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Barrier coatings for flexible packaging based on hyperbranched resins

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Abstract

Hyperbranched resins have been evaluated for use as barrier coatings. Different types of modified hydroxy-functional hyperbranched polyester resins were prepared and partially end-capped with acrylate or methacrylate units. Crystalline end-groups (poly(ϵ-caprolactone) were grafted onto some resins. The coatings were applied on poly(ethylene terephthalate) and polypropylene substrates and crosslinked by UV light and their barrier against oxygen and water vapour determined. The results show that hyperbranched coatings give a pronounced improvement in oxygen barrier on both substrates. Expressed in terms of oxygen permeability coefficient, the improvement was a factor of up to 60 times compared to polypropylene and up to 2.2 times compared to poly(ethylene terephthalate). As for other hydroxy-functional barrier polymers, the amount of hydroxyl groups in the hyperbranched resins was found to play a major role concerning the oxygen barrier, controlling both performance and water sensitivity. It was seen that humidity led to a decrease in barrier at the highest hydroxyl group concentration, whereas the barrier performance of coatings with lower concentration of hydroxyl groups instead improved under humid conditions. It was also found that crystalline end-groups did not improve the oxygen barrier and that none of the synthesised resins gave any improvement in water vapour barrier. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Hyperbranched resins; Barrier coatings; Crystalline end-groups

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 environmental impact. In order to meet the different requirements in terms of mechanical properties, barrier performance, sealability 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 high barrier against water vapour and oxygen while being flexible, mechanically resistant, transparent and of low cost. The traditional barrier layer has been aluminium, either in the form of sheet or as a vacuum-deposited layer (metallisation). These materials are obviously not transparent and also suffer from perceived negative environmental impact. Transparent metal oxide coatings, e.g. SiO_x, have been developed, but are brittle and fairly costly. Layers of barrier polymers such as poly(vinylidene chloride) (PVDC), poly(ethylene vinyl alcohol) (EVOH), poly(vinyl alcohol) (PVAL) and polyamide (PA) are available but all have drawbacks in terms of water sensitivity, environmental bad-will or high cost [1,2]. Another aspect is processing technology, where most of the alternative barrier layers require complex processing such as vacuum deposition or co-extrusion. In spite of the many options available, there is therefore still a demand for new barrier solutions.

One such solution could be the use of a new type of polymeric materials, hyperbranched polymers (HBPs) [3], as thin coatings. Materials based on HBPs have the potential of imparting high barrier properties while being mechanically flexible as well as resistant to water [4]. HBP coatings can be applied by a standard roll or spray coating operation, which opens the way for introducing the barrier layer as part of a standard printing or coating operation during packaging manufacture.

HBPs have been extensively studied as part of recent research efforts aiming at tailoring the properties of macromolecular materials by variation in the molecular architecture. HBPs are highly branched structures based on AB_x-monomers, which introduces potential branching points in every repeating unit as well as numerous end-groups. The large number of end-groups and branching points gives the polymers different properties compared to those of linear analogs. The structure of HBPs is illustrated in Fig. 1.

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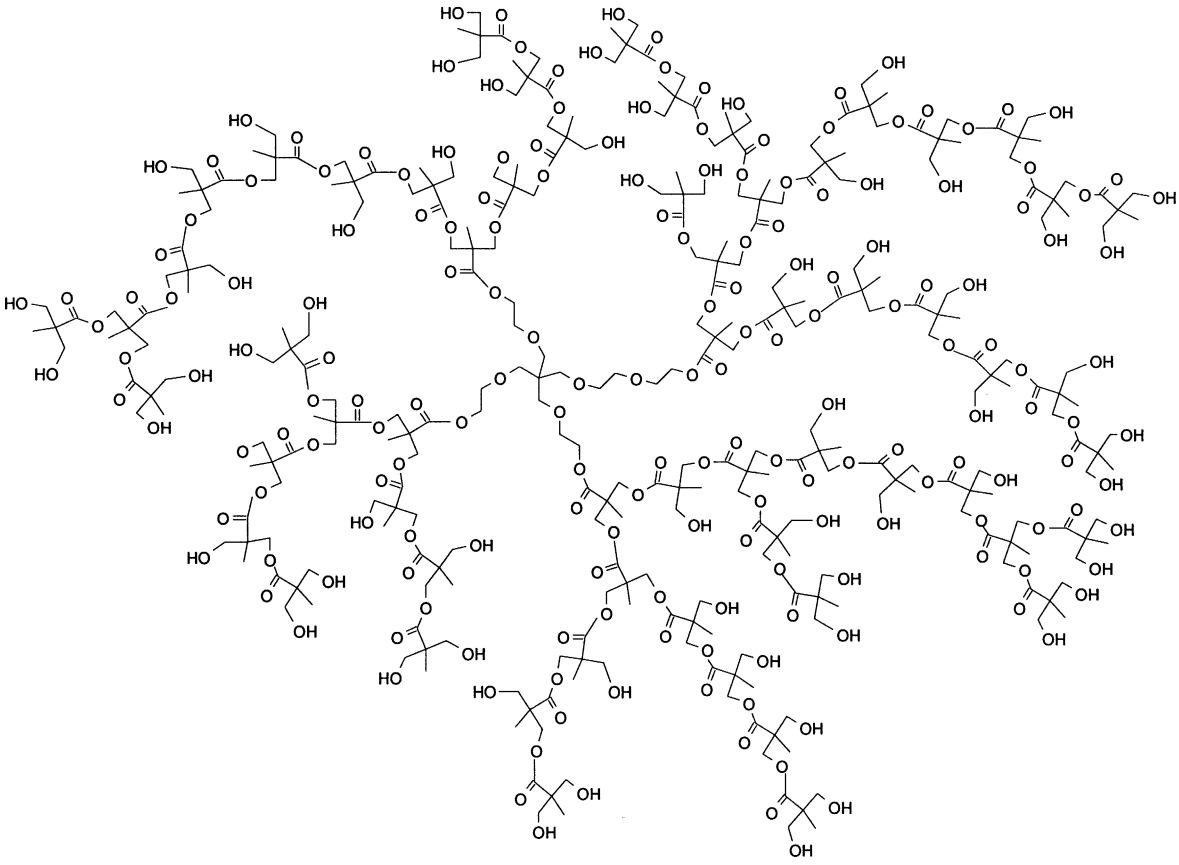

Fig. 1. General structure of a hyperbranched polymer.

HBPs have low melt and solution viscosity, high solubility, and are easy to modify in view of obtaining tailored properties [5]. Modification of the end-groups makes it possible to greatly vary the polarity of the polymer [6], introduce crystallinity [7,8] or render the polymer crosslinkable by attachment of reactive moieties [9,10]. Various HBPs, e.g. polyphenylenes [11], aromatic polyesters [12], polyethers [13], and aliphatic polyesters [14] have been prepared. Hybrid structures where linear polymers have been combined with hyperbranched polyesters have also been described [15,16]. These hybrid polymers are semi-crystalline and can be further functionalised to become crosslinkable [17].

The high degree of branching in HBPs means that they form few chain entanglements, which in turn leads to brittle behaviour below the glass transition temperature. For this reason, HBPs are rarely used alone but rather as additives for thermoplastic resins or in crosslinked thermosetting resins. Applications described so far include use as rheology modifiers for thermoplastics [18–20] and additives for thermosets where the toughness of the materials is improved through controlled phase separation [21–23]. Hyperbranched polymers have also been successfully employed as resins for coatings, where the low viscosity reduces the need of solvents [24,25].

Of particular interest for packaging applications is the fact that diffusion studies on hyperbranched aliphatic polyesters have shown that they are potentially good barrier materials [4]. Questions still remain, however, as to how the barrier performance is influenced by structural parameters such as crystallinity, cross-link density, and polarity.

In the present work, hydroxy-functional hyperbranched aliphatic polyesters have been evaluated for use as barrier-improving coatings on flexible packaging materials. Two categories of polymer resins were prepared, one with crystalline end-groups, (poly(ϵ-caprolactone) PCL) and one without. Both categories were end-capped with crosslinkable end-groups (acrylate or methacrylate moieties) to different degrees in order to investigate the influence of crosslinking density. The crystallinity was introduced with the intention of achieving improved barrier properties and the crosslinking to create sufficient material strength. The coatings were applied on poly(ethylene terephthalate) (PET) and polypropylene (PP) substrates, crosslinked by UV light and the resulting films evaluated with respect to barrier properties.

2. Experimental

2.1. Materials

The hydroxyl-functional hyperbranched polyester, **1**,

Table 1
Base polyesters with basic data

Polyester no and type	Degree of polymerization, ϵ-PCL	Theor. molecular weight (g mole^{-1})	Molecular weight by SEC, Mn (g mole^{-1})	Polydispersity by SEC
1 P4G	–	7300	2800[a]	1.8[a]
2 P4G-ϵPCL(DP10)	9.6[b]	77700[b]	29400	1.4
3 P4G-ϵPCL(DP30)	33.7[b]	226500[b]	53000	1.6

[a] Supplier data.
[b] Based on ^{1}H-NMR data.

Boltorn™ H40, with a theoretical molecular weight of 7300 g mole^{-1} and an average number of hydroxyl end groups of 64 per molecule was obtained from Perstorp AB, Sweden. Irgacure 184™ (1-benzoylcyclohexanol) was obtained from Ciba Specialty Chemicals and used as received. Acryloyl chloride, methacryloyl chloride, propionyl chloride, 4-dimethylaminopyridine (DMAP) and Sn-2-ethylhexanoic ($Sn(Oct)_2$) acid were all purchased either from Aldrich or Lancaster and used as received. ϵ-Caprolactone was obtained from Aldrich and dried over CaH_2 and distilled twice before use.

The substrates, oriented PP (Bicor MB 400, 30 μm thickness, produced by Mobil) and PET (Melinex 813, 12 μm thickness, produced by DuPont), were supplied by Lawson Mardon Packaging Services, Switzerland.

2.2. Equipment

^{1}H-NMR spectra were recorded on a Bruker AM 400 spectrometer at 400 using $CDCl_3$ as a solvent. The solvent peak was used as a reference. Size exclusion chromatography (SEC) was performed on a Waters SEC-system using a solvent delivery system (Model 510), automatic injector (WISP 710B) and a differential refractometer (Waters 410) as a detector and three PLgel 10 μm mixed-B columns from Polymer Labs. Tetrahydrofuran, THF, 1.0 ml min^{-1}, was used as the mobile phase. Calibration was carried out using linear polystyrenes of known molecular weight and low poly-dispersity.

The coatings were applied on the substrates using a Bürkle laboratory rolling mill, model BKL. UV curing was performed in a Primarc UV laboratory oven equipped with a 80 W/cm medium pressure Hg-lamp (intensity 354 W cm^{-2}, 7 m min^{-1}).

The content of residual solvents was qualitatively examined by headspace GC-MS on a HP 6890 GC analyser.

Thermal analysis was carried out using a Perkin-Elmer DSC 7 differential scanning calorimeter.

IR-spectroscopy was performed on the polymer coatings to calculate the degree of cure. The apparatus used in this analysis was a Perkin Elmer Spectrum 2000 FT-IR Single Reflection ATR with a Golden Gate accessory from Graseby Specac.

Oxygen transmission rate was analyzed with a Mocon Ox-Tran 2/20.

Water vapor diffusivity was analyzed using a MAS 1000 Moisture Diffusion System.

2.3. Synthesis and sample preparation

The starting material was Boltorn™ H40, **1**. The basic characteristics of this compound are presented in Table 1.

2.3.1. General procedure for grafting of poly(ϵ-caprolactone) (ϵ-PCL) polyesters **2** and **3** exemplified by the synthesis of P4G-ϵPCL(DP10), **2**

10.0 g (88.0 mmol hydroxyl groups) of the glassy hydroxy-functional polyester **1** was ground in a mortar and then added to a round bottomed flask and melted at 90°C in a preheated oil bath. When **1** was melted the temperature was raised to 100°C and the round bottomed flask was evacuated and refilled with Argon. This procedure was repeated five times. ϵ-Caprolactone (101 g, 888 mmol) and dry toluene (4.0 ml) were added. A catalytic amount of $Sn(Oct)_2$ was added by a syringe and the flask was purged with Argon. The reaction mixture was kept at 100°C for 20 h. The product was dissolved in THF, precipitated into cold (dry-ice) MeOH and filtered.

^{1}H-NMR ($CDCl_3$): δ (ppm) = 4.03 − 4.05 (t, 18 H, —C*H*$_2$—OOC-polyesters), 3.62 − 3.65 (t, 2H, —C*H*$_2$—OH), 2.28 − 2.32 (m, 20H, —OOC—C*H*$_2$-polyesters), 1.61 − 1.66 (m, 40H, —OOC—$CH_2CH_2CH_2CH_2CH_2$—OOC—), 1.37 − 1.39 (m, 20H, —OOC—$CH_2CH_2CH_2CH_2CH_2$—OH).

SEC (THF): M_n = 29,370, M_W = 40,450, M_W/M_n = 1.38.

Some characteristics of compounds **2** and **3** are given in Table 1.

2.3.2. General procedure for acrylation/methacrylation of the hydroxy-functional polyesters ***4–8***, exemplified by the synthesis of P4G-A, ***7***

17.0 g (148 mmol hydroxyl groups) of the glassy hydroxyl-functional polyester **1** was ground in a mortar and added to a round flask and then melted at 90°C in an oil bath. The melt was dissolved in THF and 15.0 g (148 mmol) triethylamine was added drop-wise to the solution. A catalytic amount of dimethylaminopyridine (DMAP) was added. The flask was equipped with a drying tube and cooled on a water/ice-bath after which 5.37 g (59.3 mmol) acryloyl chloride, diluted 1:3 in dichloromethane, was added drop wise to the reaction mixture. The reaction mixture was

Table 2
Acrylated and methacrylated polyesters with basic data

Polyester no and type	End group	Degree of functionalization
4 P4G-MA	Methacrylate	15%
5 P4G-MA	Methacrylate	30%
6 P4G-MA	Methacrylate	40%
7 P4G-A	Acrylate	40%
8 P4G-MA/P	Methacrylate/propionate	40/60%
9 P4G-ϵPCL(DP10)-A	Acrylate	~100%
10 P4G-ϵPCL(DP30)-A	Acrylate	65–80%

stirred at room temperature overnight. THF was evaporated and the polyester was dissolved in dichloromethane. The reaction mixture was extracted two times with 10% $NaHCO_3$ and then two times with 10% NH_4Cl. The polymers **4**–**8** were all synthesized in the same manner, with the exception for polyester **8** that had to be made in two similar steps, comprising end-capping with acrylate and propionate.

^{1}H-NMR ($CDCl_3$): δ (ppm) = 6.35 − 6.45 (br, *cis*, —CH=CH_2), 6.05 − 6.18 (br, —C*H*=CH_2), 5.85 − 5.92 (br, *trans*, —CH=CH_2), 4.1 − 4.4 (br, —CH_2—OOC—CH=CH_2), 3.6 − 3.8 (br, —CH_2—OH), 1.08 − 1.33 (br, —CH_3, bis-MPA)

FTIR (NaCl, cm^{-1}): 1728 (carbonyl), 1637 (acrylate unsaturation).

Some characteristics of compounds **4**–**8** are given in Table 2.

2.3.3. General procedure for methacrylation of the hydroxy-functional polymers *9* and *10* exemplified by the synthesis of P4G-ϵPCL(DP10)-A, 9

30.0 g of polyester **2** (240 mmol hydroxyl groups) was dissolved in dichloromethane in a round bottomed flask. Triethylamine (3.60 g, 36.0 mmol) and a catalytic amount of DMAP were added. The flask was equipped with a drying tube and cooled on a water/ice-bath after which 3.25 g (35.9 mmol) acryloyl chloride, diluted 1:3 in dichloromethane, was added slowly. The reaction mixture was stirred at room temperature overnight. The reaction mixture was precipitated into cold (dry-ice) MeOH to give the product in the form of a white, crystalline powder.

^{1}H-NMR ($CDCl_3$): δ (ppm) = 6.35 − 6.39 (d, 1H, *cis*, —CH=CH_2), 6.06 − 6.13 (m, 1H, —C*H*=CH_2), 5.78 − 5.81 (d, 1H, *trans*, —CH=CH_2), 4.11 − 4.15 (t, 2H, —CH_2—OOC—CH=CH_2), 4.03 (m, 18, —OOC—$CH_2CH_2CH_2CH_2CH_2CH_2$—OOC—), 2.28 (m, 20H, —OOC—CH_2-alkyl), 1.62 (m, 40H, —OOC—$CH_2CH_2CH_2CH_2CH_2$—OOC—), 1.36 − 1.39 (m, 20H, —OOC—$CH_2CH_2CH_2CH_2CH_2$—OOC—).

Some characteristics of compounds **9** and **10** are given in Table 2.

2.3.4. Film preparation and UV curing of Polyesters *4*–*10*

The polyesters **4**–**8** were dissolved in THF and the polyesters **9** and **10** were dissolved in toluene. Irgacure™ 184 (4% w/w) was added to all solutions. The coatings were applied on PET and PP substrates using the laboratory rolling mill. After solvent flash-off the films were melted at 70°C and immediately crosslinked by UV irradiation. The UV curing was performed with five subsequent passes under the UV lamp giving a total UV dose of 2780 mJ/cm^2.

2.4. Characterization techniques

2.4.1. Thickness measurement

Measurements of the film thickness were performed on the samples for barrier evaluation after the barrier properties had been measured. The thickness was measured using a micro-meter on four different spots from which a mean value was calculated.

2.4.2. Coating adhesion

The adhesion of the coatings to the substrate was qualitatively evaluated using the Tape test, where a pressure-sensitive tape with a given adhesion strength is applied and removed. The adhesion was evaluated by examining the amount of coating removed by the tape [26]. Results were expressed as 'good' when no coating was removed, 'fair' when some of the coating was removed, and 'bad' when all coating was removed by the tape.

2.4.3. Residual unsaturation

FTIR spectra were measured by ATR-FTIR on a diamond crystal. Both cured and uncured resins of polyesters **4**–**7** applied on PP substrates were studied. The residual unsaturation was obtained by comparing the intensity of the vinyl methacrylate peak (1640–1660 cm^{-1}) or the vinyl acrylate peak (1635–1650 cm^{-1}) with that of the carbonyl peak (1710–1730 cm^{-1}).

2.4.4. Thermal analysis

The samples were heated in the DSC from −50 to 300°C at a heating rate of 20°C min^{-1} and cooled to −50°C at a cooling rate of 100°C min^{-1}. The glass transition point was determined as the inflexion point of the curve showing the heat flow as a function of temperature (second heating).

2.4.5. Residual solvent content

Film samples with a surface area of 33 cm^2 were equilibrated in vials at 85°C for 60 min and a sample of the headspace injected in the GC-MS.

2.4.6. Oxygen transmission rate

The films were cut out in adequate pieces from the sheets to fit in an aluminium foil mask with a surface area of 5 cm^2. The samples were placed in the Ox-Tran sample cells. The analysis were performed under the conditions of 23°C/50% RH and 23°C/0% RH. The samples were run until steady-state conditions were reached.

Table 3
Thickness and adhesion of the examined coatings

Coating	Thickness (μm)		Adhesion	
	PET	PP	PET	PP
4, Methacrylated Boltorn (15%)	4 ± 1	6 ± 2	Good	Good
5, Methacrylated Boltorn (30%)	7 ± 1	9 ± 2	Fair	Bad
6, Methacrylated Boltorn (40%)	11 ± 3	11 ± 4	Fair	Bad
7, Acrylated Boltorn (40%)	3 ± 1	5 ± 2	Good	Good
8, Methacrylated Boltorn (40%) with propionate end groups	4 ± 1	–	Good	–
9, Boltorn with short PCL chains and acrylate end groups	6 ± 1	4 ± 1	Good	Good
10, Boltorn with long PCL chains and acrylate end groups	8 ± 2	9 ± 2	Fair	Bad

2.5. Water vapor transmission rate

The conditions used were 23°C at 85% RH. The samples were run until steady-state conditions were reached. The area measured was 5 cm^2.

3. Results and discussion

3.1. Coating characterisation

The thickness and adhesion of the examined coatings is given in Table 3. As can be seen the thickness was between 3 and 11 μm. Transition temperatures as determined by DSC are presented in Table 4. The results show that the samples **4**–**8** all were amorphous and that the samples **9** and **10** were crystalline. All coatings were transparent. The adhesion of the coatings to the PET and PP substrates expressed in qualitative terms is also given in Table 3. It can be seen that the adhesion was good or fair for all coatings on PET substrates and for most of the coatings on PP substrates. However, some of the coatings, e.g. those with high degrees of methacrylate functionalization, did not adhere well to PP.

The degree of cure is shown in Table 5. It can be seen that there was significant amounts of residual unsaturation left in the coatings after cure. This is due to the fact that during UV-cure at ambient temperature, the cross-linking reaction becomes limited by vitrification as the T_g increases to the cure temperature [27]. Table 4 shows that this temperature was around 50°C for both acrylate and methacrylate coatings. It can be seen in Table 5 that the degree of cure was higher for the acrylated coating than for the methacrylated ones. The reason for this is that the ultimate T_g, i.e. the T_g at full cure [27], is lower for acrylates than for methacrylates [28], which means that the amount of cross-linking and thus the degree of cure required to reach a given T_g will be higher for the acrylate.

Table 4
Degree of cure for coatings on PP substrates

Coating	Residual unsaturation	Degree of cure
4, Methacrylated Boltorn (15%)	0.6	0.4
5, Methacrylated Boltorn (30%)	0.4–0.7	0.3–0.6
6, Methacrylated Boltorn (40%)	0.5–0.6	0.4–0.5
7, Acrylated Boltorn (40%)	0.3	0.7

Table 5
Transition temperatures for the different coatings (°C)

Coating	Glass transition temperature	Melting peak temperature
4, Methacrylated Boltorn (15%)	45 ± 2	
5, Methacrylated Boltorn (30%)	50 ± 1	
6, Methacrylated Boltorn (40%)	54 ± 2	
7, Acrylated Boltorn (40%)	49 ± 2	
8, Methacrylated Boltorn (40%) with propionate end groups	Not detectable	
9, Boltorn with short PCL chains and acrylate end groups		41 ± 1
10, Boltorn with long PCL chains and acrylate end groups		49 ± 2

The residual solvents detected were butyl acetate and tetrahydrofuran, present in coatings **5** and **6**. Some triethyl amine (residue from synthesis) was also found in coatings **4**, **8** and **10**.

3.2. Oxygen transport

In Fig. 2 the oxygen transmission rates through the neat and coated substrates are presented. It should be noted that the thickness is not considered in these data.

It can be observed that the substrates coated with coating **5**–**7** gave improved oxygen barrier properties compared to the uncoated substrates for on both PET and PP and under both dry and humid conditions. The improvement was up to a factor 15 on PP and about 2.3 on PET compared to the neat substrates. Coating **4** gave an improvement in all cases except on PET under humid conditions. The films coated with coating **9** and **10**, i.e. containing PCL, gave only a very slight or no improvement compared to the neat PP and PET substrates. This result was surprising since the hypothesis was that the crystalline PCL end-groups would lead to improved barrier properties.

To render the oxygen barrier data more comparable, the permeability coefficients for each coating were calculated using the following relationship:

$$\frac{1}{T_R} = \frac{L_S}{P_S} + \frac{L_C}{P_C} \quad (1)$$

where T_R is the transmission rate of the coated substrate, L_S and P_S the thickness and permeability of the substrate and L_C and P_C the thickness and permeability of the coating [29]. The coating permeability coefficients obtained through calculations from data for both PET and PP substrates are presented in Table 6. A comparison with the results in Fig. 2 shows that the same trend with respect to oxygen barrier

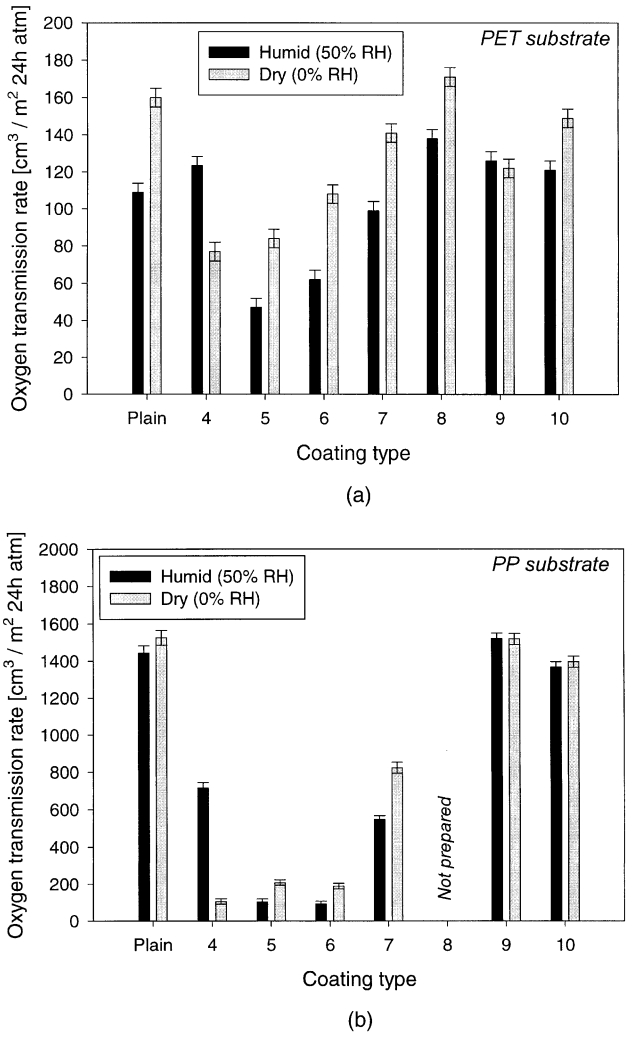

Fig. 2. Oxygen transmission rate for plain and coated: (a) PET and (b) PP substrates.

Table 6
Oxygen permeability for the coatings. The data for the three last materials are taken from literature [32]

Material	Permeability at 23°C 50%RH (cc mm/m² 24 h atm)	Permeability at 23°C 0%RH (cc mm/m² 24 h atm)
Coating **4**	9.0 ± 1.6	0.9 ± 0.3
Coating **5**	0.7 ± 0.2	1.4 ± 0.4
Coating **6**	1.1 ± 0.3	2.2 ± 0.6
Coating **7**	3.0 ± 1.0	7.0 ± 3.0
Coating **8**	> 50[a]	> 50[a]
Coating **9**	> 50[a]	> 50[a]
Coating **10**	> 50[a]	> 50[a]
PET	1.3 ± 0.1	1.8 ± 0.1
PP	42 ± 0.5	44 ± 0.5
Polyamide	–	0.1–1
Polyvinylidene chloride (PVDC)	0.01–0.3	0.01–0.3
Ethylene vinyl alcohol (EVOH)	–	0.001–0.01

[a] Estimated value, calculation unreliable.

performance is obtained irrespective of if total transmission rate or permeability coefficient is used.

Looking in further detail at the data in Fig. 2 and Table 6, while keeping the characteristics of each coating in mind, makes it possible to make further observations. Comparing coatings **6** and **7** thus shows the influence of the type of crosslinker, where methacrylate moieties appear to yield coatings with higher oxygen barrier than acrylate groups. This difference is not related to variations in T_g (see Table 5) or in cross-link density (see Table 4), unless a higher cross-link density imparts a lower oxygen barrier. The measurements of residual solvent content are also unable to offer an explanation, since less volatiles were detected in the acrylate coating than in the methacrylate coatings. The reason for this difference in barrier performance between acrylate and methacrylate functional coatings is not clear and further research is required to understand the mechanism behind the observations.

Another factor that is known to play a role for oxygen barrier performance is the presence and quantity of hydroxyl groups. For other hydroxy-functional barrier polymers it is generally found that hydroxyl moieties improve the oxygen barrier under dry conditions, but make the materials more sensitive to water vapour [1,30]. Comparing the barrier performance of coatings **4**–**6** on one hand with the behaviour of coating **8** on the other, it can be seen that a barrier improvement is only obtained when hydroxyl groups are present. Regarding the influence of the concentration of hydroxyl groups on oxygen permeability, data for dry and humid conditions are presented in Fig. 3. Under dry conditions the expected behaviour, i.e. increasing barrier performance with increasing hydroxyl content in the coating, is observed. Under humid conditions the behaviour is more

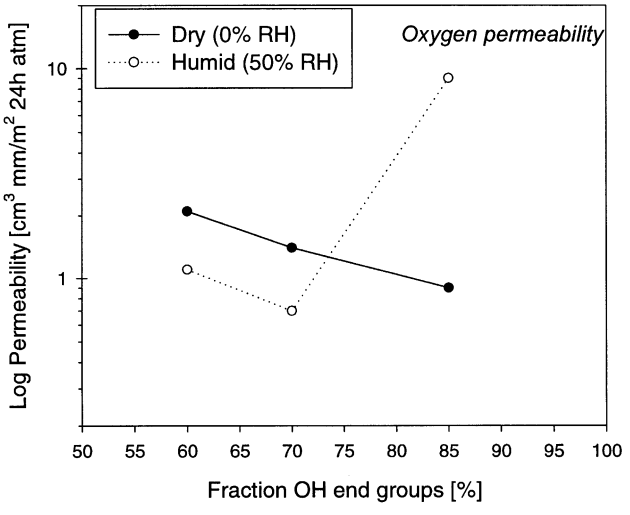

Fig. 3. Oxygen permeability coefficient as a function of hydroxyl end group fraction for methacrylated coatings.

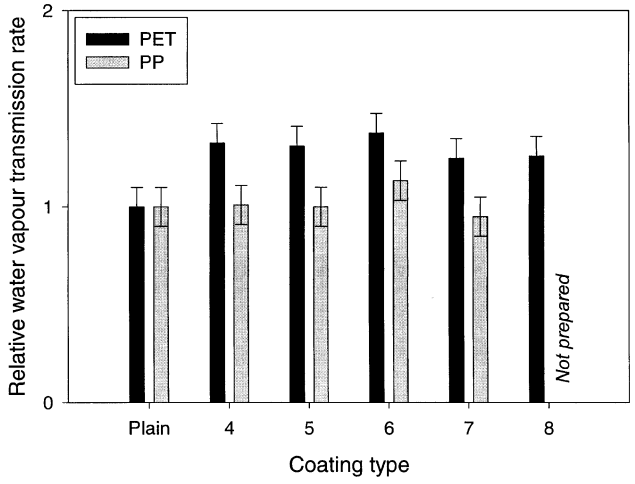

Fig. 4. Relative water vapour transmission rate for coatings on PET and PP substrates. The values for the plain substrates are 12 and 1 g/m^2 day for PET and PP, respectively.

complex with a minimum in permeability observed at a hydroxyl end group fraction of about 70%. This is presumably due to the plasticizing effect of water competing with and ultimately dominating over the increase in density as the concentration of hydroxyl groups grows. A linear extrapolation to 100% hydroxyl groups would give values of about 0.7 under dry conditions and more than 60 under humid conditions, which can be compared with the values 0.5 and 7 obtained for a similar 100% hydroxy-functional HPB in previous work [4].

Furthermore, it can be seen in Fig. 3 that the presence of humidity leads to a decrease in oxygen barrier only for the coating with the highest fraction of hydroxyl groups, whereas the barrier performance of the other two coatings instead improves under humid conditions. The latter type of behaviour is not typical for other hydroxy-functional polymers such as EVOH and PVAL, but is observed in amorphous PA [30], certain polyethers [2] as well as for PET (see Table 6). For the polyethers, the reason for this behaviour is believed to be that water not only occupies free volume but actually enhances the material cohesion [2]. A similar explanation involving mixed gas permeation has been suggested for PET [31]. Further research will be required to elucidate the exact mechanism in the present hyperbranched polyester hydroxy-functional structures.

If the permeability coefficients of the best coatings are compared with those of the PP and PET materials, it can be seen that the values are 2.2 times higher than the one for PET and 60 times higher than the one for PP (data in Table 6). If the permeability coefficients instead are compared with those of current barrier polymers it can be seen that the best hyperbranched coatings have permeabilities comparable to those of dry PA. However, the hyperbranched resins are far behind materials such as PVDC and EVOH.

3.3. Water vapour transport

In Fig. 4 the total water vapour transmission rate (WVTR) through the polymer coatings **4**–**8** on the substrates relative to the total water vapour transmission rate through the uncoated substrate materials are presented. As in the case of the O2TR results, this data does not take the thickness of the coatings into account. It can be seen in Fig. 4 that none of the coatings gave any improvement in water vapour barrier.

4. Conclusions

Acrylated and methacrylated hyperbranched coatings gave a clear improvement in oxygen barrier on both PP and PET substrates. For the coating thicknesses examined in the present work, the improvement was at the most of the order of 15 for PP and 2.3 for PET compared to the uncoated substrates. Since the oxygen transmission rate does not consider the thickness, a more accurate comparison is the permeability coefficient. Depending on the coatings and the conditions, the permeability coefficients were 6–60 times lower than for plain PP and 1.2–2.2 times lower than for plain PET. This puts the best coatings on par with dry polyamide. All coatings were transparent and adhered well to PET substrates. Some coatings only showed limited adhesion to PP.

The amount of hydroxyl groups was found to play a major role concerning the oxygen barrier, controlling both performance and water sensitivity. The coatings showed increasing barrier performance with increasing hydroxyl content under dry conditions. Under humid conditions a maximum in barrier was observed at a hydroxyl end group fraction of 70%. Comparing dry and humid data, it was also seen that humidity led to a decrease in barrier at the highest hydroxyl group concentration, whereas the barrier performance of coatings with lower concentration of hydroxyl groups instead improved under humid conditions.

The coatings that were made from methacrylated resins showed better oxygen barrier performance than the one made from acrylated resins. The difference could not be explained by differences in T_g, cross-link density or residual solvent content of the coatings. The results also showed that crystalline end-groups did not improve the oxygen barrier as expected. Finally, it was found that that none of the synthesized resins gave any improvement in water vapour barrier.

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