

차세대 Barrier 물질 개발 동향

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A Practical Engineering for Advanced Barrier Materials: A Brief Review

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요약: 고분자의 용이한 가공성과 우수한 투명성, 그리고 합리적인 비용 효율로 인해 식품 포장 산업에서 금속이나 유리 용기들을 고분자 기반의 포장 소재들로 대체하려는 경향이 전 세계적으로 널리 퍼지고 있다. Barrier 고분자들은 산소, 이산화탄소, 수증기 등 대기 가스에 대한 낮은 투과성을 나타내고 있어 식품 포장 산업 이용에 유용하다. 이러한 식품 포장 산업의 전반적인 추세와 함께, 산소에 민감한 주스, 착향 음료, 그리고 에너지 음료 등 새로운 식품 산업의 성장으로 인해 고성능의 barrier 특성, 특히 O₂와 CO₂에 대해 낮은 투과성을 지닌 고분자 포장 소재의 개발이 시급한 상황이다. 기존의 고분자 기반한 barrier의 성능 향상은 새로운 식품 포장 산업에 급격한 변화를 줄 것이다. 본 총설에서는 (1) antiplasticization을 유도한 barrier 소재들, (2) antiplasticization과 crystallization을 사용한 barrier 성능 상승 효과, (3) 새로운 barrier 고분자들, (4) 나노합성 소재, (5) 혼합 고분자 등과 더불어, 차세대 포장 소재들의 특성 분석을 소개하고자 한다.

Abstract: A global trend of replacing metal or glass containers with polymer-based packaging materials has been prevalent in the food packaging industry due to their ease in processibility, excellent transparency, and good cost efficiency. Barrier polymers tend to show low permeabilities for atmospheric gases such as oxygen, carbon dioxide, and water vapor, which allow them to be utilized in the food and beverage packaging industry. With the current global trend, expansion of polymeric packaging materials to new markets such as oxygen sensitive juices, flavored water, and energy drinks requires improved CO₂ and O₂ barrier properties. The improvement of the existing polymer-based barrier platform will enable a rapid market impact. In this paper, the current barrier technologies such as (1) antiplasticization-induced barrier materials, (2) synergistic effect of antiplasticization and crystallization, (3) new barrier polymers, (4) nanocomposite materials, and (5) polymer blending are introduced with their characterization techniques for the development of advanced packaging materials.

Keywords: Barrier, polymer, packaging, characterization

1. Introduction

Polymeric materials exhibiting low permeabilities for atmospheric gases such as oxygen, carbon dioxide, and water vapor, are termed barrier polymers. Their ease of processibility and low permeability for those penetrants have promoted a general trend to replace glass with

plastic bottles in the food and beverage packaging industry. In general, barrier polymers tend to contain polar groups such as nitrile, ester, halogen (e.g., -Cl or -F), cyano, and etc, which induce strong chain-to-chain forces, subsequently reducing permeability by restricting the chain motion[1]. Fluoropolymers like polyvinylidene fluoride, poly(vinylidene chloride) (PVDC), ethylene vi-

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Table 1. Permeability of Oxygen, Carbon Dioxide and Water Vapor in Commonly Used Barrier Materials[2]

Polymer	Oxygen Permeability* cc.mm/m ² · day · atm [‡]	Carbon Dioxide Permeability* cc.mm/m ² · day · atm [‡]	Water Vapor Transmission g.mm/m ² · day
Poly(vinyl alcohol)	0.024 (24°C)	0.040	1247 (40% RH)
Poly(vinyl alcohol)-75% RH	0.09	-	-
Ethylene vinyl alcohol-dry (EVOH)	0.00008	0.000192	Poor barrier
Vectran V100P TM (dry) [#]	0.03	-	0.01
Vectran V100P TM (wet) [#]	0.02	0.05	-
Poly(ethylene)-LDPE	150.00	790.00	2.50
Poly(ethylene)-HDPE	69.57 (30°C)	229.70 (30°C)	-
Poly vinylidene chloride-Saran TM	0.47 (75% RH)	-	0.13 [‡]
Polyamide-Nylon 6	0.61-0.71 (40% RH)	5.90 (30°C)	15-16
Polyamide-Nylon 6	-	63.00 ^δ	-
Poly acrylonitrile	0.02	1.47	147 (100% RH)
Poly (ethylene terephthalate) oriented	1.2-2.4	5.9-9.8	0.39-0.51
Polycarbonate	102.4	307.1	14.9
Polypropylene	39	865	0.79
Polystyrene	118-157	394-590	0.79-3.9

* All permeability values are at 23°C, 0% RH unless otherwise specified.

‡ 1 cc.mm/m² · day · atm = 65.62 Barrer and 1 Barrer = 1 × 10⁻¹⁰ ccSTP · cm/cm²/s/cmHg[3]

An aromatic polyester produced by the polycondensation of 4-hydroxybenzoic acid and 6-hydroxynaphthalene-2-carboxylic acid.

‡: At 38°C, 90% RH

δ: At 30°C, 95-100% RH

nyl alcohol (EVOH), polyesters such as poly(ethylene terephthalate) and poly(ethylene naphthalate), and poly vinyl alcohol (PVAL) are examples of commonly used polymeric packaging materials. Many of these polymers (e.g., EVOH and PVAL) exhibit excellent barrier properties against oxygen in the absence of water and typically they are protected by water vapor barrier coatings in order to maintain their oxygen barrier function. Some of those barrier polymers, however, are less consumed mainly due to the environmental concern. For instance, PVDC containing chlorine produces toxic dioxins during the waste disposal, which induces a global trend to avoid chlorine. Table 1 shows the oxygen, carbon dioxide, and water vapor permeability of various barrier polymers being used.

Permeability is the most important practical transport parameter, and it gives an indication of barrier efficiency. The permeability of a single gas i , P_i , across a membrane of thickness l is defined as:

$$P_i \equiv \frac{(Flux)_i}{\Delta p_i / l} \quad (1)$$

where Δp_i is the pressure difference across the membrane, which is the driving force of permeation.

The overall driving force for the movement of a penetrant in membranes is the chemical potential gradient. The flux, J_i , of a component, i , is described by the Equation (2) where the chemical potential gradient is replaced by the concentration gradient.

$$J_i = -D_i \frac{dc_i}{dx} \quad (2)$$

Where J_i is the diffusive flux of penetrant i (mol/cm²/sec), D_i is the diffusion coefficient (cm²/sec), C_i is the concentration of penetrant i (mol/cc), and x is the diffusion distance (cm). The concentration gradient (really chemical potential gradient, which usually corre-

lates to the concentration gradient), a driving force for diffusion, enables a net diffusive flux to occur in a specific direction. Each gas penetrant tends to execute random movement due to its inherent nature called *Brownian motion*, but the overall flux occurs in the direction of decreasing concentration on statistical grounds. The sorption coefficient quantifies how much gas penetrant is taken up by a polymer at a given pressure. The gas penetrant in the gas phase is in equilibrium with that in the polymer phase and its distribution is expressed by using a sorption coefficient as follows:

$$C = S(p)p \quad (3)$$

where C is the concentration of the penetrant in the polymer phase, S is the apparent sorption coefficient, and p is the pressure of the penetrant in the gas phase. The combination of Equations (1), (2), and (3) shows that the permeability can be simply expressed as a product of the diffusion coefficient, D , and the sorption coefficient, S , as follows:

$$P = D \times S \quad (4)$$

Equation (4) shows that the permeation consists of two different processes: (i) diffusion (a kinetic factor) and (ii) sorption (a thermodynamic factor). Many research verified the effect of Fractional Free Volume (FFV) on gas permeability in dense and nonporous polymers by using an Equation (5)[4-7].

$$P = A_p \exp\left(-\frac{B_p}{FFV}\right) \quad (5)$$

Where A_p and B_p are adjustable constants depending only on temperature and penetrant type. The FFV is defined as:

$$FFV = \frac{\hat{V}_g - \hat{V}_0}{\hat{V}_0} \quad (6)$$

where \hat{V}_g is the specific volume of a glassy polymer at a given temperature and pressure and \hat{V}_0 is the specific occupied volume of a glassy polymer. In order to develop a better barrier material, it is critically important to understand the transport mechanism of penetrants through the polymer.

Packaging materials should have a low permeability to oxygen in order to reduce oxidative degradation and to preserve the quality of the product[8]. The presence of oxygen not only leads to an increase in the oxidation of fats and important nutrients like vitamin C, but it also results in the decomposition of proteins, discoloration, formation of harmful peroxides, etc. In addition, the oxygen concentration may also influence microbiological growth and metabolism[9]. Carbonated beverage packaging should have low carbon dioxide permeability since loss of carbonation limits its shelf life. Along with their low permeability against oxygen and carbon dioxide, they need to be easily processible since consumers prefer to have different options in regards to shape, size and color[10]. Furthermore, consumers like to see the contents inside a container so that they feel comfortable when they enjoy their soft drinks. General requirements that the packaging barrier films should meet are summarized as below:

1. Good barrier properties to gases and vapors
2. High mechanical strength
3. High thermal stability
4. Excellent optical transparency
5. Good chemical stability
6. Recyclability

This paper introduces various approaches for the barrier improvement with their corresponding performance as well as the principle behind each technology. Also, different characterization techniques for the evaluation of barrier efficiency will be discussed.

2. Recent Advances of Barrier Materials

2.1. Antiplasticization-induced barrier materials

Poly(ethylene terephthalate) (PET) has been widely used in the packaging industry, especially in beverage

packaging, due to its easy processibility, and excellent transparency as well as its good barrier properties. Extensive research has been performed to characterize PET for application in the packaging industry[11-16]. In the early stage of barrier material development, the question arose as to the relationship between barrier morphology and sample permeability. It has been found that crystallinity and orientation play a significant role in improving barrier property[1,17]. Michaels et al.[18,19] proposed that the crystallites are randomly distributed with respect to the solution-diffusion process, and behave as impermeable regions, reducing permeability. The reduction in permeability due to crystallinity results from two aspects: (1) diffusion coefficient is reduced due to the tortuous path caused by crystallites and (2) sorption coefficient is also reduced due to the reduction in amorphous volume phase.

Although PET is an excellent, broadly accepted barrier material for current generation applications, expansion to new markets requires improved barrier property compared to that of the state-of-the-art PET. When a low molecular weight diluent (LMWD) is introduced into a polymer at low concentration level, its modulus increases while its glass transition temperature decreases with reduction in permeability, which is the so-called antiplasticization. Antiplasticization is attractive for the improvement of PET barrier properties since it involves minimal modifications to the current processing platform. Jackson and Caldwell[20-22] pioneered that the incorporation of some LMTDs into polymers causes antiplasticization and suggested that the effect is attributed to the filling of free volume. Many research groups support the notion that antiplasticization occurs mainly via a simple "hole filling" mechanism, where the diluents reduce the free volume of the mixture by filling a portion of the excess free volume in the non-equilibrium glass[23-28]. Robeson and Faucher[29] first pointed out the importance of secondary loss transitions induced by antiplasticization by using dynamic mechanical measurement. They elucidated that the decrease in free volume contributes to hin-

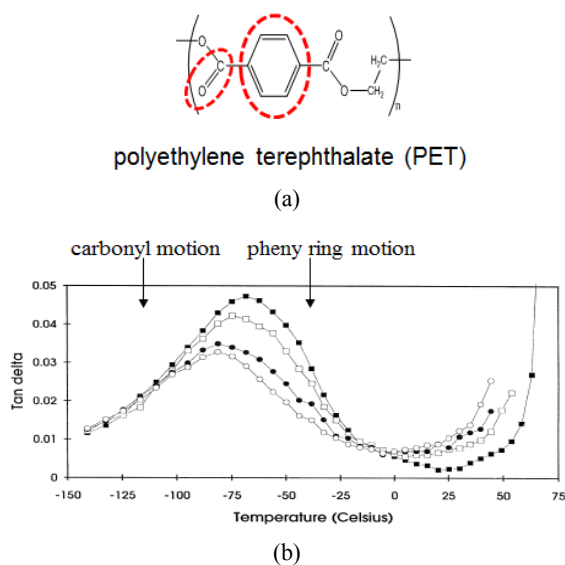


Fig. 1. (a) The chemical structure of PET, (b) The effect of different concentrations of dimethyl terephthalate (DMT) on the mechanical relaxation processes in PET at 1 Hz; ■, pristine PET; □, 2% DMT; ●, 10% DMT; ○, 20% DMT[30].

dering the motions of polymer segmental chains which are associated with the secondary transition. Maxwell et al.[30] well described the history of studies on relaxation processes associated with PET in their introduction. Illers and Breuer[31] suggested the mechanical relaxation peak for PET consists of more than one relaxation process. English[32] proposed that molecular motions of PET below the α relaxation should be attributed to motion of the phenyl rings. Since then, Maxwell et al.[30] confirmed that the β relaxation peak consists of two different relaxation processes based on dynamic mechanical and dielectric measurements; the lower temperature side is due to the motion of carbonyl groups while the higher temperature process is attributed to the motion of phenyl rings. They observed that a low concentration of additives suppress the flipping motion of the phenyl rings, while the motion of the neighbouring carbonyl groups are virtually unaltered (See Fig.1).

With investigations on relaxation processes, many researchers demonstrated reduction in permeability associated with antiplasticization in polymers[33-38]. Vrentas et

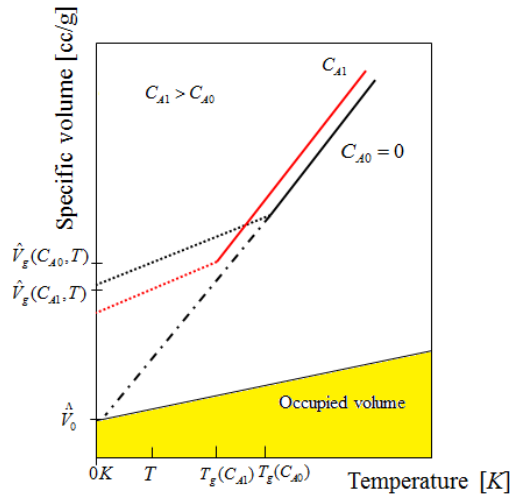
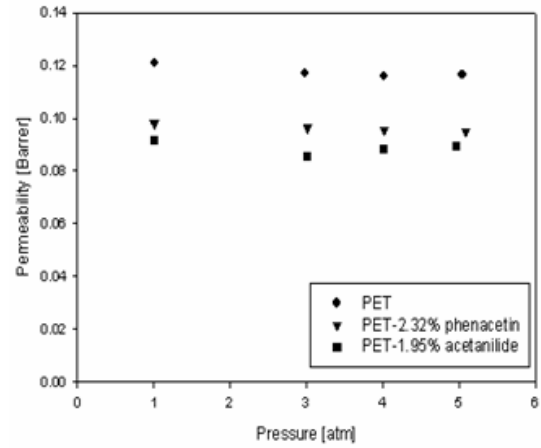


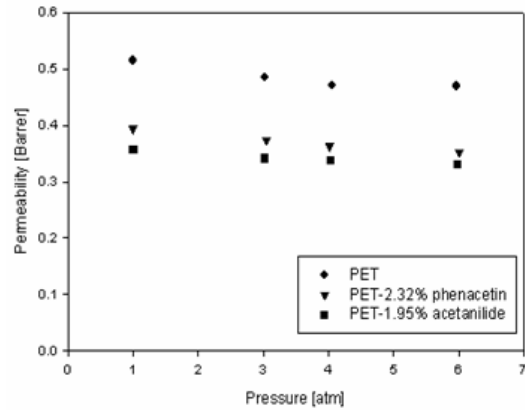
Fig. 2. Schematic of a temperature dependence of a specific volume behavior for antiplasticization.

al.[39] proposed a model that describes the change in the volumetric and the free volume properties of a glassy polymer upon antiplasticization. Antiplasticization is verified to be caused by a loss in free volume and a subsequent suppression of motions in the polymer chain. Maeda and Paul[33,34,40] elucidated the reduction in permeability induced by antiplasticization by a simple free volume treatment. Ruiz-Treviño and Paul[41] proposed a more user-friendly mathematical model for the specific volume change in the Polymer-LMWD system and suggested that its volume contraction is due to the decrease in nonequilibrium region of the mixture compared to that of the pure polymer.

Fig. 2 illustrates the effect of antiplasticization on glass transition temperature, T_g , and specific volume change[42]. The specific volume vs. temperature change of a pure polymer is indicated as the line labeled “ C_{A0} ”. For the case of antiplasticization, C_{A1} in the *rubbery state*, the specific volume of the mixture is greater than that of pure polymer assuming ideal mixing. The specific volume of polymer-additive mixture, $\hat{V}_g(C_{A1}, T)$, in the glassy state can be less than the specific volume of pure polymer, $\hat{V}_g(C_{A0}, T)$ in the glassy state at an arbitrary temperature, T below T_g (See red line curve labeled “ C_{A1} ”). This phenomenon is accompanied by antiplasticization. It is noticed that antiplasticization re-



(a) O₂ barrier properties at 35°C



(b) CO₂ barrier properties at 35°C

Fig. 3. Permeability for O₂ and CO₂ in PET, PET-2.32% phenacetin, and PET-1.95% acetanilide at 35°C (kindly borrowed from[28]).

duced its corresponding glass transition temperature, $T_g(C_{A1})$ compared to that of the pure polymer, $T_g(C_{A0})$. From Fig. 2, it is obvious that the *FFV* value at the arbitrary temperature, T , is clearly lower for the red (antiplasticization) case vs. the pure polymer case, which leads to reduction in both diffusion coefficient and permeability.

Lee et al.[28] demonstrated the barrier improvement of PET by incorporating model additives such as phenacetin and acetanilide into PET at a low concentration (i.e., ~2 wt%). They defined the barrier improvement factor (BIF) as the ratio of permeability of pure polymer to that of antiplasticized polymer and demonstrated that their antiplasticized PET samples (i.e.,

PET/phenacetin and PET/acetanilide) exhibited an average BIF value of ~ 1.23 and ~ 1.38 for O_2 and CO_2 , respectively (See Fig. 3). Also, they explained the antiplasticization based on the combination of free volume and interaction between PET and diluents. Larocca and Pessan[36] also claimed that the extent of antiplasticization depends on diluents' size, free volume of mixture, and interaction between polymer and diluents. Slark[43] has also found that the glass transition temperature, T_g , of polymer-LMWDs blends depends on the degree of interaction between polymer and LMWDs and the averaged polar/hydrogen bonding solubility parameters produce good correlations with change in T_g of polymer-LMWDs system. The solubility parameter approach assumes that the compatibility between polymer and LMWDs is inversely proportional to the quantity, $(\delta_{polymer} - \delta_{additive})^2$, where δ is the averaged polar/hydrogen bonding solubility parameter.

Most recently, Burgess et al.[44] thoroughly investigated caffeine-induced antiplasticization of amorphous PET using detailed oxygen and carbon dioxide transport studies, free volume characterization, and thermal/mechanical techniques. Caffeine is generally considered "safe" for human consumption, and consequently, is more practical as diluents compared to previously considered antiplasticizers for both PET[2,845,46] and other polymers[26,27,36]. This "safety" factor of antiplasticizers is most critical for food/beverage packaging applications, to address concerns regarding additive migration into the container contents. Besides safety advantages, high solubility of caffeine in the PET matrix makes it attractive as an antiplasticizer in PET. All the PET/caffeine samples studied in their work substantially improved barrier properties of PET (i.e., $>3\times$ for PET/caffeine (89.3/10.7 wt/wt)). Dynamic mechanical data recorded via $\tan \delta$ (i.e., E''/E' , or the ratio of loss modulus to storage modulus) as a function of temperature and frequency can provide useful information regarding the viscoelastic relaxations in PET. Specifically, characteristics of the sub-ambient beta (β) relaxation have been previously correlated with a wide variety of

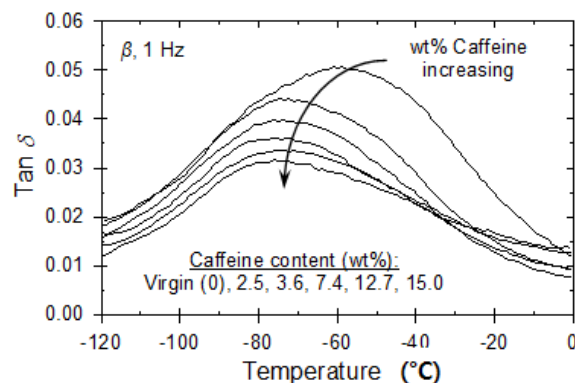


Fig. 4. Example $\tan \delta$ data at 1 Hz plotted over the temperature range of the β relaxation for various PET/caffeine samples. Data were smoothed over an interval of 10°C prior to plotting (kindly borrowed from[44]).

macroscopic properties for PET[45-50] and other polymers[47,50]. The β peak for PET, which occurs at approximately -60°C , differs from the alpha relaxation (α , or T_g) in that only localized chain motions can exist at temperatures so far below T_g in the glassy state[47,51,52]. The activation energy (E_A , kJ/mol) of the β relaxation can be calculated by applying the Arrhenius relationship in Equation (7) to data corresponding to the shift in β peak temperature (T , Kelvin) as a function of the dynamic test frequency (f , Hz), where A is a constant and R (8.314 J/mol \cdot K) is the gas constant.

$$f = A \exp\left(-\frac{E_A}{RT}\right) \quad (7)$$

Further information regarding the energetics of the β relaxation can be obtained via the activation entropy (ΔS), which is provided from Starkweather[53] in Equation (8).

$$E_A = RT \left[1 + \ln\left(\frac{k}{2\pi h}\right) + \ln\left(\frac{T}{f}\right) \right] + T\Delta S \quad (8)$$

In Equation (8), ΔS is the activation entropy of the β relaxation, k and h represent Boltzmann's and Planck's constants, respectively, and T , f , R , and E_A are the same respective parameters employed in Equation (7). The acti-

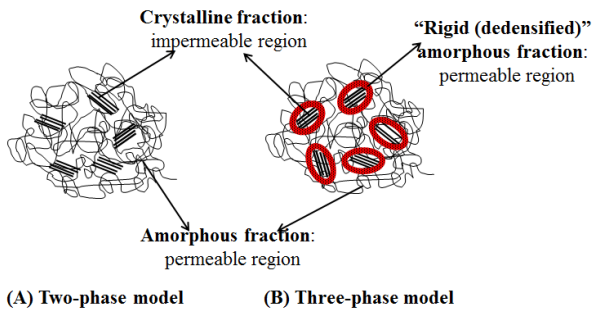


Fig. 5. Schematic illustration of different morphologies for semicrystalline polymers.

vation entropy, in the context of Starkweather, provides an estimate of the cooper activity between moieties and neighboring polymer chains involved in the respective relaxation[53-55]. Viscoelastic relaxations which involve significant long-range motion, such as the glass transition, incur large values of ΔS , while values pertaining to the β relaxation are significantly smaller in magnitude[52,53]. Example $\tan \delta$ data at 1 Hz over the temperature range of the β relaxation are plotted in Fig. 4 for various PET/caffeine samples.

2.2. Synergistic effect of antiplasticization and crystallization

Lasoski and Cobbs[56] demonstrated that water vapor permeability in semicrystalline PET increases directly as the square of the amorphous volume fraction. The square dependency of permeability with amorphous volume fraction is based on two assumptions: (1) a semicrystalline PET consists of two phases (i.e. the amorphous and crystalline phases) and (2) both sorption and diffusion happen only in amorphous phases. Michaels et al.[11] also observed that the diffusion in semicrystalline PET is inversely proportional to the tortuosity factor induced by the crystallites in the case of unoriented crystalline PET. However, it should be noted that their permeation experiment for carbon dioxide was performed within the Henry's law region to avoid complication due to concentration effects. As for the solubility, Michaels et al.[57] elucidated that gas solubility in semicrystalline PET is reduced with an increase in crystallinity, but not in di-

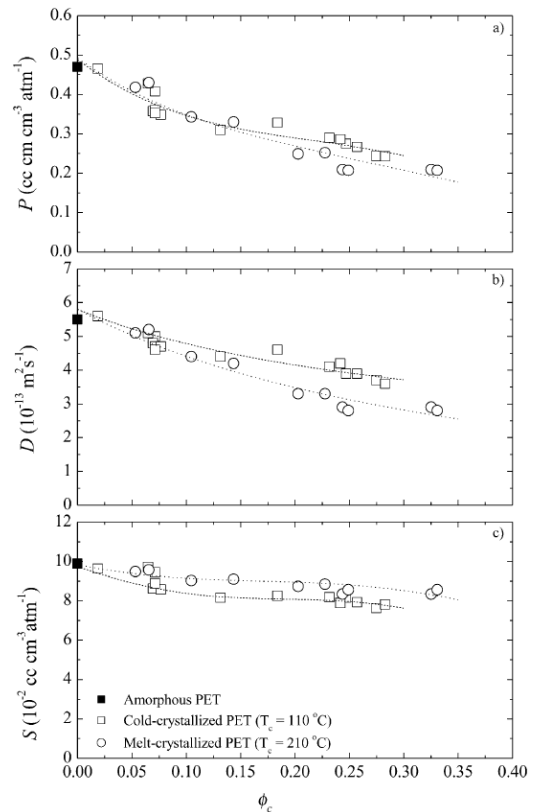


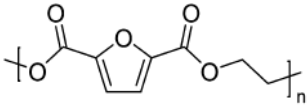
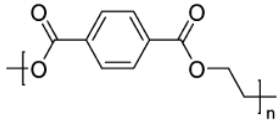
Fig. 6. Effect of crystalline volume fraction on O₂ transport results: (a) permeability, (b) diffusivity, (c) solubility for cold-crystallized at 110°C and melt-crystallized at 210°C PET (Kindly taken from[59]).

rect proportion with the decrease in amorphous volume as expected. They suggested that the non-equilibrium regions are higher in concentration in a glassy semi-crystalline PET than in the amorphous material, leading to higher solubility than expected. Since then, a third phase at the interface between bulk amorphous regions and impermeable crystalline regions for a semi-crystalline polymer has been considered by many researchers (See Fig. 5)[58-62].

More recently, Sekelik et al.[63] demonstrated that the reduction of oxygen permeability in PET as a function of crystallinity is described by Nielsen's model as follows:

$$P = P_0 \frac{1 - \phi}{1 + \alpha \phi / 2} \tag{9}$$

Table 2. Structural and Physical Property Information for Amorphous PEF and PET[52]

Polymer	Structure	ρ (g/cc)	Tg (°C)
Poly(ethylene furanoate)		1.4299	85
Poly(ethylene terephthalate)		1.3346	76

where ϕ is the crystalline volume fraction and P_0 is the permeability of perfectly amorphous polymers. For $\alpha = 1$, Equation (9) becomes Maxwell's solution for impermeable spheres. Lin et al.[59] also proposed that the overall oxygen solubility in crystallized PET consists of two independent contributions; the solubility of the bulky amorphous phase and that of the interfacial amorphous phase (See Fig. 6). All researchers mentioned above except Lasoski et al.[56] directly or indirectly pointed out that there certainly exists an intermediate phase between the bulk amorphous phase and the crystalline phase in semicrystalline PET. At this point, it is not clear why water vapor follows square dependence of its permeability in semicrystalline PET. Nevertheless, the presence of the interfacial phase in semicrystalline PET has been investigated by other researchers[64-69].

Reducing dedensification of the interfacial phase in semicrystalline PET is of key interest to achieve a more effective barrier improvement of crystallized PET. Hu et al.[70] demonstrated that copolymerization of PET with isophthalate prevented dedensification of the interfacial phase in crystallized PET since comonomers are forced to be excluded from the PET crystalline lattice[71] and thereby, cold crystallization induces comonomer units to be located in the amorphous phase. It was proposed that the segregation of kinked isophthalate units to the amorphous regions of the spherulite facilitates the polymer segmental relaxation in the interlamellar amorphous region[70].

2.3. New barrier polymers

Recently, a translucent liquid crystalline polymer (LCP) in a thin layer was developed by Ticona and its oxygen barrier properties are 50-100 fold higher than those of PET[72]. However, it is quite costly and so it is not commercialized to date. The Dow Chemical Company developed the thermoplastic epoxy resins [poly(amino ethers)] with a trade name of Blox[73,74]. These resins typically exhibit a 50-fold reduction in O_2 permeability compared to that of PET. Gandini et al.[75] synthesized poly(ethylene furanoate) (PEF), the furan-derived analogue to PET (See Table 2), using an antimony catalyst in the transesterification step and subsequently characterized the results using various characterization techniques including differential scanning calorimetry (DSC), infrared spectroscopy (IR), and NMR. Recently, Burgess et al.[52] performed a thorough investigation on the barrier, mechanical and thermal properties of PEF. The results from various characterization techniques including DMA, ^{13}C -CP/MAS solid-state NMR variable contact-time experiments, and center-band-only detection of exchange (CODEX) measurements reflect that the furan ring-flipping in PEF was highly suppressed due to the energy penalty associated with the nonlinear axis of ring rotation and ring polarity. Fig. 7 compares the CODEX spectra for amorphous PEF vs. PET, reflecting that the flipping motion of the furan ring in PEF was greatly suppressed.

2.4. Nanocomposite materials

Nanocomposites have been extensively investigated for various applications (e.g., medicine, microelectronics,

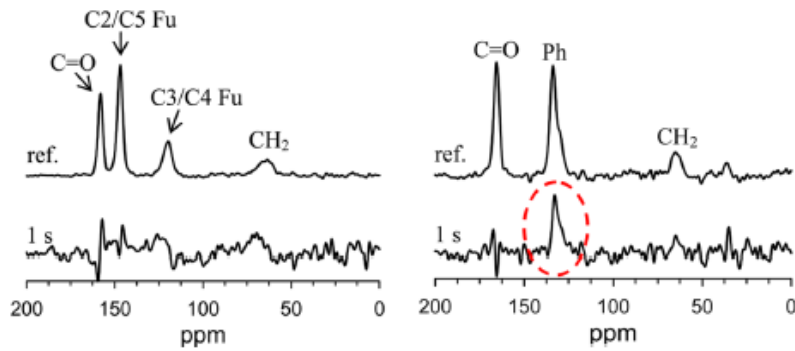


Fig. 7. CODEX spectra (bottom) for amorphous PEF (left) and PET (right) measured at room temperature for $t_m = 1$ s. The top curve represents the corresponding reference spectra. Conclusive evidence for an aromatic peak in the CODEX spectrum is found only for PET (encircled), while the absence in the PEF spectra provides evidence for the hindrance of furan ring flips (kindly taken from[52]).

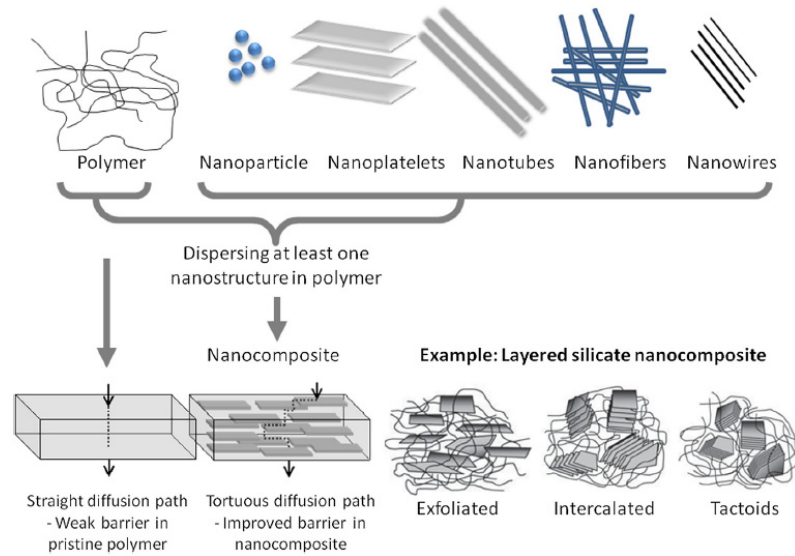


Fig. 8. Schematic illustration of the morphology for different nanocomposites and improvement of the barrier properties (kindly taken from[78]).

and the chemical industry) since Toyota’s Central Research Laboratory has prepared clay mineral-nylon nanocomposites for the automotive applications in the 1980s[76,77]. Their macroscopic properties including thermomechanical or barrier performance are determined mainly by the structure and dynamics in nanocomposites so that the extent of filler dispersion and the strength of matrix-nanoparticle interactions are critical. The clay nanoparticles behave as impermeable physical barriers in a nanocomposite matrix that they decelerate the diffusion of gas or vapor penetrants, improving barrier properties. Nevertheless, the precautionary approach

should be applied especially on the migration of nano-materials in the food contents for safety. Fig. 8 describes different types of nanocomposites and illustrates how these materials improve the barrier properties compared to the pristine polymeric materials.

Many research groups have investigated polymer/clay nanocomposite materials for the barrier property improvement. The incorporation of 5 wt% nanoclay to PET enhanced O_2 barrier properties by a factor of 15 with relatively lower reduction in H_2O permeability by 13%[79]. Xie et al.[80] demonstrated that their low density polyethylene (LDPE)/organic montmorillonite (OMMT) sample

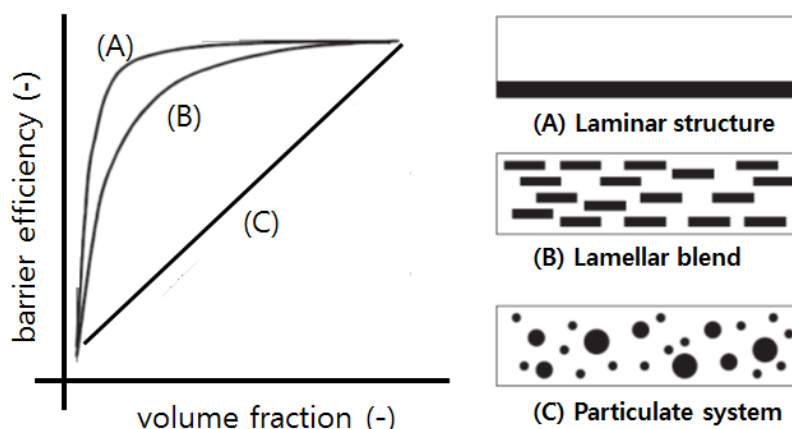


Fig. 9. Schematic of barrier efficiency as a function of high-barrier volume fraction in barrier blends (kindly borrowed from[10]).

improved the O₂ barrier properties by 7 times compared to the LDPE. Frounchi and Dourbash[81] also confirmed that two different montmorillonite-based organoclays containing PET samples enhanced O₂ barrier properties compared to those of PET. They observed that nanocomposites with lower organoclay contents were exfoliated while those with relatively higher organoclay contents were mostly intercalated.

2.5. Polymer blending

Blending is a simple and economical approach to improve the barrier efficiency by incorporating an excellent, but expensive barrier material in low-cost polymer matrix. However, it should be noted that blends are difficult to recycle. Fig. 9 illustrates the barrier efficiency of a blend as a function of the morphology. The structure of blends can be (a) a fully laminar system, where the barrier polymer is present as a continuous layer, (b) lamellar blends, where the barrier polymers are interleaved in a polymer matrix or (C) a particulate system where an isotropic form of barrier polymers is present.

The ethylene vinyl alcohol (EVOH), an excellent oxygen barrier was blended in polypropylene or polyamide[82-84]. Faisant et al.[82] successfully demonstrated that the extruded polypropylene (PP)/ethylene vinyl alcohol (EVOH) (80/20 vol/vol) blends induced a significant reduction in O₂ permeability by 85% compared to the extruded PP. Jang and Lee[85] blended

PP with polyvinyl alcohol (PVA) and demonstrated that their biaxially oriented PP/PVA blend film exhibited a substantial enhancement for the oxygen barrier property compared to the biaxially oriented PP film (i.e., BIF = 140).

3. Conclusions

Plastic packaging materials are attractive in food and beverage industry due to their ease of processibility, excellent optical transparency, and good cost efficiency. There are a number of important issues to consider for the development of polymer-based food packaging materials. The most critical one is the safety concern due to possible migration of additives from the packaging materials into the food contents and their toxicological effects. Besides, their barrier properties should be improved to replace metal or glass packaging materials. Several different approaches are considered to improve the barrier efficiency of the current packaging materials including (1) antiplasticization-induced barrier materials, (2) synergistic effect of antiplasticization and crystallization, (3) new barrier polymers, (4) nanocomposite materials, and (5) polymer blending. In addition to transport characterization, various characterization techniques such as DMA and NMR can be also utilized to evaluate the barrier efficiency of polymeric packaging materials.

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