

Designing Polyethylene Terephthalate-Based Barrier Resins

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ABSTRACT: We have studied the efficiencies of commercially available barrier resins used for food packaging and beverage bottle applications and compared them with resins made using copolymer and blending approaches. The effects of various copolymer related parameters that influence oxygen barrier performance and the underlying mechanisms for these effects in PET-based copolymers and blends were investigated. Using these approaches, it is possible to make highly effective PET-based copolymers for gas barrier applications. Blending

of PET with phenolic and other organic materials shows equivalent barrier performance in PET copolymers having comonomer levels of <8-mole %. Reduction in oxygen permeation rates results from the reduction or elimination of short range molecular motion of polyethylene terephthalate molecules. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: barrier; block copolymers; blends; gas permeation

INTRODUCTION

Polyesters are suitable materials for forming into biaxially oriented films, containers, and bottles for use in packaging foodstuffs and beverages.^{1–6} Polyethylene terephthalate (PET) has good mechanical strength, chemical stability, transparency, injection moldability, as well as good resistance to gas permeation in comparison to polyolefins and other resins. However, the performance of PET is less than adequate for packaging carbonated beverages, fruit juice beverages, liquid flavorings, edible oils, liquor, wine, beer, etc. In these applications, the permeability to carbon dioxide and oxygen influences the flavor of the packaged contents.

The barrier properties of PET can be improved by coating the polyester film, container, or bottle with a layer of barrier material, which has low gas permeability.^{7,8} However, coated materials have disadvantages such as the need for a thick coating layer, the extra cost involved with the use of another polymer, additional process steps, and toxicity of some of the coating formulations. Another approach for improving the gas barrier properties involves the preparation of multilayered articles, such as bottles, containing individual barrier layers.⁹ This approach is not

very attractive because of the additional costs of the barrier resin and the process steps for adding extra layers. In addition, multilayered articles are difficult to recycle.

Extensive studies on polyester copolymers and blends have been carried out to develop high barrier resins that are safe and cost-effective and are capable of reducing oxygen and carbon dioxide permeability of polyester-based resins.^{10–30} The barrier properties of such resins have been summarized by several authors.^{1–6} However, the design of such a resin is challenging. All new high barrier resins available in the market cost at least \$2.50/lb and need to be recyclable when used in multilayer construction.

To develop a moldable resin for packaging applications, a number of PET copolyesters containing ortho-, meta-, or para-substituted terephthalic acid (TA) or naphthalene dicarboxylic acid (NDCA) have been synthesized.^{10–19} Studies included the effect of comonomer type and content on the melting point (T_m), glass transition temperature (T_g), nucleating characteristics, and mechanical properties. Donohue and Paschke¹² and Sakaguchi and Yoshida¹⁵ prepared a PET-copolymer containing a biphenyl unit, but the barrier properties were not investigated. Asrar⁶ studied the oxygen permeability of a PET copolymer containing 4,4'-biphenyl dicarboxylic acid (BDA) and compared it with PET containing NDCA as a comonomer. Mitsubishi Chemical developed a copolymer formulation containing resorcinol dioxyacetic acid (RDOA), while Mitsui Chemical Corporation developed a copolymer containing 1,3-bis

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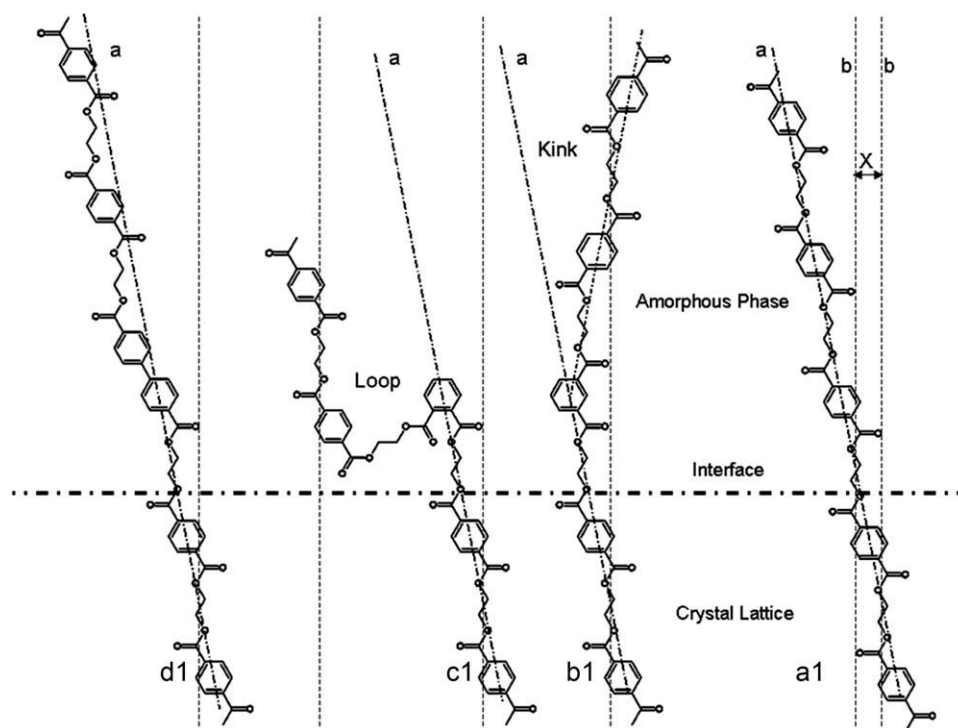


Figure 1 This shows the chain conformations of a PET molecule and PET copolymers containing IPA, PA, and BDA. The area below the horizontal dotted line represents the crystal lattice of PET while the area above the crystal surface is the amorphous phase containing copolymer units like IPA or PA. The axes passing through the PET molecules and EG units are denoted by "a" and "b," respectively.

(hydroxyethyl) ether of resorcinol (HER) and compared their results for oxygen and carbon dioxide permeability and other properties with commercial barrier resins.³ Seko¹⁶ made a PET-based copolymer containing Phthalic acid (PA) for improving the fragrance retention property of hollow containers. However, Seko did not investigate the effect of meta- and ortho-substituted TA. Barbee^{17,18} made PET containing PA as a comonomer and found improvement in oxygen and carbon dioxide barrier properties. Most of the previous work on PET-based copolymers is published in the patent literature, and the effects of various comonomers on barrier properties and the mechanism for barrier improvement were not systematically explored in detail. Our goal is to extend these studies, investigate, and develop an approach for making highly efficient barrier resins.

The chain conformations of PET and several copolymers are shown in Figure 1. Fig 1(a1) depicts the planar chain conformation of a PET molecule. Various chain conformations of PET molecules were discussed by Nicholson et al.³¹ The effect of replacing one TA unit with IPA, PA, or BDA comonomer on PET chain conformation is shown in Figure 1(b1–d1), respectively. An axis passing from ethylene glycol (EG) units of PET molecules is denoted by "b". Addition of each TA unit to EG will shift the axis passing through EG by distance "X." The molecular axis passing through the benzene rings is denoted by "a".

If TA is replaced by IPA then a kink will be introduced in the PET molecule [Fig. 1(b1)] while it forms a loose loop if the TA is replaced by PA [Fig. 1(c1)]. The change in the PET conformation by replacing TA with BDA is shown in Figure 1(d1), which also shows the creation of a defect in the chain conformation. The area below the horizontal dotted line represents the crystal lattice of PET, while the area above the crystal surface is the amorphous phase containing comonomer units like IPA or PA. The molecules in the amorphous state shown here are just at the crystal-amorphous interface. Loose PET copolymer molecules (molecules where one or both chain ends are not directly connected to the crystal lattice in the amorphous phase) are not shown in Figure 1. All the conformation defects shown here and any branching or crosslinks in PET chains can be considered as molecular heterogeneities.

Gas or water vapor is not permeable from the crystalline phase; therefore, the state of amorphous phase plays an important role for determining the barrier properties of semicrystalline polymers. In this respect, factors such as orientation of molecules, the nature of the comonomer in polymer and the presence of antiplasticizers or monomeric materials play a vital role.

In polymers, the motion of molecules results from cooperative movements of other molecules in the amorphous phase. In PET, the carboxylic acid group

is at the para-position; therefore, the benzene ring can “flip” or rotate around the polymer axis easily in the amorphous phase. As the position of the dicarboxylic acid on the benzene ring changes from para- to meta- or para- to ortho-, flipping of the benzene rings of PET in the amorphous phase becomes sterically constrained. Flipping of the benzene ring in copolymers containing IPA (meta-) or PA (ortho-) is constrained due to the position of the carboxylic acid groups. This, in turn, influences the segmental motions of other PET copolymer molecules in the amorphous phase.

The barrier properties of aromatic polymers are governed by the degree of short-range motion of the polymer molecules in the amorphous phase. Increased molecular mobility in the amorphous phase will allow increased permeation of gases, and restricted mobility analogously decreases permeation. It is therefore expected that the presence of rigid folds or loops in the amorphous phase will rigidify the amorphous phase or reduce molecular motions and thereby reduce the permeation of gases.

The presence of comonomer units can distort the crystal lattice, which then leads to reduction in the lateral size of the PET crystals. This can lower the T_m of the crystal. In addition, it is possible that the presence of IPA or PA in PET creates heterogeneities in PET molecules so that this part of the molecule is rejected from the PET crystal lattice and resides on the crystal-amorphous interface. This effect can hinder the solid-state thickening of lamellar crystals allowing the lamellae to melt at lower temperature.³¹

The molecular motion of PET homopolymers can also be reduced by blending with the appropriate low molecular weight organic materials and antiplasticizers capable of reducing flipping of the benzene rings. This approach can also reduce OPR values.

This study is intended to investigate two approaches to decreasing OPR in PET: (a) preparing PET-based copolymers containing kinks or rigid folds and (b) blending of PET with antiplasticizers. The effect of various molecular-level variables on oxygen barrier and the underlying mechanisms for such effects are also investigated. The goal is to make highly effective barrier polyester resins by substituting the appropriate groups on the benzene ring of the comonomers and to assess the advantages and disadvantages of the different approaches.

EXPERIMENTAL

Materials

Abbreviations for various compounds and polymers are as follows: PA, isophthalic acid (IPA), acetylsalicylic acid (SA), dihydroxy naphthoate, TA, BDA, 5-hydroxy-isophthate (5-OHIPA), sodium sulfonated

isophthalic acid (Na-sulfo IPA), lithium sulfonated isophthalic acid (Li-sulfo IPA), NDCA, methyl-4-hydroxybenzoate (M4HB), para-4-hydroxybenzoate (P4HB), phenyl-hydroxynaphthoate (PHN), 4,4'-sulfonyl diphenol (4,4'-SFDP), 2,7'-naphthalene diol (2,7 ND), bisphenol A (BISP-A), biphenol (BP), RDOA, HER, phenolphthalein, and hydroquinone (HQ). Boltorn H20 is a dendritic polymer obtained from Perstorp, Sweden. MIXXIM AO-30 is 1,1,3-Tris (2-methyl-4-hydroxy-5-*tert*-butylphenyl)-butane anti-oxidant product from Fairmount Chemical.

Copolymers

PET copolymer containing lithium-sulfonated isophthalic acid, PET copolymer containing sodium-sulfonated isophthalic acid, PET copolymer containing 5-hydroxy-isophthalate, PET copolymer containing bis-(hydroxyethyl) ether of resorcinol, PET copolymer containing resorcinol dioxyacetic acid (PET-*co*-RDOA), PET copolymer containing Phthalic acid (PET-*co*-PA), PET copolymer containing isophthalic acid (PET-*co*-IPA), PET copolymer containing acetylsalicylic acid, PET copolymer containing naphthalene dicarboxylic acid (PET-*co*-NDCA), and PET copolymer containing 4,4'-biphenyl dicarboxylic acid.

Preparation of PET and copolymers

A vessel equipped with agitation, a cooling column, and an in-line condenser was charged with the following ingredients: 194 g of dimethyl terephthalate, 113 mL of EG, and 2.7 mL Zn(OAc) solution (1 g/100 mL EG). These were mixed in a flask equipped with a distillation column and methanol was distilled off at 200°C. After an hour, 7.0 mL solution of Sb₂O₃ (1 g/100 mL EG) was added. After collection of 70 mL of methanol, the temperature was slowly raised to 280°C. EG was then distilled out under vacuum. The polymer was then cooled with nitrogen gas, powdered, and dried in vacuum at 120°C. The same procedure was used to prepare copolymers with PA, IPA, SA, and other copolymers mentioned in the above section.

Blends of PET and copolymers

Blends of PET were made at 270–280°C while blends of PET containing 3% isophthalic acid (PET-*co*-3% IPA) were made at 265–270°C using a 28 mm twin screw extruder (Werner and Pfleiderer, Stuttgart, Germany, Model ZDSK-28 II).

Preparation of biaxially oriented film and heat setting procedure

Films and bottles used for food and beverage packaging are biaxially oriented. Therefore, to compare

the required barrier and other properties the cast films were biaxially oriented.

Amorphous cast films were prepared by pressing dried polymeric material at 280°C with a pressure of 140 MPa (20 kpsi) for 3 min. Cast films were biaxially oriented by simultaneously stretching in a tenter frame in perpendicular directions.³² Film stretching was carried out on a modified T.M. Long Laboratory Stretcher with a draw ratio of 3.5×3.5 and at strain rate of 9000%/min at 88°C. These conditions were kept constant for most of the samples unless stated otherwise. The biaxially oriented films were then heat-set in the temperature range of 180–200°C with the film edges constrained in a frame.³³

The inherent viscosity measurements

The inherent viscosity (IV) of the polyesters was measured according to the ASTM method D2857 using a Cannon Ubbelohde viscometer using a polymer concentration of 0.5% by weight in a 25/75% (volume/volume) trifluoroacetic acid/methylene chloride solution at $30^\circ\text{C} \pm 0.1^\circ\text{C}$.

Oxygen and carbon dioxide permeability measurements

Oxygen permeability was measured at 24°C with relative humidity (RH) of 65% using a Mocon Ox-Trans Twin DL200 oxygen permeability instrument.³² Carbon dioxide permeability was measured at 25°C using the Mocon instrument. Oxygen permeation rate (OPR) is expressed as cubic centimeters of oxygen permeating a 1-mil (25.4 μm) thick sample, per 100 inches square, over a 24-h period under an oxygen partial pressure difference of one atmosphere at 25°C (cc-mil/100 sq inch/day/atm, which is equivalent to 15.5 cc-mil/m²/day/atm).

Differential scanning calorimeter

Glass transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_c), and heat of fusion values were determined by differential scanning calorimetry (DSC) (TA Instrument-DSC-2920) at a heating rate of 20°C/min. To determine the T_g , the polymers were heated to higher than their T_m , quenched, and reheated for a second scan.

Isothermal crystallization studies were performed on a Perkin-Elmer DSC-7. A total of 6–8 mg of amorphous films of PET or PET blends were heated from 60°C to their T_c (between 140 and 210°C) at 200°C/min. Samples were allowed to crystallize for 10–25 min until completion. The exothermic peak position was marked as the crystallization half time, $t_{1/2}$.³⁴

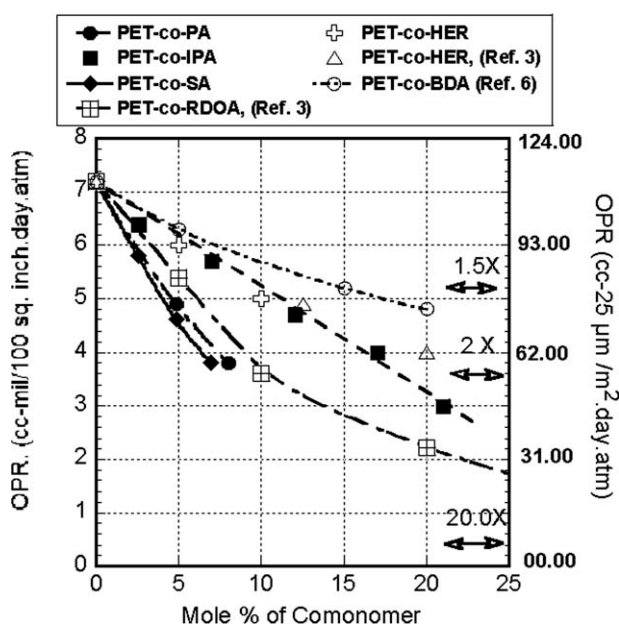


Figure 2 This shows the results for OPR plotted against mole % of comonomer content for PET copolymers containing different amounts of various meta- and ortho-substituted comonomers.

Mechanical properties measurement

Instron measurements on thin film samples were carried out following a modified ASTM Method D882. For quickly achieving equilibrium at 50% RH, samples were first conditioned for at least 48 h at 23°C at 65% RH. Films were cut into strips measuring 0.25" wide using a Thwing-Albert cutter. Strips were exposed to 50% RH (to satisfy ASTM requirements) at 23°C for at least 45 min and then tested on a load frame using a 2000 g maximum load cell. Test speed was 5"/min with grip separation (gage length) of 0.986".

Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was carried out on biaxially oriented films using a Seiko DMS210 instrument in the temperature range of 0–250°C using a frequency of 1 Hz, a heating rate of 2°C/min, and sample dimensions of 5.67×2 mm.³⁵

RESULTS AND DISCUSSION

PET copolymer containing kinks or rigid folds

We prepared PET copolymers containing different amounts of various meta- and ortho-substituted comonomers. The results for the oxygen permeability rate (OPR) are plotted against the mole % of comonomer in Figure 2. All of the measurements were carried out on biaxially oriented heat-set films using the conditions discussed in the experimental

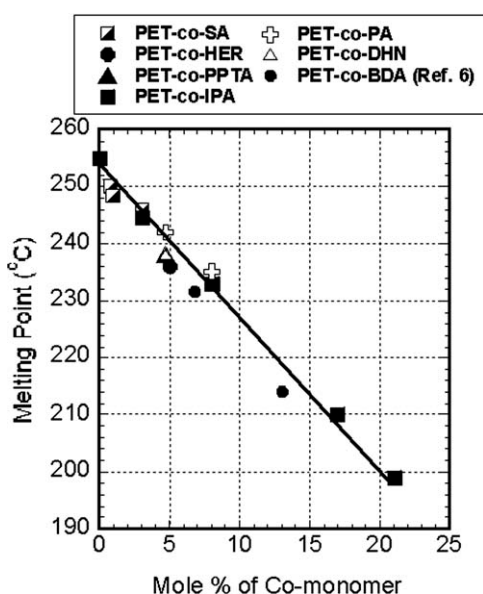


Figure 3 This shows the T_m of PET copolymers versus the mole % of comonomer.

section. The plot shows that addition of IPA in PET decreases oxygen permeability. However, the rate of decrease of OPR is much lower than the rate observed when the PET copolymer contains PA or SA units. These results suggest that the position of dicarboxylic acid groups on benzene rings of PET plays an important role in the flipping of benzene rings of PET molecules.

The PET copolymer containing 5% PA can provide the oxygen permeability level required for making two-liter (67 oz.) bottles for soft drinks requiring a shelf life of 12 weeks, that is, $1.5\times$ improvement over PET homopolymer. Twelve-Ounce (355 mL) bottle resins require a $2\times$ oxygen barrier improvement over PET for the same shelf life because of the increased surface area to volume ratio in the smaller bottles. This requirement can be met with a resin containing $<10\%$ PA in PET. Designing bottle resins for beer bottle applications, however, requires $>20\times$ improvement in oxygen barrier properties because even the presence of a very small amount of oxygen can alter the taste of beer. The required OPR values for all these bottle types are indicated by double-arrows in Figure 2.

The OPR of commercial products containing RDOA and HER are also plotted in Figure 2, after being normalized to the OPR of our PET sample. The reported oxygen permeability of the HER-containing PET-copolymer is similar to PET-co-IPA up to 15% HER content and then starts decreasing.³ Our results for this copolymer follow a similar trend. The OPR for BDA-containing copolymer⁶ shows no improvement over the copolymer containing HER. The PET copolymer containing RDOA showed considerable improvement in OPR values

versus the PET-co-IPA sample. The barrier efficiency of each resin can be ranked by comparing the values of OPR at 5-mole % of comonomer added to PET, or in terms of a % reduction in OPR with respect to PET. In conclusion, PA and SA are more effective comonomers in improving PET barrier properties than RDOA, HER, and BDA.

The T_m of PET copolymer resins decreases with addition of comonomers as seen in other copolymers.^{6,15} Figure 3 demonstrates the T_m of resins as a function of mole % of comonomer. The solid line is a best fit for the T_m as a function of mole % of IPA. The type of monomer used to make the PET copolymers seems to have no consequential influence on T_m . From Figures 2 and 3, it is seen that at 5% mole of comonomer, the T_m of the copolymer remains unchanged while the OPR varies considerably.

When the heterogeneity in the polymer chains increases, the crystal lattice becomes imperfect and, as a result, the percent crystallinity is reduced. This leads to formation of small crystallites having smaller lateral dimensions and, hence, the polymer melts at a lower temperature. Gohil and Peterman³⁶ have shown that polystyrenes containing a low level of heterogeneity in the molecules are rejected from the crystal lattice and reside on the crystal surface. The observed melting behavior of polystyrene crystals that were heated directly in the electron microscope showed that this heterogeneity hinders solid-state thickening of lamellae; hence, those regions of lamellae melt at lower temperature than the rest of the lamellae.

With the addition of comonomer in PET, crystallinity decreases analogously, and so there is a considerable depression in T_m with increasing comonomer content. High crystallinity is required to maintain the dimensional stability of containers, which are normally hot-filled above room temperature. Addition of 5 mole % comonomer in PET results in T_m s near 242°C , while the copolymer having 10 mole % of comonomer will have a T_m near 228°C . These temperatures are much higher than the T_m s of polypropylene and polyethylene. The T_g of PET copolymers studied here are well above room temperature. So all the permeability measurements carried out are well below T_g where long-range molecular motions are frozen, hence the contribution to OPR is mainly from short-range molecular motions. These thermal characteristics at a low level of comonomer indicate that crystallinity remains high enough in these PET copolymers to allow one to make sufficiently dimensionally stable containers.

The glass transition temperature of PET homopolymer, PET-co-2.5% PA and PET-co-6.5% PA determined by DSC are, respectively, 83.3 , 80.0 , and 76°C . In the case of PET-co-IPA, the T_g is reduced

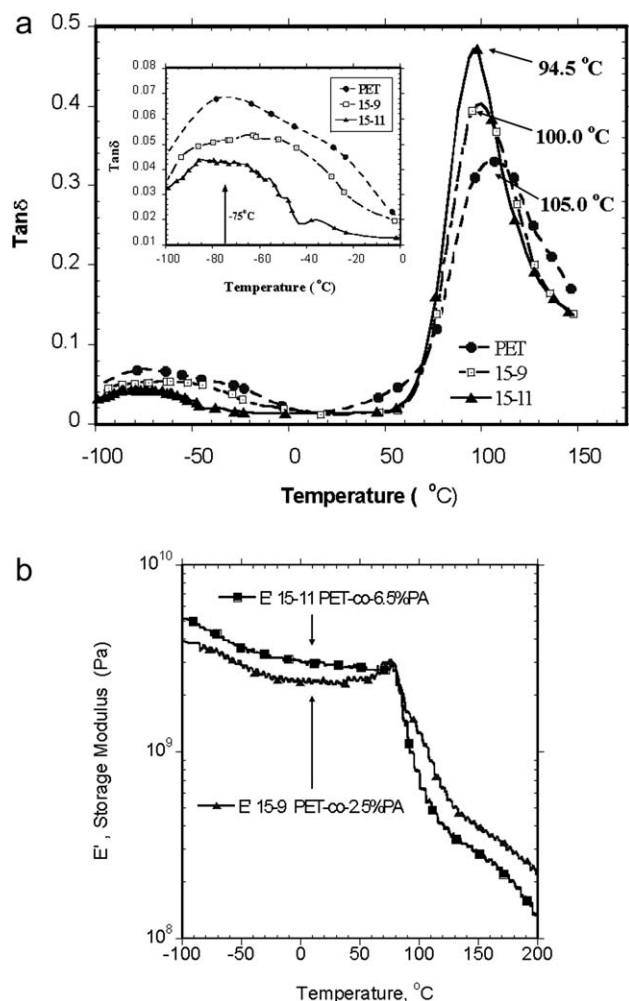


Figure 4 (a) This shows the storage modulus (E') of PET copolymers containing PA at various temperatures. (b) This shows the $\tan \delta$ -temperature scans of PET (IV = 0.62 dL/g), PET-co-2.5% PA (IV = 0.625 dL/g) and PET-co-6.5% PA (IV = 0.64 dL/g). The inset figure shows the effect of different amounts of PA on the magnitude of the sub- T_g peak.

approximately by $0.26^{\circ}\text{C}/\text{mol}$ of IPA,³⁴ while in PET-co-PA the reduction in T_g is $1.1^{\circ}\text{C}/\text{mol}$ of PA. In PET-based copolymers, comonomers like HQ,¹⁵ 2,2',6,6'-tetramethylbiphenyl-4,4'-diol and 2,2',6,6'-tetramethylbiphenyl-4,4'-dicarboxylic acid,¹² isosorbide (I), and cyclohexane dimethanol (CHDM)³⁴ initially increase the T_g of the copolyesters. Thus, an increase or decrease in T_g of a PET-copolymer is dependent on the nature of the comonomer and the positions of the diols or dicarboxylic acid groups on the benzene ring.

The storage modulus (E') of PET-co-PA copolymers containing different amounts of PA was studied at various temperatures [Fig. 4(a)]. The storage modulus at temperatures below T_g is higher for PET-co-6.5% PA than PET-co-2.5% PA. The trend reversed above T_g . With increasing amount of PA in copolymers, crystallinity of copolymer decreases or

amorphous content increases. However, increasing PA content enhances rigidity of the amorphous phase, which leads to reduce OPR.

Figure 4(b) shows variation in $\tan \delta$ with temperature for PET, PET-2.5% PA (15-9), and PET-co-6.5% PA (15-11). $\tan \delta$ peak temperatures that occur at 105, 100, and 94.5°C are related to long-range molecular motions of polymer molecules. These temperatures are similar to T_g measured by DSC. Higher $\tan \delta$ peak temperature observed is due to use of different method.

The flipping of the benzene ring in PET can be monitored from the magnitude of the $\tan \delta$ peak at the sub- T_g peak. The effect of different amounts of PA on sub- T_g peak magnitude or reduction in β transition peak (also known as secondary loss transition) is shown in Figure 4(b). Enlarged area covering temperature range of -100.0 – 0°C is shown in insert. Increasing the amount of PA in PET copolymer reduces the magnitude of the $\tan \delta$ peak. This demonstrates samples having rigid loops in the amorphous phase are more effective at reducing the flipping of the benzene ring or short-range molecular motion of PET molecules in the amorphous phase. This phenomenon leads to local rigidification of polymer chains below T_g . Therefore, the OPR of PET-co-PA is much lower than the PET-co-IPA copolymer molecules containing kinks.

In PET-co-IPA copolymer, we determined the effect of substituted groups on the IPA. These PET copolymers are designated as PET-co-Li-Sulfo IPA and PET-co-5OH-IPA. Figure 5 shows that incorporation of any of these hydroxy- or sulfo-substituted IPA comonomers greatly reduced the OPR as compared with a PET copolymer containing unsubstituted IPA; there is no appreciable difference in OPR between copolymers made using Li-Sulfo IPA or Na-Sulfo IPA. PET copolymer containing $<2\%$ substituted IPA monomer was more effective at reducing OPR than the PET copolymer containing PA. Incorporation of only 2% substituted IPA comonomer in PET reduced OPR to 4.8, a value that requires incorporating 12% IPA in PET. Thus, it is possible to increase the OPR efficiency of PET-co-IPA by substituting the appropriate group on the IPA monomer. This demonstrates that a comonomer capable of forming a rigid loop is not an essential requirement for improving the barrier property to more useful levels.

We have also investigated the effect on OPR of other PET-copolymers containing comonomers like NDCA and BDA, which do not contain the rigid loop conformation like in PET-co-PA. From Figure 5, it is seen that when the concentration of the comonomer is $<5\%$ the effect of these monomers is similar to PA. In the copolymer containing NDCA, the carboxylic acid groups are in the meta-position while in

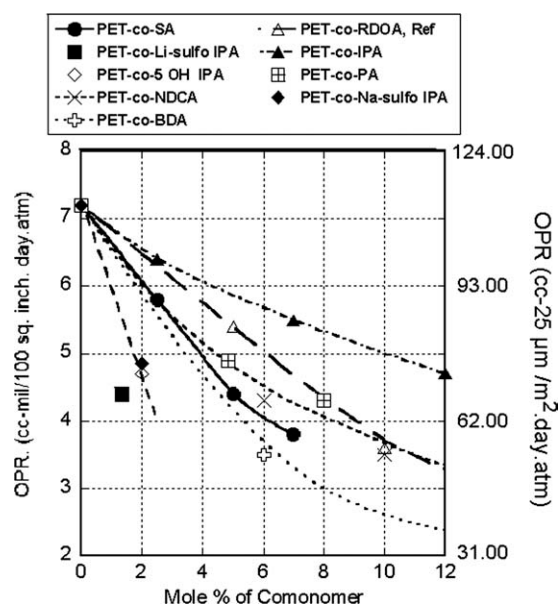


Figure 5 This shows the results for OPR plotted against mole % of comonomer content for PET copolymers.

BDA they are in the para-position. The effectiveness of BDA and NDCA in reducing OPR is very similar in spite of the different positions of the carboxylic acid groups. It is also seen in Figure 5 that the RDOA is less effective than BDA and NDCA. Thus, using this type of comonomer, we can avoid using a rigid loop in PET and get equivalent OPR.

There are several different comonomer options for reducing OPR in PET-copolymer while not sacrificing other useful properties. At a low level of comonomer content, the PET-co-Na-sulfo IPA, PET-co-Li-sulfo IPA, and PET-co-5OH IPA, are more efficient at reducing OPR than most of the commercial barrier resins.

Polymer blends

In this section, we intend to explore blending PET with low molecular weight organic additives that are capable of reducing flipping of benzene rings in polymer chains.^{19–30} In previous sections, we have discussed that the reduction in OPR in PET copolymers is due to a reduction in flipping of the benzene rings of PET molecules, which is indicated by a reduction in the magnitude of the sub- T_g peak of the PET copolymer in a DMA scan. The elimination of the secondary loss transition (reduction in β transition peak) in polyvinyl chloride and polysulfone by blending with antiplasticizers was observed previously.³⁷ Gohil and Lee,²⁰ Miles,³⁰ and Seymour and Light²⁵ showed that blending PET with the appropriate antiplasticizer, usually phenols or substituted phenolic compounds, reduces OPR. They have also shown the effect of various antiplasticizers on the T_g

of PET blends. Their results show that T_g decreases as the percentage of antiplasticizers increases. In spite of the decrease in T_g , oxygen permeability decreases. Below T_g , the reduction in permeability is mainly due to the reduction in short range molecular motion. To explain the reduction in permeability to gases Maeda and Paul³⁸ established a correlation between permeability and free volume of some antiplasticized blends of polymers. They found a correlation in some systems but some blends failed to follow the same trend. This suggests further study is needed to firmly establish the dependency of gas permeability on free volume. Plotzker et al.,²¹ made PET blends with antiplasticizers such as M4HB, P4HB, and PHN. Stretched PET film containing 2.48 wt % M4HB exhibited almost a two-fold reduction in OPR.

We have studied the effectiveness of blending PET with several substituted and nonsubstituted phenolic compounds at reducing the OPR and the underlying mechanism of OPR reduction. OPR measurements were carried out on biaxially oriented films in the temperature range of 80–95°C. All the films were heat set at 180°C unless otherwise noted. The experimental conditions, OPR values, and intrinsic viscosity (IV) of several PET and PET-co-3% IPA blends made using BP, BISP-A, and IPA are presented in Table I.

As seen in Figure 6, compared with PET-co-PA and PET-co-RDOA copolymers, the oxygen permeability in PET blends is reduced dramatically. The OPR of the blends of PET with each of BISP-A, 2,7-naphthalene diol (2, 7 ND) and PHN follow the trend of the PET/BP blend. The blend of BP with PET-co-3% IPA shows slightly lower oxygen permeability than the PET/BP blend. However, the total mole % of comonomer used is high and hence the crystallinity of the resin will be lower than PET.

BPs' have been investigated by many authors. Seymour and Light²¹ made PET blends with bisphenol-A (BISP-A), 4,4'SFDP, and 2,7 ND. Except for BISP-A, the OPR for each of these blends follow the curve shown by the PET-co-3% IPA/BP blend (Fig. 6). Variation in the values of OPR is indicated by the error bar. All these results led us to conclude that the specific nature of the BPs used for blending with PET does not have a drastic effect on reduction of OPR values of PET blends.

It is necessary to blend only 5–6% BP with PET to achieve a 50% reduction in the OPR of PET. Achieving similar OPR in PET-co-IPA copolymer requires addition of 20% IPA comonomer PET (Fig. 2).

We have also investigated a PET blend with the dendritic polymer, Boltorn H20. The OPR values at 5% Boltorn are shown in Figure 6, which is slightly higher than the PET/BP blend. However, the OPR for a PET blend containing 8% Boltorn is similar to the curve for PET/BISP-A and falls below the PET/

TABLE I
Stretching Ratio and Stretching Temperature (TS) Used to Stretch Cast Films to Make Biaxially Oriented Films, OPR Values, and Intrinsic Viscosity (IV) of PET Blends and PET Copolymers

Composition	MD × TD	TS (°C)	OPR	IV (dL/g)
PET	3.5 × 3.5	85	6.8	0.72
PET (not heat set)	3.5 × 3.5	95	8	0.72
PET (cast film)	Cast	–	9.9	0.72
PET/5% BP	3.5 × 3.5	80	3	0.58
PET/11%BP	3.5 × 3.5	85	2.3	0.55
PET/5% BISP A	3.5 × 3.5	95	4.6	0.6
PET-co-3%IPA	3.5 × 3.5	85	5.9	0.72
PET-co-3% IPA / 5% BP	3.5 × 3.5	85	2.8	0.57
PET-co-3% IPA / 8% BP	3.5 × 3.5	85	2.1	0.55
PET-co-3% IPA / 10% BP	3.5 × 3.5	85	2	0.55

BP curve. This is an example of a nonphenolic compound that shows improvement similar to a PET/BP blend.

The effect of different substitutions in BPs on the percent reduction in OPR values of PET blends at 5% loading is presented in Table II. The OPR of PET blends with phenolic compounds having sulfonyl or methylene groups, substituted phenol, hindered phenol, and acetylated BP was determined at 5% loading. The T_m s of various phenols are also shown in Table II. From the percentage change in OPR at 5% loading of various phenols, we can make the following conclusions: (a) the hydroxyl group position in BP has no significant effect on OPR values; (b) polar or nonpolar bridging groups between two phenyl rings have no effect on OPR (Table II, 4,4' sulfonyl diphenol, bisphenol A, *p*-cresol Novolac resin); (c) the phenolic group is effective in lowering the OPR whereas biphenyl and acetate derivatives of phenols are not effective. However, addition of 5% biphenyl in PET showed a 25% reduction in OPR; (d) the presence of bulky hindering groups as shown by *p*-cresol novolac resin or octadecyl 3,5-di-*tert*-butyl-4-hydroxy-hydrocinnamate has no effect on OPR.

The OPR values of PET blended with biphenyl, *p*-cresol novolac resin, and octadecyl 3,5-di-*tert*-butyl-4-hydroxy-hydrocinnamate are similar (Table II). This indicates that blends of a hindered phenol such as octadecyl 3,5-di-*tert*-butyl-4-hydroxy-hydrocinnamate retain the same barrier performance as 4,4' BP. The percent reduction in OPR values in the range of 42–45% for PET blends containing MIXXIM AO-30, 5-hydroxyisophthalate, and *p*-vinylphenol polymer is also observed. It should be noted that the cast film PET blend containing 5% polymeric phenolic resin showed 45% reduction in OPR. However, biaxial stretching of cast films of a PET/5% polymeric phenolic resin blend induces porosity in films, which reduces the oxygen barrier properties of the oriented films. Thus, there are wide varieties of phenolic compounds having T_m in the range of 50–280°C that are capable of reducing the OPR of PET.

Figure 7 shows the carbon dioxide permeation rate (CPR) as a function of comonomer content in PET copolymers as well as in the PET blends. The goal CPR for commercial applications of interest is 16 cc-mil/100 sq/ inch/day. While the PET-co-IPA comonomer requires 19–20% comonomer to achieve CPR of 16, <5% of phthalimide, Saccharin, or BP is required to achieve a similar CPR. PET-co-PA requires 8% comonomer to achieve the goal CPR. PET blended with the dendritic polymer, Boltorn H20, shows similar improvement in the CPR. The PETG blend with BISP-A follows the curve of PET-co-PA. In addition to OPR and CPR, the water vapor permeation rate also decreases²⁵ for the PET blends with BPs. These results led to the conclusion that this approach can improve both gas and water barrier properties.

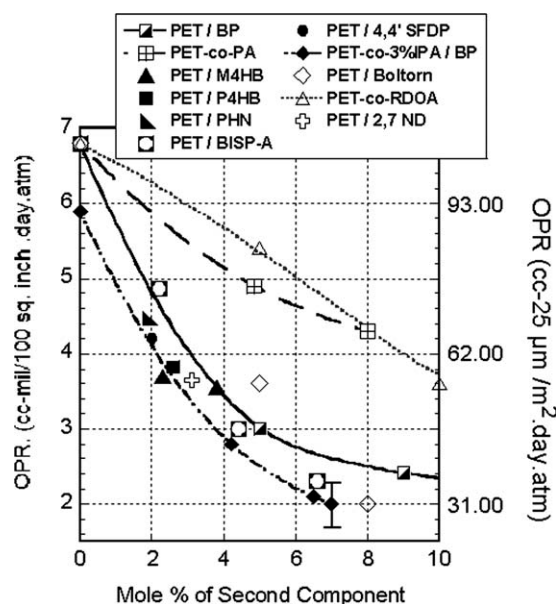
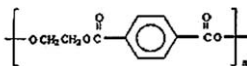
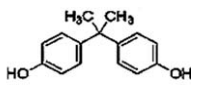
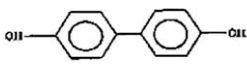
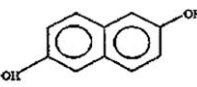
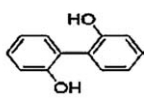
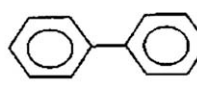
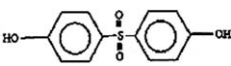
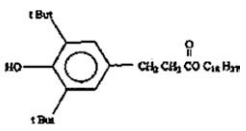
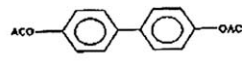
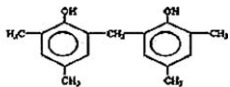


Figure 6 This shows the results for OPR plotted against mole % of comonomer content for PET blends and PET copolymers.

TABLE II
Structural Effect of Different Biphenols Having Different Group Positions on the Reduction in OPR Value at 5% Loading of Phenol in PET Blends

Structure of additives	% Reduction In OPR	T_m (°C)	Structure of additives	% Reduction in OPR	T_m (°C)
 PET	OPR for PET is 6.5	255°C	 Bisphenol A	40% ± 5%	159°C
 4,4' Biphenol	44% ± 5%	280°C	 2,6 Naphthalene diol	45% ± 5%	225°C
 2,2' Biphenol	45% ± 5%	110°C	 Biphenyl	25% ± 5%	72°C
 4,4' Sulfonyl diphenol	45% ± 5%	247°C	 Octadecyl 3,5-di-tert-butyl-4-hydroxy-hydrocinnamate	44% ± 5%	52°C
 Biphenyl Acetate	25% ± 5%	167°C	 p-Cresol Novolac Resin	43% ± 5%	2% wt loss at 275°C

The melt temperature of PET/BP blends as a function of BP content is presented in Figure 8. The T_m decreases as the percentage of BP increases, which is very similar to the PET copolymers (Fig. 3). Compared with PET, the T_m of PET-co-3% IPA copolymer is reduced from 255 to 246°C. As the mole % of BP increases, the T_m of the blends decreases at a similar rate in both the PET-co-3% IPA/BP and PET/BP blends up to 6% BP content.

The crystallization rate as a function of temperature for PET and PET blends with BP, HQ, and BISP-A is presented in Figure 9. The maximum crystallization rate for PET homopolymer occurs at 180°C.^{15,34,39,40} Blending BP with PET enhances the rate of crystallization considerably, but the temperature at the maximum crystallization rate (T_{max}) does not change. However, blending HQ with PET reduces the T_{max} from 180 to 170°C, and the crystallization rate decreases above T_{max} . Blending BISP-A with PET drastically depresses the rate of crystallization. A similar enhancement in crystallization rate of PET is also observed in PET-copolymers containing 4, 4'-BP and 4, 4'-diphenyldicarboxylic acid units

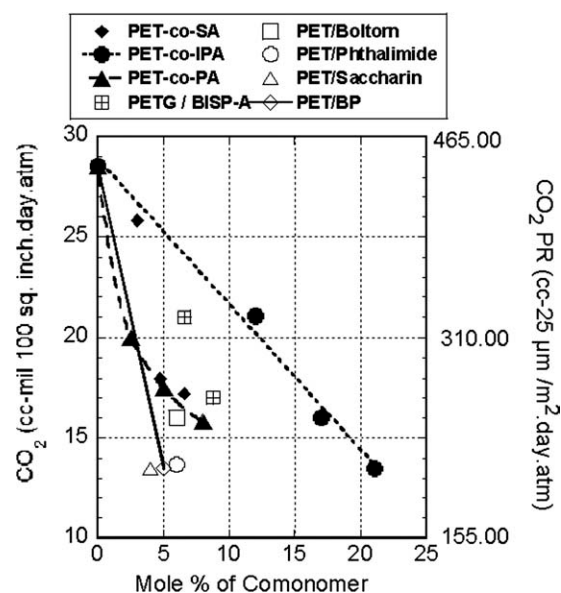


Figure 7 This shows the CPR as a function of the percentage of comonomer in PET blends and PET copolymers.

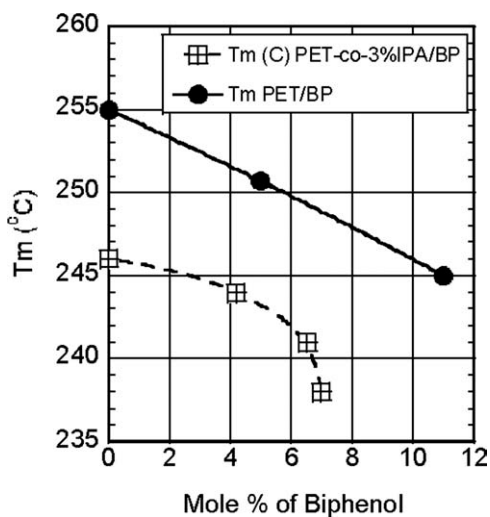


Figure 8 This shows the T_m of PET blended with BP as a function of BP content.

and it is shown that the crystallization rate increases with increasing comonomer content from 4 to 8 mole %.^{39,40} At 5 mole % a higher crystallization rate is noted below 160°C , while a much higher rate occurs when copolymer content is 8 mole %. This indicates that the increase in molecular heterogeneity in the PET-copolymer increases nucleation and crystallization rates, which was also observed by Gohil and Phillips^{41,42} in lightly crosslinked PE. It should be noted that the crystallization rate of the polymer is dependent on the molecular weight. The crystallization characteristics of the resin determine the dimensional stability of films and articles, that is, the shrinkage and mechanical properties.

To examine the changes in long and short-range interaction parameters resulting from the blending of BP with PET having IV of 0.72 dL/g, we have

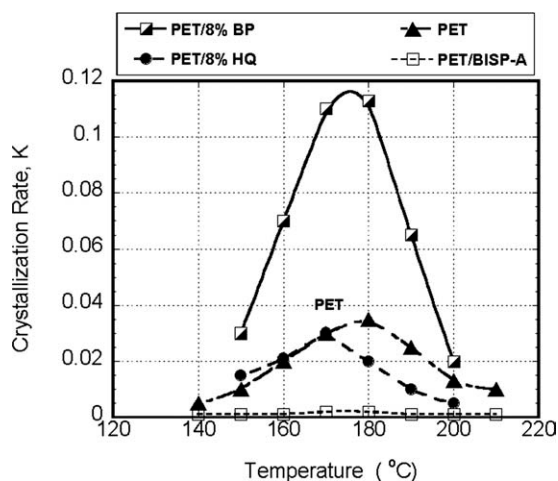


Figure 9 This shows the crystallization rate as a function of temperature for PET and PET blends with BP, HQ, and BISP-A.

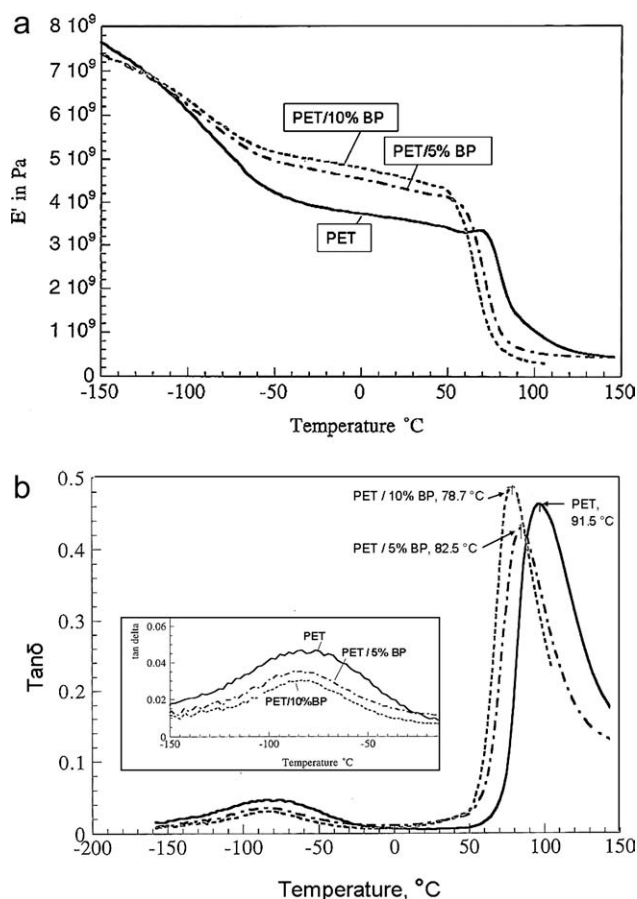


Figure 10 (a) This shows the variation in storage modulus as a function of temperature for PET (IV = 0.72 dL/g) and its blends with BP. (b) This shows the $\tan \delta$ -temperature scans showing a reduction in $\tan \delta$ peak temperature (in the range of T_g) and the magnitude of sub- T_g peaks with increasing BP content in PET blends.

carried out DMA for PET and PET/BP blends.³⁷ Figure 10(a) shows the variation in storage modulus (E') as a function of temperature for PET blends with BP. The storage modulus increases with increasing BP content below T_g . As seen in Figure 10(a), the storage modulus of PET/BP blends above T_g begins to earlier than PET. Figure 10(b) shows the $\tan \delta$ -temperature DMA scans, which demonstrate that the glass transition temperature (T_g) decreases with increasing BP content. The DMA scan also shows a sub- T_g peak at about -85°C , which has been associated with the short-range interaction parameter or flipping of benzene ring. This area is enlarged in the inset of Figure 10(b). This figure shows that with increasing amounts of BP the magnitude of the sub- T_g peak decreases, indicating that the antiplasticizer hinders the flipping of the benzene ring, which in turn is responsible for the observed reduction in OPR. As seen previously, the reduction in flipping of the benzene ring in copolymers occurs by introducing rigid folds or kinks in

TABLE III
Tensile Properties, Stretching, and Heat Set Conditions of PET, PEN, the PET Blends and Copolymers

Polymer composition	Modulus (MPa)	TS (MPa)	% Elongation	F-5 (MPa)	IV (dl/g)	HST (°C)	Stretching conditions
PET	3300	238	94	105	0.62	180	3.5 × 3.5, TS=90°C
PET	4200	322	77	116	0.72	180	3.5 × 3.5, TS=90°C
PEN	5000	265	70		0.63	180	3.5 × 3.5, TS=90°C
PET/5% Biphenol Blend	5500	217	71	137	0.59	180	3.5 × 3.5, TS=90°C
PET/5% Bisphenol A Blend	4800	245	84	131	0.59	180	3.5 × 3.5, TS=90°C
PET/2,6' Hydroxynaphthalen o Rlonrl	4500	203	95	105		180	3.5 × 3.5, TS=90°C
PET-co-6.5% PA	3300	214	103	99	0.64	180	3.5 × 3.5, TS=90°C
PET-co-8% SA	3000	156	88	100	0.63	180	3.5 × 3.5, TS=90°C
PET-co-8% PA	3400	224	81	101	0.62	180	3.5 × 3.5, TS=90°C
PET-co-DRL124	3300	161	92	95	0.6	180	3.5 × 3.5, TS=90°C
PET-co-DRL6	3400	194	113	99	0.63	180	3.5 × 3.5, TS=90°C

PET molecules (Fig. 2). However, in the PET blends the reduction in flipping of the benzene ring is due to the interaction of the phenolic groups of the BP with the ester links of the PET molecules. From this study, it became evident that besides phenolic compounds there are several other classes of materials capable of hindering the flipping of the benzene rings of PET molecules. This provides a new opportunity to explore for designing new effective barrier resins in the future.

DMA of the blends showed a decrease in $\tan \delta$ peak temperature. Figure 10(b) shows $\tan \delta$ peak temperature of PET at 91.5°C. PET/5%BP and PET/10% blends exhibited a $\tan \delta$ peak at 82.5 and 78.7°C, respectively. These results show that T_g decreases with increasing BP content in PET.

The tensile properties, stretch ratio, and heat set conditions of PET, PEN, and blends are presented in Table III. The influence of IV on the mechanical properties of the two different PET samples is shown in Table III. The tensile modulus of PET (IV = 0.72 dL/g) is 4200 MPa. Upon addition of 5% BP, the modulus increases to 5500 MPa. This value is very similar to the tensile modulus of inherently stiff chain molecules like PEN (Table III). The stress at 5% strain ("F-5" value) for PET is 116 MPa and at 5% loading of BP it is 137 MPa. Addition of BP to PET enhances the modulus and F-5 values while decreasing the percent elongation. As seen from Table III, PET copolymers made with various comonomers show lower values of tensile modulus, tensile strength, and F-5 values. Previous work shows that the antiplasticizers are diluents, which when added to polymers result in higher tensile strength, tensile modulus, hardness, and oxygen barrier, and decreases in the elongation, impact strength, and heat-distortion temperature.^{37,43} For example, it has been shown that the antiplasticizing of polycarbonate leads to a clear, stiff, tough, self-extinguishing molding plastic with good electrical properties, and improved resistance to stress cracking.⁴³

Next we will consider the following: (a) the possibility of preparing PET blends using other classes of monomeric materials which can replace BPs and have barrier properties similar to PET/BP blends; (b) the possibility of making PET copolymers that are as effective as PET/BP blends; and (c) comparing the advantages and disadvantages of both approaches and the preferred approach for preparing barrier resins. Our conclusions are summarized below.

- (a) Our study reveals that besides BP, there are other monomeric materials like phthalimide, dendritic polymers, and saccharin whose blends with PET give OPR values similar to PET/BP or PET-co-3% IPA/BP blends (Fig. 11). Therefore, the BPs' are not the only class of materials capable of reducing the flipping of the benzene ring of PET molecules. The

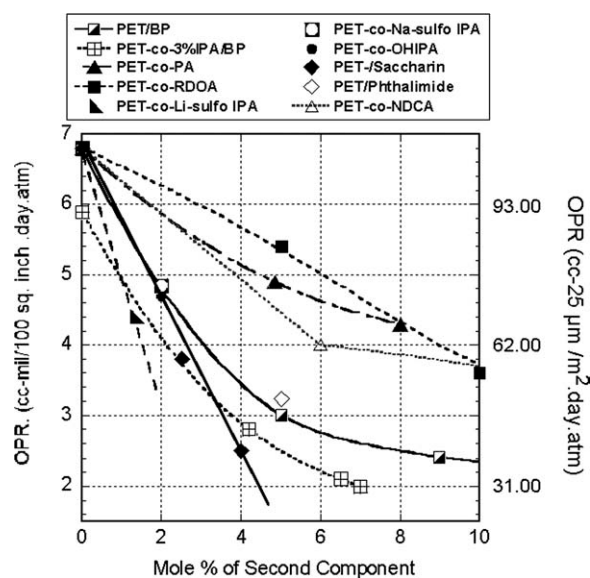


Figure 11 This shows the results for OPR plotted against mole % of comonomer content for PET copolymers, PET blends, and blends of PET copolymers.

results presented in Figure 11 also indicate that the barrier properties of PET-co-NDCA are better than the barrier properties of the commercial products PET-co-RDOA and PET-co-IPA. At <10% comonomer loading, PET-co-PA showed very similar barrier performance to PET-co-RDOA and PET-co-NDCA. PET-co-NDCA is a more expensive copolymer than PET-co-PA. Figure 11 shows that phenolic, phthalimide, and saccharin blends of PET outperform the PET-copolymers discussed so far.

- (b) We have prepared PET copolymers containing sulfonated IPA with different ions (Na⁺ or Li⁺) and hydroxylated IPA. The OPR values of these copolymers are summarized in Figure 11. The barrier performance of these copolymers is identical or better than the PET blends studied so far. These results provide guidance for choosing the comonomer required to make efficient PET copolymers for barrier resins.
- (c) During the processing of PET blends, we discovered that there is a tendency for low molecular weight and low melting BP to bloom out on the surface of films or containers, which is not desirable for food packaging applications. These phenolic molecules can also be deposited in the extruder or be released into the atmosphere during processing. As seen in Table I, addition of BP in PET reduces IV (molecular weight), so one has to start with high molecular weight PET. This adds an additional step of solid-state polymerization of PET, which increases the resin cost. Therefore, considering the limitations of the PET-blending approach, the copolymer approach seems more appealing. Taking into account the safety and cost aspects, the preparation of PET-copolymers containing comonomers like Na-sulfo IPA and 5OH-IPA is an attractive approach for making barrier resins.

SUMMARY

We investigated two approaches for designing beverage bottle resins with improved oxygen barrier characteristics. Several PET copolyesters having kinks and rigid loops in polymer molecules were prepared by selecting suitable meta- and ortho-substituted monomers. The PET copolymer approach using PA to introduce rigid loops is more effective at reducing OPR than introducing kinks using IPA. However, copolymers made using substituted isophthalate provide OPR similar or lower than copolymers containing rigid loops. It is therefore not essen-

tial to use ortho-substituted monomers capable of forming rigid loop conformations to make an efficient barrier resin.

The barrier properties of the PET-copolymers are compared with PET/antiplasticizer blends made with suitable molecules capable of reducing segmental motion of PET. The blending of PET with a variety of phenolic compounds is found to be effective in reducing the oxygen permeability. It is shown that neither the phenolic group position (para-, ortho-, and meta-) nor the substitution hindering the phenolic groups has very little effect on OPR. Acetate derivatives of BP are not effective in reducing OPR. The crystallization rate of PET is enhanced by either blending with BP or copolymerization. This observation leads one to believe that the introduction of molecular heterogeneity into PET molecules enhances the crystallization rate, which is helpful for dimensional stability of films and articles. We have also demonstrated that compounds other than phenolics such as saccharin and phthalimide, are as effective as BPs in reducing OPR. In both copolymer and blend approaches, the reduction in OPR occurs by inhibiting the flipping of the benzene rings of the PET molecules. The PET copolymer approach is more appealing for making high-barrier resins and the criteria needed to select the appropriate comonomers to make effective high-barrier resins have been demonstrated.

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