glass transition temperature could not be correlated with the permeability. However, it was found that a polarity index, calculated as the sum of the concentrations of hydroxyl and amine moieties weighted by their individual cohesive energy density, was a good predictor of oxygen permeability for all types of formulations. © 2002 Published by Elsevier Science Ltd.

Keywords: Epoxy coatings; Barrier properties; Cohesive energy density

1. Introduction

Polymer-based flexible packaging materials provide a very efficient way to tailor-make packages for food products in terms of performance, economics and environment. In order to meet the different requirements regarding mechanical properties, barrier performance, scalability and cost efficiency, a flexible packaging film is generally composed of several layers, each with a specific function. In many cases the layer imparting the barrier is the most critical and represents the highest fraction of the total cost of the laminate [1]. Ideally, the barrier layer should have a low permeability to water vapour and oxygen while being flexible, mechanically resistant, transparent and of low cost. In general, the barrier against oxygen is the most difficult to achieve. Although a number of barrier technologies have been developed they all have their limitations and there is still a demand for new solutions [1].

Crosslinked coatings based on epoxy–amine chemistry are interesting candidates for use as barrier layers. These materials are known for their chemical stability, good adhesion and attractive optical properties, and are used in a wide range of applications. The coatings are mechanically flexible and resistant to water, and they can be applied by a simple roll or spray coating operation. This opens the way for introducing the barrier layer as part of a standard printing or coating operation during packaging manufacture. Alternatively, the materials could be employed as adhesive layers between films in a laminate. As regards barrier properties, it has been shown that linear, thermoplastic polymers based on epoxy and amine compounds can have very low permeability to oxygen [2–4], and poly-(hydroxy amino ethers) for use as barrier layers in packaging applications have been developed [2,5]. Certain crosslinked epoxy–amine coatings also exhibit low oxygen permeability [6–9], and such coatings are being introduced to improve the oxygen barrier of poly(ethylene terephthalate) containers [10,11].

In order to utilise the full potential of crosslinked epoxy–amine coatings as barrier materials and extend the use

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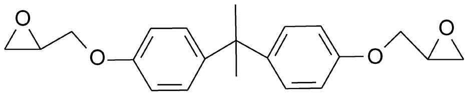
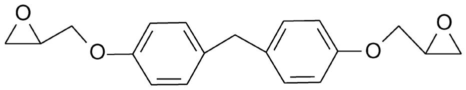
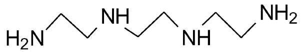
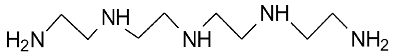
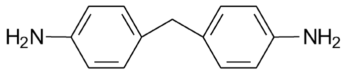
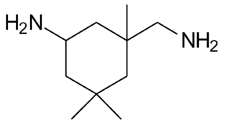
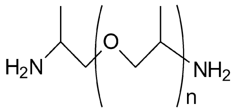
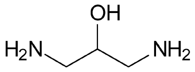
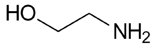
Table 1
Chemical structure of the monomers

Name	Structure
Diglycidyl ether of bisphenol A (DGEBA)	
Diglycidyl ether of bisphenol F (DGEBF)	
Diglycidyl ether of butanediol (DGEBD)	
Triethylene tetramine (TETA)	
Tetraethylene pentamine (TEPA)	
Bis-(4-aminophenyl)methane (MDA)	
Hexamethylene diamine	
Isophorone diamine	
Jeffamine (D230, *n* = 2.6, D400, *n* = 5.6)	
Diamino propanol	
Ethanol amine	

beyond current applications, a fundamental understanding of the relationship between chemical structure and barrier performance is required. However, to date no systematic studies have been published and information is available only through the patent literature. Unsurprisingly, patents describe a wide range of coatings prepared from a number of different amines and epoxies. The examples mention epoxy resins based on the diglycidyl ethers of 2,2′-bis(4-hydroxyphenyl)propane (bisphenol A), bis(4-hydroxyphenyl)-methane (bisphenol F) and butanediol, reacted with amines such as triethylene tetramine and tetraethylene pentamine [6–8]. It is stated that the barrier properties improve when the concentration of amine nitrogen and of hydroxyl groups is increased, and that coatings prepared with an excess of amine generally show better barrier performance. It is also mentioned that the presence of pendent methyl groups, such as in bisphenol A compared to bisphenol F, is detrimental to the barrier properties.

Examination of the literature available on linear aromatic poly(hydroxy ethers) and poly(hydroxy amino ethers) gives some further indications on the structure barrier property relationship for this type of compounds. Work reported by White et al. [12] and Silvis [2] on these polymers has shown that the oxygen permeability strongly depends on the type and substitution of the aromatic moieties in the polymer chain. Phenyl groups give better barrier properties than biphenyl groups, and changing from a *para*- to a *meta*-substituted phenyl yields a significant improvement in barrier performance. For biphenyl groups, a detrimental effect of pendant methyl groups is again observed. It is shown that although the lowest oxygen permeability is obtained with amines present in the polymer, good barrier properties can be achieved also without amine functionality. Only *tertiary* amine groups are considered. Furthermore, it is seen that adding pendant hydroxyl groups strongly improves the barrier properties.

Although somewhat different in composition, aromatic poly(hydroxy amide ethers) may also provide useful insights. Work on these polymers by Brennan et al., has shown that the chemical moieties present, as well as the configuration of the polymer backbone, have an influence on the barrier properties [13,14]. High barrier is favoured by

Table 2
Composition of the prepared coatings

Number	Epoxy resin	Amine	Stoichiometric ratio, amine to epoxy	Total N conc. (wt%)	OH conc. (wt%)
1	DGEBF	TEPA	1	5.5	9.2
2	DGEBF	TEPA	3	12.7	7.2
3	DGEBF	TETA	1	5.2	9.5
4	DGEBF	Hexamethylene diamine	1	3.8	9.1
5	DGEBF	Isophorone diamine	1	3.5	8.5
6	DGEBF	Jeffamine D 230	1	3.3	8.0
7	DGEBF	Jeffamine D 400	1	2.7	6.7
8	DGEBF	MDA	1	3.4	8.3
9	DGEBF	50% Jeffamine D 400, 50% TETA	1	3.0	6.4
10	DGEBF	50% TETA, 50% diamino propanol	1	4.3	10.0
11	DGEBF	50% MDA, 50% diamino propanol	1	3.6	10.0
12	DGEBF	50% MDA, 50% ethanol amine	1	3.6	10.8
13	DGEBF	50% TEPA, 50% diamino propanol	3	11.1	10.2
14	DGEBF	50% TEPA, 50% ethanol amine	3	10.5	12.3
15	DGEBA	TEPA	1	5.1	8.6
16	DGEBA	TEPA	3	12.0	6.8
17	DGEBA	TETA	3	11.5	7.0
18	DGEBA	MDA	1	3.2	7.8
19	DGEBD	TETA	1	7.4	13.6
20	50% DGEBD 50% DGEBF	TETA	1	6.1	11.2

a tight packing of the polymer, which in turn depends on the compactness and hydrogen bonding capacity of the structures present [13]. The main factors were seen to be the *meta*- or *para*-substitution of the phenylene units and the concentration of amide and hydroxyl groups. It was observed that amide groups should be separated by as few non-polar units as possible, but that at least one spacer unit was required for optimum barrier. It was also found that adding OH groups in close proximity to amide groups did not improve barrier performance, presumably because the OH and amide units form one single hydrogen-bonding site rather than different sites [14]. The type of amide groups present, i.e. primary, secondary or tertiary, also influences barrier properties, with increasing N-alkylation reducing the barrier performance due to diminished hydrogen bonding.

Although the work cited above gives some indications as to what governs the relationship between structure and oxygen permeability for crosslinked epoxy–amine coatings, several questions remain unanswered. For instance, the understanding of the influence of structure, e.g. aliphatic versus aromatic, linear versus branched or cyclic, on barrier properties is limited. It is also not known to what extent the oxygen permeability is dominated by the presence and amount of polar groups, e.g. ether, amine and hydroxyl moieties, or if some of the groups are more important than others. On a more general level, it would also be desirable to be able to relate the oxygen permeability to one or a few structural, chemical or physical parameters of the polymer.

In the present work, a series of coatings based on diglycidyl ethers of bisphenol A, bisphenol F and butanediol reacted with a wide range of amines in different stoichiometric ratios have been prepared. The oxygen permeability of the coatings has been determined and the data are discussed with respect to the structure in general and concentration of polar functional groups in particular. The optical and mechanical properties of the coatings are also briefly examined.

2. Experimental

2.1. Materials

Epoxy resin GY 285, diglycidyl ether of bisphenol F (DGEBF) was obtained from Vantico (formerly Ciba SC), Switzerland. DER 330 epoxy resin, a diglycidyl ether of bisphenol A (DGEBA), was obtained from Dow Chemical. Two aliphatic poly(ether amines) (Jeffamine D230 and D400) were obtained form Huntsman Chemical, US. Diglycidyl ether of butanediol (DGEBD), triethylene tetramine (TETA), tetraethylene pentamine (TEPA), 2-aminoethanol, 1,3-diamino-2-propanol, hexamethylene diamine and bis-(4-aminophenyl)methane (MDA) were all purchased from Aldrich, Switzerland. The monomers are presented in Table 1. Silicone surface additive BYK 310, a polyester modified dimethyl polysiloxane, was received from BYK Chemie, Germany. All chemicals were used as received.

The substrate material, polyethylene terephthalate (Melinex 813, 12 μm thickness, produced by DuPont) was supplied by Alcan Packaging Services, Switzerland.

2.2. Sample preparation

A number of formulations were prepared and evaluated. They are listed in Table 2. The epoxy resin and the amine

Table 3
Glass transition temperature of the different formulations and thickness of the coatings analysed for oxygen permeability. The reported values are for the thickest and thinnest sample of each coating formulation

Number	Composition	Glass transition temperature (°C)	Coating thickness (max and min of 4) (μm)
1	DGEBF + TEPA	98	32 ± 4–40 ± 4
2	DGEBF + TEPA ($r = 3$)[a]	37	28 ± 5–36 ± 4
3	DGEBF + TETA	100	24 ± 5–34 ± 5
4	DGEBF + hexamethylene diamine	57	23 ± 4–39 ± 4
5	DGEBF + isophorone diamine	98	24 ± 2–28 ± 4
6	DGEBF + Jeffamine D 230	51	40 ± 5–160 ± 5
7	DGEBF + Jeffamine D 400	30	34 ± 4–110 ± 5
8	DGEBF + MDA	110	39 ± 5–80 ± 5
9	DGEBF + Jeffamine D 400 + TETA	50	34 ± 4–54 ± 4
10	DGEBF + TETA + diamino propanol	100	26 ± 3–32 ± 4
11	DGEBF + MDA + diamino propanol	97	28 ± 4–38 ± 5
12	DGEBF + MDA + ethanol amine	68	27 ± 3–31 ± 2
13	DGEBF + TEPA + diamino propanol ($r = 3$)[a]	43	20 ± 2–24 ± 2
14	DGEBF + TEPA + ethanol amine ($r = 3$)[a]	35	25 ± 3–29 ± 3
15	DGEBA + TEPA	108	28 ± 5–38 ± 3
16	DGEBA + TEPA ($r = 3$)[a]	46	27 ± 3–35 ± 4
17	DGEBA + TETA ($r = 3$)[a]	45	25 ± 2–29 ± 3
18	DGEBA + MDA	115	63 ± 3–73 ± 3
19	DGEBD + TETA	75	33 ± 4–43 ± 4
20	DGEBD + DGEBF + TETA	54	39 ± 3–49 ± 5

[a] Stoichiometric ratio amine to epoxy of 3:1.

used were mixed together at the calculated stoichiometric ratio, r, equal to a/e (amino hydrogen over epoxy), and 0.15% surface additive was added. For the solid amines the mixing was carried out under heating whereas the mixtures with liquid amines were prepared at room temperature. The mixture was stirred and then de-gassed under vacuum to remove bubbles. To prepare the coatings, the PET substrate was first fixed on a glass plate to obtain a smooth surface. The formulation was then applied on this substrate with a bar coater. The wet thickness of the coating was about 60 μm. After application, the coating was cured at 100 °C for 100 min.

2.3. Analysis

The coatings were analysed with differential scanning calorimetry (DSC) using a Perkin Elmer DSC 7. The samples (coating on substrate) were heated from 0 to 200 °C at a heating rate of 10 °C/min. The glass transition point was determined as the inflexion point of the curve showing the heat flow as a function of temperature. The heating curves were also checked for the presence of a residual exotherm.

The oxygen transmission rate was measured with a Mocon Oxtran 2/20 at 23 °C and 50% relative humidity. The coated substrates were placed in a foil mask which gave a sample area of 5 cm^2. The coated side was oriented towards the O_2 side. Data was collected until a constant value of transmission rate was obtained (steady-state conditions). No attempt was made to determine the absorption and desorption profiles. Four samples of each coating formulation were measured. The permeability coefficient for each sample was calculated using the following relationship [15]

$$\frac{1}{T_R} = \frac{L_S}{P_S} + \frac{L_C}{P_C} \tag{1}$$

where T_R is the transmission rate of the coated substrate, L_S and P_S the thickness and permeability coefficient of the substrate and L_C and P_C the thickness and permeability coefficient of the coating sample. The permeability coefficient for each coating formulation was taken as the average of the results from the individual samples.

Measurement of the film thickness was performed using a Minitest 600 coating thickness gauge from Erichsen, Germany. Ten different spots were measured from which a mean value was calculated. The thickness was determined individually for each sample subjected to measurement of oxygen transmission rate.

The mechanical properties and adhesion of the coatings was evaluated qualitatively by flexing and wrinkling the coated substrates and visually observing the behaviour of the coating. The colour, gloss and clarity of the coatings was also evaluated by visual inspection.

3. Results and discussion

3.1. Coating characteristics

The glass transition temperature of the different cured formulations was measured and the results are presented in Table 3. As can be seen the transition temperatures varied quite widely, from 30 to 115 °C. It can be noted that all formulations with the possible exception of

7 (DGEBF + Jeffamine D 400) are in the glassy state. During heating in the DSC, no residual exotherm could be detected. This indicates that all coatings were fully cured. However, the limited sensitivity of the DSC technique with respect to small residual exotherms should be kept in mind. It is worth noting that the ultimate glass transition temperatures of the formulations based on MDA (8 and 18) are above 150 °C [16], which means that these formulations cannot be completely cured at 100 °C. Nevertheless, the DSC results still show that the residual reactivity is limited. The thickness of the samples for permeability measurement is presented in Table 3. The results are given as maximum and minimum thickness for the samples from each formulation together with the standard deviation for the respective measurements. As can be seen, the standard deviation for each individual coating was 5 μm or less, indicating that all coatings were quite even.

Manual flexing showed that all coatings had fair to excellent flexibility and adhesion to the substrate. It was seen that the coatings with the highest glass transition temperatures showed the lowest flexibility. The optical characteristics were checked visually, and it was seen that all coatings were transparent and uncoloured. However, it was observed that the coatings prepared from a combination of amines in many cases were slightly more hazy than the other formulations. This is believed to be due to limited miscibility of some of the amines.

3.2. Influence of monomer structure and stoichiometry on oxygen permeability

In order to examine the influence of the structure of the epoxy resin on coating permeability, coatings were prepared using DGEBF, DGEBA and DGEBD together with aliphatic amines (TEPA and TETA). The results are shown in Table 4. As can be seen, the permeability of coatings prepared from DGEBF with TEPA (formulation 1) is a less than half of that of coatings made from DGEBA and TEPA (formulation 15). A similar permeability reduction (60%) when changing from DGEBA to DGEBF was observed for the MDA aromatic amine (data not shown). The only difference between DGEBA and DGEBF is the pendent methyl groups on the central carbon atom. This effect of the pendent methyl groups as such is expected and has been reported for both linear and crosslinked systems by others. However, the differences reported in the literature were only of the order of 30% [2].

The data in Table 4 also shows that the coatings prepared with DGEBD have much higher permeability than those prepared with DGEBF (formulation 19 versus formulation 3). However, if a mixture of DGEBF and DGEBD is used (formulation 19), the barrier properties become comparable to or better than those of the pure DGEBF formulations. Here it should be noted that formulation 19, prepared from DGEBD and TETA, had a very low viscosity which meant that it was difficult to prepare good, even coatings. In spite of the care taken to avoid defects, it is therefore, possible that the coatings contained imperfections. The high standard deviation in permeability for this formulation also points in this direction. The presence of defects could be one reason why these coatings exhibit so high permeability. Why a mixture of the two epoxies produces coatings with such low permeability is not fully understood. However, similar observations, but without any data on barrier performance, have been qualitatively described in the patent literature and attributed to increased packing efficiency of the polymer backbone [17]. It could be that the difference in reactivity between DGEBF and DGEBD, where the DGEBF epoxy groups will react before those of the DGEBD, results in a particular network structure which somehow improves properties. Further work, e.g. on mixtures with different ratios of DGEBF to DGEBD and involving analysis of the network structure, will be required to explain this behaviour.

The oxygen permeability of a series of coatings prepared from DGEBF with different amines is presented in Table 5. The results show that the formulations based on linear aliphatic amines yield the lowest permeability, that the aromatic amine gives intermediate properties, and that polyether amines produce coatings with very high permeability. For the aliphatic amines, it can be seen that the permeability increases as the number of amine functionalities decreases. This will be further discussed below. It can also be seen that a cyclo-aliphatic amine structure gives coatings with much higher permeability than the linear structures. This can presumably be explained by the higher free volume brought by the cyclic moieties in combination with the detrimental effect of the pendent methyl groups. The reason why the polyether amines yield coatings with such a high permeability is not fully understood. One possible explanation is the presence of a number of pendent methyl groups in the structure. As regards the barrier properties of poly(hydroxy ethers) in general, they are otherwise expected to have a low permeability to oxygen [12]. The very high values for the formulation with Jeffamine D400 (formulation 7) might be due to it being close to its rubbery state (see the glass transition temperature in Table 3), but the value for the D230 formulation 6 is also high in spite of its glassy nature. It should be noted that the high standard deviation in the permeability data suggests that the quality of the prepared coatings might be uneven. However, no defects were seen in the coatings. Another possibility is that the high thickness of some of the samples of formulations 6 and 7 could have produced erroneous permeability results. However, it is reminded that it was ensured that all data was obtained under steady-state conditions. Furthermore, any error in this respect would lead to an under-estimation of the permeability coefficients and could thus not explain the high values obtained. Further work will be required to fully explain these observations.

The data in Table 5 also show what happens when hydroxy-functional amines are added to the formulations. It

Table 4
Influence of epoxy composition on oxygen permeability at 23 °C and 50% RH (cm^3 μm/m^2 24 h atm)

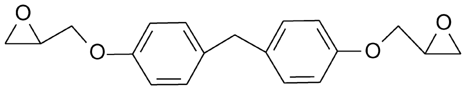
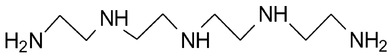
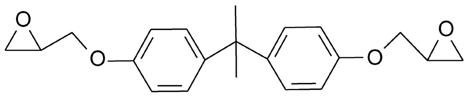
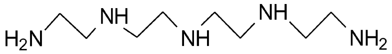
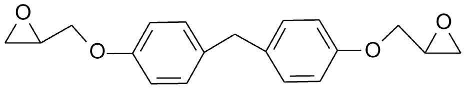
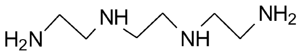
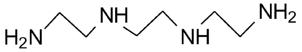
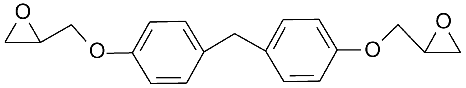
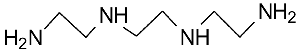
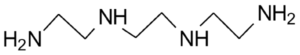
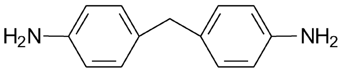
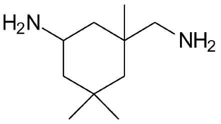
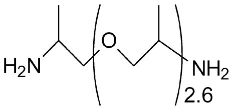
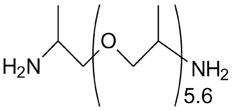
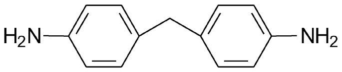
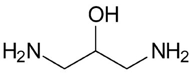
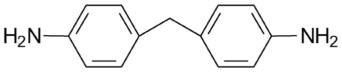
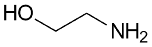
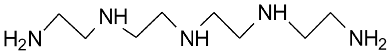
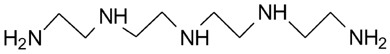
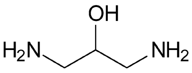
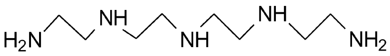
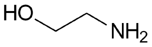
Formulation number	Coating composition	Epoxy structure	Amine structure	Oxygen permeability
1	DGEBF + TEPA			340 ± 30
15	DGEBA + TEPA			780 ± 60
3	DGEBF + TETA			230 ± 20
19	DGEBD + TETA			1300 ± 600
20	DGEBF + DGEBD + TETA	 		180 ± 30

Table 5
Influence of amine composition and stoichiometric ratio on oxygen permeability at 23 °C and 50% RH (cm^3 μm/m^2 24 h atm) of coatings prepared with DGEBF

Formulation number	Coating composition	Amine structure	Oxygen permeability
3	DGEBF + TETA		230 ± 20
4	DGEBF + hexamethylene diamine		450 ± 70
8	DGEBF + MDA		620 ± 80
5	DGEBF + isophorone diamine		1400 ± 200
6	DGEBF + Jeffamine D 230		2000 ± 800
7	DGEBF + Jeffamine D 400		4700 ± 2000
11	DGEBF + MDA + diamino propanol	 	440 ± 40
12	DGEBF + MDA + ethanolamine	 	470 ± 70
2	DGEBF + TEPA, $r = 3$		170 ± 20
13	DGEBF + TEPA + diamino propanol, $r = 3$	 	190 ± 20
14	DGEBF + TEPA + ethanolamine, $r = 3$	 	150 ± 20

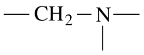
can thus be seen that for the case of the aromatic amine, addition of hydroxy-functional amines yields a reduction in permeability. For the linear aliphatic polyamines, however, there is virtually no change in barrier performance when hydroxy-functional amines are added.

As regards the stoichiometric ratio, Table 6 shows that increasing the amount of amine with respect to the epoxy gives a pronounced reduction in permeability (compare the data in Table 5 with the values for the balanced DGEBF–TEPA formulation in Table 4). Similar effects of changing stoichiometry were observed also for other mixtures (a) formulation of DGEBA with TEPA at a stoichiometric ratio of 3 gives a permeability of 240 ± 30 (cm^3 μm/m^2 24 h atm) as compared to the 780 ± 60 of the balanced formulation). These results are in agreement with expectations, i.e. that barrier performance depends on amine group concentration. This will be further discussed below.

3.3. Quantitative analysis and prediction of oxygen permeability

The observations cited above show that a number of

Table 6
Calculated cohesive energy density (CED) of selected chemical groups. The values were obtained through group contribution calculations using data presented by Van Krevelen [23]

Structure	CED calculated using the cohesive energy values and molar volumes of Fedors (J/cm^3)	CED calculated using the cohesive energy values of Fedors and the van der Waals volumes of Bondi et al. (J/cm^3)
$-CH_2-OH$	1300	1900
$-CH_2-O-$	420	530
$-CH_2-NH_2$	500	590
$-CH_2-NH-$	650	940
 $-CH_2-N-$	1300	630
$-CH_2-CH_2-$	310	480

structural features in the formulations play a role for the barrier properties. However, in order to further the understanding and simplify the formulation of new coatings it would be useful to identify common parameters that predict barrier performance for a wider range of formulations including different structural elements.

It is well known that many of the characteristics that influence the barrier properties, e.g. packing density, structure stiffness, polarity, mobility, and free volume, also influence the glass transition temperature. Intuitively, it might therefore, be expected that the glass transition temperature could be useful for predicting the barrier performance. However, it has been shown for different poly(hydroxy ethers) [2,13,14], as well as for a series of polycarbonates based on bisphenol [18], that there was little correlation between barrier performance and glass transition temperature. A plot of the permeability coefficient of the different formulations versus their glass transition temperature, presented in Fig. 1, shows that this absence of a correlation is observed also for crosslinked epoxy–amine coatings. It is worth noting that although factors such as cohesive energy density and chain stiffness are known to favour both a high glass transition temperature [19] and a high resistance to diffusion [20], the activation energy of diffusion is actually seen to decrease as the glass transition temperature increases [21]. This apparent contradiction could be one explanation why there is no correlation between glass transition temperature and barrier properties.

As previously mentioned, the concentration of amine groups in the coating plays an important role for the barrier properties. It is also well-known that hydroxyl groups promote barrier performance. Figs. 2 and 3 show the permeability coefficient of the different formulations plotted against the concentration of amine nitrogen (Fig. 2) and against the hydroxyl group concentration (Fig. 3). It should be noted that no distinction is being made between secondary and tertiary amines. In Fig. 2 it can be seen that although there is a significant amount of scatter, there is some correlation between the total amine nitrogen concentration and the logarithm of permeability. As opposed to this, Fig. 3 shows that there is little correlation between OH concentration and log (permeability). However, if one does not consider the previously discussed DGEBD–TETA formulation, i.e. data point 19, the correlation improves. It is also worth noting that the three data points in the bottom left corner of Fig. 3, i.e. 2, 16 and 17, correspond to the formulations with an excess of aliphatic amines, and thus to coatings with a high concentration of amine nitrogen.

Since both amine and hydroxyl groups contribute to barrier performance, it can be expected that the combined

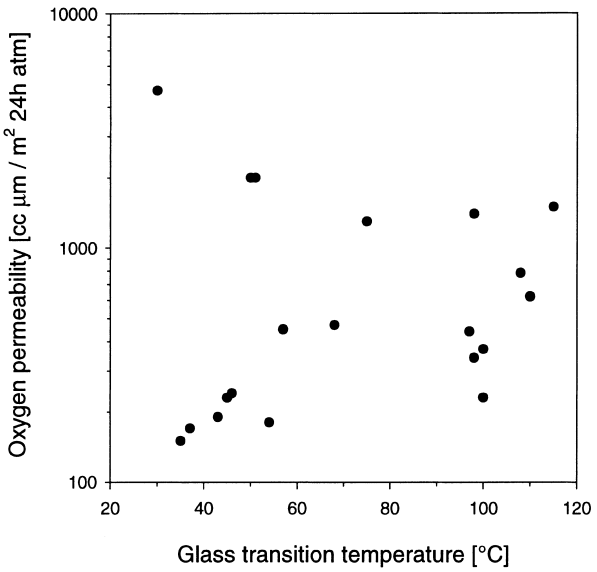


Fig. 1. Oxygen permeability coefficient versus glass transition temperature for all formulations.

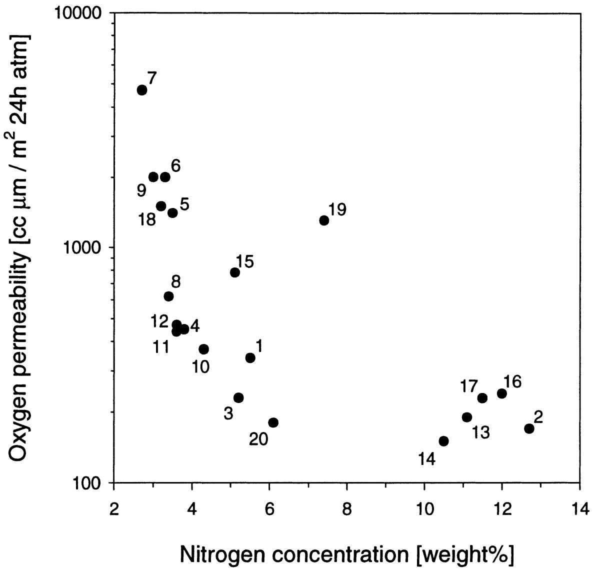


Fig. 2. Oxygen permeability coefficient versus concentration of amine nitrogen for all formulations. The numerals in the graph correspond to the formulation number as defined in Table 2.

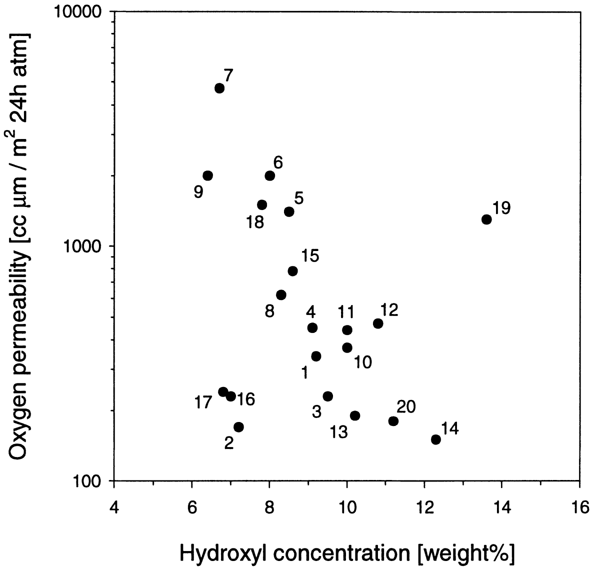


Fig. 3. Oxygen permeability coefficient versus concentration of hydroxyl groups for all formulations. The numerals in the graph correspond to the formulation number as defined in Table 2.

concentrations would be a good predictor of permeability. However, the differences in hydrogen bonding capacity and thus in contribution to barrier performance between the different groups have to be taken into account. In order to compare the contribution of hydroxyl groups relative to that of amines, and to estimate the differences between primary, secondary and tertiary amines, two methods were evaluated. The first was the Permachor approach developed by Salame. This method combines cohesive energy density (CED) and fractional free volume data for structural units to predict polymer permeability and has been shown to work well for a number of polymers [22]. However, although Permachor values for a number of groups have been published, unfortunately no data for amine structures are available.

The second method was the calculation of the CED of the different moieties. Table 6 presents CED values calculated using the group contribution method and data presented by Van Krevelen [23]. The definition of the structures, i.e. the size and type of units to include with each functional group, is of course somewhat arbitrary. Nevertheless it is believed that the structures in Table 6 provide a reasonable basis for comparison. The data in Table 6 was calculated using two different sets of molar volumes (the details are given in Table 6). The data show that for all structures except the tertiary amine, the results obtained are similar. The difference of 20–50% between the two sets of data reflects the general difference between the Van der Waals volumes presented by Bondi et al., and the general molar volume given by Fedors. It can thus be seen that the hydroxyl group has the highest and the ether unit the lowest CED of all polar moieties, with the primary and secondary amines in between. However, for the tertiary amine there is a significant difference in result. Using Fedors' volumes gives a CED for the tertiary amine that is twice as high as the CED of the primary and secondary amines, and equal to the CED of the hydroxyl group. If Bondi's volumes are employed, the CED of the tertiary amine instead falls between those of the primary and secondary amines and well below that of the hydroxyl group.

When trying to judge which one of the two CED values for tertiary amines is the most reasonable, it is useful to re-examine the influence of stoichiometric ratio on structure and permeability. Changing r from 1 to 3 roughly doubles the overall amine concentration (see data in Table 1). At the same time the form in which the amine is present in the cured coating changes. If it is assumed that all primary amines react first and that all epoxy groups are consumed, a simple theoretical analysis shows that for $r = 1$ all amine groups will be tertiary, whereas for $r = 3$ they will almost exclusively be secondary. Therefore, if the CED values from Fedors data are correct, a change in stoichiometry from 1 to 3 should yield only a small change in permeability, as the increase in total amine concentration would largely be offset by a decrease in amine CED. As opposed to this, the CED values obtained using Bondi's volumes suggest that the change from tertiary to secondary amine should increase the polarity of the material. In combination with the overall increase in amine concentration this indicates a pronounced decrease in permeability, which also is what is observed in practice. For this reason it is believed that the CED values obtained using the volumes of Bondi are more accurate. However, it should be noted that these values certainly can be improved upon and should be taken only as indications.

Looking in further detail at the data in Table 6 it can be seen that a secondary amine has a CED value of about 1/2 and a tertiary amine 1/3 of that of an hydroxyl group. Therefore, in order to obtain a good measure of the overall hydrogen binding capacity and contribution to barrier properties of a formulation, it is hypothesized that an overall polarity index, I_P, can be calculated from the weight concentrations of the different species according to the following equation

$$I_P = C(\mathrm{OH}) + \frac{C(\mathrm{N}_{sec})}{2} + \frac{C(\mathrm{N}_{tert})}{3} \qquad (2)$$

where OH refers to hydroxyl groups and N_{sec} and N_{tert} to secondary and tertiary amine nitrogen atoms, respectively. As it proved impractical to directly analyse the concentration of secondary and tertiary amines in the cured coatings, the concentrations were instead estimated as described above. Fig. 4 shows the oxygen permeability coefficients of the different formulations plotted against I_P calculated from Eq. (2) using the estimated amine nitrogen concentrations. As can be seen, the data shows a good correlation between concentration and log(permeability) except for the point corresponding to the DGEBD–TETA mixture. It thus appears that the concentration of polar moieties calculated in this fashion is a good overall predictor of barrier performance. It is reminded that Fig. 4 includes a variety of formulations containing quite different

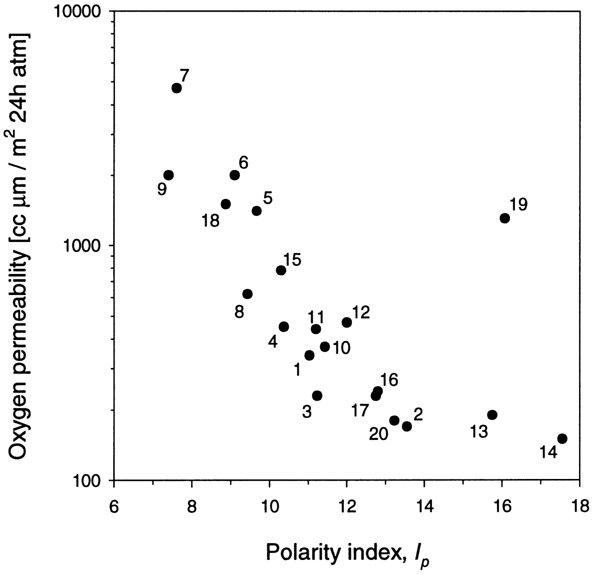


Fig. 4. Oxygen permeability coefficient versus polarity index I_P (as defined by Eq. (2)) for all formulations. The numerals in the graph correspond to the formulation number as defined in Table 2.

chemical structures. In spite of this, there is only limited scatter in the data. Apparently, the influence of structural differences (aromatic versus aliphatic, linear versus branched and cyclic) is either limited, or can be accounted for by the changes in concentration of polar moieties. It is also worth noting that the data on the polyether-containing formulations falls within this general relationship.

4. Conclusions

The barrier properties of a series of coatings prepared from different types of epoxy and amine resins have been investigated. A number of qualitative observations on the influence of structure on oxygen barrier were made. It was thus found that pendant methyl groups had a strong detrimental effect on barrier properties, that formulations based on aliphatic amines showed good barrier performance, and that coatings prepared from polyether amines had very poor barrier. It was also observed that using hydroxy-functional amines improved barrier performance in some but not all cases, and that using an excess of amine monomer significantly improved the barrier properties. Attempts at predicting the oxygen permeability from physical and chemical characteristics of the coatings showed that the glass transition temperature could not be correlated with the barrier properties. However, a polarity index, calculated as the sum of the concentrations of hydroxyl and amine moieties weighted by their individual cohesive energy density, was found to be a good predictor of oxygen permeability for all types of formulations.

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