

# Plasticizer Effect on Oxygen Permeability of $\beta$ -Lactoglobulin Films

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Plasticizer effect on oxygen permeability (OP) of  $\beta$ -lactoglobulin ( $\beta$ -Lg) films was studied. Propylene glycol (PG), glycerol (Gly), sorbitol (Sor), sucrose (Suc), and polyethylene glycol at MW 200 and 400 (PEG 200 and PEG 400, respectively) were studied due to their differences in composition, shape, and size. Suc-plasticized  $\beta$ -Lg films gave the best oxygen barrier (OP < 0.05 cm<sup>3</sup>· $\mu$ m/m<sup>2</sup>·day·kPa). Gly- and PG-plasticized films had similar OP values, and both had higher OP than Sor-plasticized films. PEG 200- and PEG 400-plasticized films were the poorest oxygen barriers. Empirical equations including plasticizer efficiencies for OP were employed to elucidate the relationships between OP of plasticized  $\beta$ -Lg films and plasticizer type and content. Plasticizer efficiency ratios between mechanical and OP properties of  $\beta$ -Lg films show the relative efficiency of plasticizers in modifying mechanical and OP properties. A large ratio is desirable.

**Keywords:**  $\beta$ -Lactoglobulin; edible films; plasticizer; oxygen permeability

## INTRODUCTION

The transfer of oxygen to food from the environment has an important effect on food quality and shelf life. Oxygen causes food deterioration such as lipid and vitamin oxidation, leading to sensory and nutrient changes. Edible films and coatings can prevent deterioration for many food products because they often possess excellent oxygen barrier properties (Miller and Krochta, 1997). Edible films and coatings can also control respiration in fruits and vegetables, depending on film formation materials used (Cuq et al., 1998). The potential applications of edible films also include coatings on fruits, for example, apples, citrus fruits, and pears, to prevent moisture loss and improve gloss (Grant and Burns, 1994). Nevertheless, basic research is still needed to gain more understanding on film structure–property relationships to improve opportunities for food applications.

$\beta$ -Lactoglobulin ( $\beta$ -Lg) is the principal component (~56.5% of total whey protein, MW = 18300 Da) in whey protein (Dybing and Smith, 1991).  $\beta$ -Lg film properties such as transparency, water vapor permeability (WVP), oxygen permeability (OP), and mechanical properties are identical or quite similar to properties of whey protein isolate (WPI) films (Mate and Krochta, 1996; Anker et al., 1998).  $\beta$ -Lg and WPI are generally heated to denature protein and expose the internal sulfhydryl groups to allow formation of intermolecular disulfide bonds, which affect the film structure (McHugh et al., 1994; Mate and Krochta, 1996). Both  $\beta$ -Lg and WPI require plasticizer addition to overcome film brittleness. However, studies of  $\beta$ -Lg and WPI films have mainly involved only one type of plasticizer at a time. Very little research has examined the effect on film properties of different types of plasticizer.

Generally, plasticizers are required for both polysaccharide- and protein-based edible films. Plasticizers are low molecular weight substances that are incorporated into the polymer matrix (protein or polysaccharide) to increase film flexibility and processability. Plasticizers increase the free volume or molecular mobility of polymers by reducing hydrogen bonding between polymer chains. A plasticizer's composition, size, and shape influence its ability to disrupt protein-chain hydrogen bonding, including its ability to attract water to the plasticized protein system. Water is an effective plasticizer for protein films. Thus, attracted water influences the plasticizing ability of an added plasticizer. A previous study on the effect of plasticizer on  $\beta$ -Lg film mechanical properties showed that plasticizer improved mechanical properties to varying degrees depending on plasticizer type and concentration (Sothornvit and Krochta, 2000). Oxygen barrier properties have been shown to be important properties for films from several proteins, such as wheat gluten (Gennadios et al., 1993), soy protein isolate (Brandenburg et al., 1993), WPI (McHugh et al., 1994; Mate and Krochta, 1996), and  $\beta$ -Lg (Mate and Krochta, 1996). Our study examined the effect of several plasticizers on plasticized  $\beta$ -Lg films to determine plasticizer efficiency on film OP. The six plasticizers studied, including glycerol (Gly), propylene glycol (PG), polyethylene glycol at molecular weights of 200 and 400 (PEG 200 and PEG 400, respectively), sorbitol (Sor), and sucrose (Suc), possess various compositions, sizes, and shapes. Among these, Gly and PG have the best water binding, followed by PEG 400, Sor, and Suc (Sloan, 1976). We hypothesized that these differences would affect film OP. Therefore, our objective was to compare and quantify effects of plasticizer composition, size, and shape on  $\beta$ -Lg film oxygen permeability.

## MATERIALS AND METHODS

**Materials.**  $\beta$ -Lg [98.2% protein dry basis (db)] supplied by Davisco Foods International (Le Sueur, MN) was used to make films. PG, PEG 200, and PEG 400 were purchased from

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Aldrich (Milwaukee, WI). Gly, Sor, and Suc were purchased from Fisher Scientific Inc. (Fair Lawn, NJ).

**Film Formation.**  $\beta$ -Lg solutions (10% w/w) at pH  $\sim$ 7 were used to form films as described in a previous study (Sothornvit and Krochta, 2000). Plasticizer concentrations in the  $\beta$ -Lg solutions were 0.34, 0.44, 0.54, or 0.64 M. A  $\beta$ -Lg and plasticizer solution containing 3 g of total solids was pipetted onto a 14.7 cm internal diameter, rimmed, smooth high-density polyethylene (HDPE) casting plate. The casting plate was placed on a leveled surface at ambient temperature [23 °C and 35  $\pm$  5% relative humidity (RH)] until dried film could be peeled from it. Three film replications were used to determine oxygen permeability (OP).

**Film Thickness.** Film thickness was measured with a micrometer (No. 7326, Mitutoyo Manufacturing Co., Ltd., Japan) to  $\pm$ 0.0001 in. (0.00254 mm) at four random positions. An average was used to determine OP.

**OP Measurement.** An Ox-Tran 2/20 ML modular system (Modern Controls, Inc., Minneapolis, MN) was used to determine the OP of plasticized  $\beta$ -Lg films at 23 °C and 50  $\pm$  1% RH, according to the American Society of Testing and Materials Standard Method D3985 (ASTM, 1995). A stainless steel mask with 5 cm<sup>2</sup> of open testing area was used to reduce oxygen transfer in a film. One side of the film was exposed to nitrogen gas flow, and the other side was exposed to oxygen gas flow at 23 °C and 50  $\pm$  1% RH.

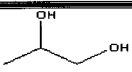
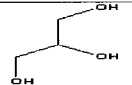
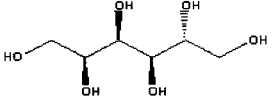
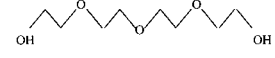
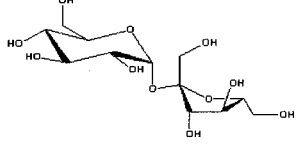
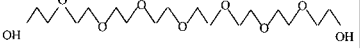
**Statistical Analyses.** A completely randomized experimental design was used to study the following factors: (1) plasticizer type, (2) plasticizer concentration, and (3) interaction between plasticizer type and concentration. SAS system software program, release 6.12 (SAS Institute Inc., 1996), was utilized to calculate analysis of variance (ANOVA) using the General Linear Models Procedure PROC GLM, and a Duncan's multiple-range test was used to determine the significant treatments at 95% confidence interval.

## RESULTS AND DISCUSSION

Polymer science principles can be used to explain the behavior of food biopolymer films, including the plasticization effect. The barrier properties of polymer films are generally related to the physical and chemical nature of the polymers. The chemical structure of the polymer backbone, the degree of crystallinity and orientation of molecular chains, and the nature of the plasticizer added all affect barrier properties (Salame, 1986). Plasticizers need to be compatible with the polymer, permanent in the system and efficient to accomplish the desirable film properties (Banker, 1966). Table 1 shows the plasticizers we studied to determine the effect of plasticizer composition, shape, and size on  $\beta$ -Lg film oxygen barrier.

**Plasticizer Effect and Bases of Comparison.** Plasticizer not only reduced film brittleness but also generally increased film permeabilities. All plasticized  $\beta$ -Lg films were colorless and transparent. Sor- and Suc-plasticized  $\beta$ -Lg films at the highest plasticizer content tended to crystallize after 1 month of storage at ambient temperature and intermediate RH (35  $\pm$  5% RH), because both are solid forms in this condition. Sor was more likely to crystallize than Suc. This might be due to the bulky molecules and low hygroscopicity of Suc (Sloan, 1976), which retard migration and crystallization. Plasticizer type, concentration, and interaction between type and concentration of plasticizer produced significant difference ( $p \leq 0.05$ ) in OP. Salame (1986) defined a barrier polymer as a polymer having an OP value of  $<38.9 \text{ cm}^3 \cdot \mu\text{m}/\text{m}^2 \cdot \text{day} \cdot \text{kPa}$  at 23 °C. Broadly, the plasticizers we studied can be classified in two groups according to this criterion. PG-, Gly-, Suc-, and Sor-plasticized  $\beta$ -Lg films were excellent oxygen barriers,

**Table 1. Plasticizers Selected for Study and Their Properties**

Plasticizer Type	MW	Chemical Structure
Propylene glycol (PG)	76	
Glycerol (Gly)	92	
Sorbitol (Sor)	182	
Polyethylene glycol 200 (PEG 200)	200	
Sucrose (Suc)	342	
Polyethylene glycol 400 (PEG 400)	400	

ers, whereas both PEG 200- and PEG 400-plasticized films were poor oxygen barriers.

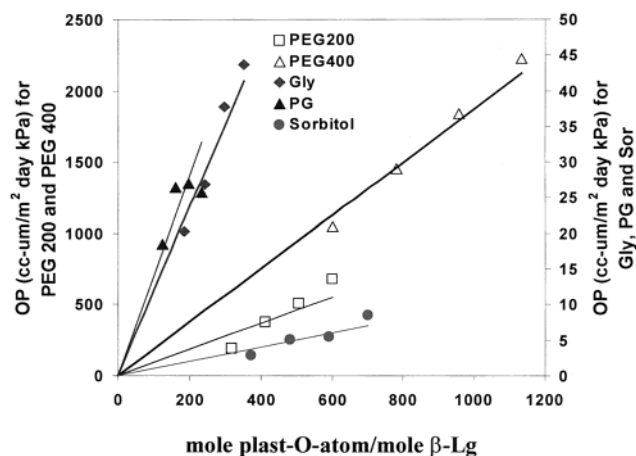
To compare the plasticizers studied, three different bases was employed, namely, moles of plasticizer multiplied by the number of oxygen atoms in each plasticizer per mole of  $\beta$ -Lg (Figure 1), moles of plasticizer per mole of  $\beta$ -Lg (Figure 2), and mass of plasticizer per mass of  $\beta$ -Lg (Figure 3). The reason for these bases was explained in previous work (Sothornvit and Krochta, 2000).

**Effect of Suc.** The OP of Suc-plasticized  $\beta$ -Lg films could not be exactly determined because it was below the limit of detection ( $0.05 \text{ cm}^3 \cdot \mu\text{m}/\text{m}^2 \cdot \text{day} \cdot \text{kPa}$ ) of the Ox-Tran 2/20 ML at each film content studied. Thus, the OP of Suc-plasticized  $\beta$ -Lg films was reported as  $<0.05 \text{ cm}^3 \cdot \mu\text{m}/\text{m}^2 \cdot \text{day} \cdot \text{kPa}$ . This very low OP is attributed to the ring structure and size of Suc, which prevent efficient disruption of hydrogen bonding between protein chains. This result corresponds to previous results on film mechanical properties, showing that Suc is also the least efficient plasticizer in terms of lowering  $\beta$ -Lg film elastic modulus and tensile strength values (Sothornvit and Krochta, 2000).

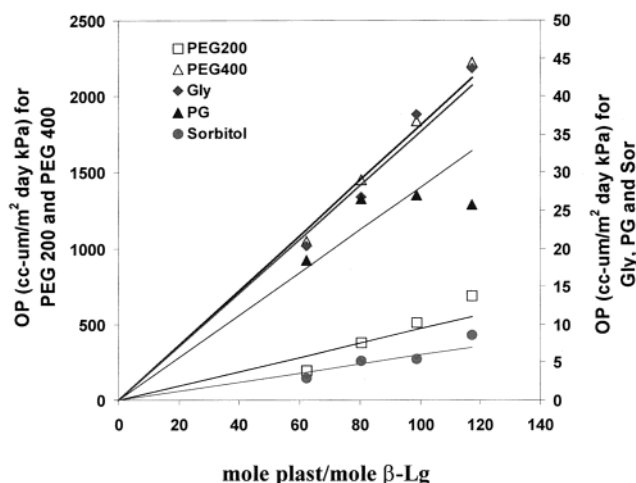
Cherian et al. (1995) reported that Suc-plasticized gluten films had a higher glass transition temperature ( $T_g$ ) than Gly-plasticized gluten films. They found that Suc crystallized during the increase of the temperature through the  $T_g$  region at lower moisture content [5–13% wet basis (wb)]. Therefore, Suc-plasticized  $\beta$ -Lg films are stronger than Gly-plasticized  $\beta$ -Lg films.

**Effect of PG, Gly, Sor, PEG 200, and PEG 400.** All of these plasticizers are considered as polyols and possess different compositions, shapes, and sizes. For each basis, OP of each plasticized film displayed linear dependence on plasticizer content.

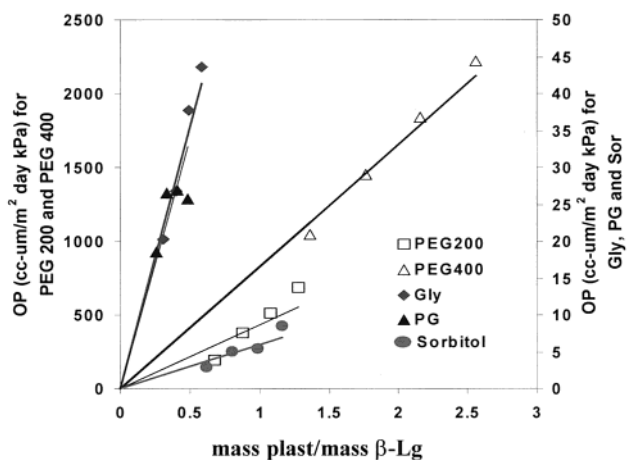
**Determination of  $k_{OP}$ .** From the lowest value to the highest value of OP, films plasticized with Sor, Gly, and



**Figure 1.** Effect of plasticizer on OP of  $\beta$ -Lg films based on moles of plasticizer oxygen atoms per mole of  $\beta$ -Lg. The symbols represent the data sets, and the lines represent the empirical fitting results with zero intercept.



**Figure 2.** Effect of plasticizer on OP of  $\beta$ -Lg films based on moles of plasticizer per mole of  $\beta$ -Lg. The symbols represent the data sets, and the lines represent the empirical fitting results with zero intercept.



**Figure 3.** Effect of plasticizer on OP of  $\beta$ -Lg films based on mass of plasticizer per mass of  $\beta$ -Lg. The symbols represent the data sets, and the lines represent the empirical fitting results with zero intercept.

PG were excellent oxygen barriers, whereas films with PEG 200 and PEG 400 were poor oxygen barriers. As mentioned earlier, OP values showed a linear dependence on plasticizer content.  $\beta$ -Lg films without plasti-

**Table 2. Plasticizer Efficiencies ( $k_{OP}$ ) for OP ( $\text{cm}^3\text{-mm}/\text{m}^2\text{-day}\cdot\text{kPa}$ ) for Different Plasticizers**

plasticizer	$k_{OP}$ value <sup>a</sup> based on		
	mol of plasticizer O atoms per mol of $\beta$ -Lg	mol of plasticizer per mol of $\beta$ -Lg	mass of plasticizer per mass of $\beta$ -Lg
PG	0.13994	0.27984	67.395
Gly	0.11774	0.35321	70.255
Sor	0.00993	0.05959	5.9918
PEG 200	0.91746	4.7117	431.16
Suc	<0.00014 <sup>b</sup>	<0.00043 <sup>b</sup>	<0.08492 <sup>b</sup>
PEG 400	1.86867	18.102	828.23

<sup>a</sup> From the general equation  $OP = k_{OP}x$ , where  $x$  = plasticizer content on bases indicated in table. <sup>b</sup> Estimated from OP value at detection limit and the highest sucrose content studied.

cizer are far below their  $T_g$  and extremely brittle and present an extremely good oxygen barrier. Unfortunately, it is difficult to produce films in this brittle condition and test for film OP. Thus, an assumption was made that no discontinuities in OP occurred at lower plasticizer concentration, and extrapolation of all data to zero OP at zero plasticizer content was employed. In fact, a linear dependence between OP and plasticizer content through the origin fit experimental data well:

$$OP = k_{OP}x \quad (1)$$

where  $k_{OP}$  is plasticizer efficiency for OP and  $x$  is plasticizer content/ $\beta$ -Lg content depending on the basis. For Suc-plasticized films,  $k_{OP}$  can be estimated from the OP value at the Ox-Tran 2/20 ML detection limit and the highest Suc content (Table 2). The higher the  $k_{OP}$  is, the higher the plasticizer efficiency is in terms of increasing OP. The  $k_{OP}$  values for all three different bases are shown in Table 2, based on the best fits between OP and plasticizer contents shown in Figures 1, 2, and 3, respectively, on all three bases. Overall,  $k_{OP}$  increased in the following order for all bases: Suc < Sor < PG, Gly < PEG 200 < PEG 400. Therefore, the following discussion refers to results for all three bases.

(1) *Plasticizer Size (MW) Effects.* Three plasticizer categories were identified related to size effects. First, PG- and Gly-plasticized  $\beta$ -Lg films showed no significant difference ( $p > 0.05$ ) in OP, presumably due to plasticizer structure and hygroscopic similarity. In addition, the number of O atoms did not cause any differences between these two plasticizers.

Second, Sor- and Gly-plasticized  $\beta$ -Lg films also have similarity in their straight-chain structure. However, Sor gave lower OP values and lower  $k_{OP}$  values than Gly (Table 2). This corresponds to the higher EM and TS for Sor- $\beta$ -Lg films compared to Gly- $\beta$ -Lg films from the earlier work (Sothornvit and Krochta, 2000). This seems to suggest that the larger size and lower hygroscopicity of Sor compared to Gly reduces its ability to affect hydrogen bonding between protein chains. Moreover, the higher number of O atoms of Sor did not provide a higher plasticization effect. The result is Sor- $\beta$ -Lg films, which have lower OP, have higher EM and TS compared to Gly- $\beta$ -Lg films at the same plasticizer content, no matter what the basis. Sor also imparted a lower OP than Gly in whey protein films (McHugh and Krochta, 1994) and casein-based films (Chick and Ustunol, 1998). However, Sor-plasticized gelatin-soluble starch films (Arvanitoyannis et al., 1997), sodium caseinate-soluble starch films (Arvanitoyannis and Billaderis, 1998), and methylcellulose-soluble starch films

(Arvanitoyannis and Biliaderis, 1999) had higher OP values than Gly-plasticized films on mass basis.

Third, a comparison between PEG 200 and PEG 400 is possible because of the similarity in molecular composition and shape. In this case, PEG 400 imparted a higher  $k_{OP}$  value than PEG 200 (Table 2). The result is contradictory to the above comparison of Gly- and Sor- $\beta$ -Lg films, where the larger Sor was a less efficient plasticizer. This might be due to the difference in the arrangement of O atoms among Gly, Sor, and PEGs. PEG-O atoms alternate with two carbon atoms along the molecule backbone. Therefore, there may be more room to form H-bonds with protein chains, compared to the OH groups which are on adjacent C atoms in Gly and Sor. Our result with PEGs is also contradictory to the result from Donhowe and Fennema (1993), who studied the effect of PEG plasticizer (PEG 400, PEG 1450, PEG 8000, and PEG 20000 at 30% db) on OP of methylcellulose (MC) films. They found that PEG with higher MW gave smaller film OP values. They hypothesized that higher MW PEG resulted in reduced interaction between PEG and MC. This may be right in their case, because they were working with higher MW PEGs than in our study. Also, PEG with MW >400 is solid at ambient temperature, so it might be less compatible with MC. This makes it difficult to compare our results and their results.

However, our results with PEG are consistent with those of di Gioia et al. (1998), who concluded that increasing plasticizer MWs from 60 to 300 (urea < Gly < diethanolamine < triethanolamine < PEG 300) increased the plasticizing efficiency by lowering the  $T_g$  values of corn gluten meal films.

(2) *Plasticizer Shape Effects.* Our main focus was on the shape comparison between PEG 200 and PEG 400 (straight chains) and Suc (ring structure with MW 342). The estimated extremely low  $k_{OP}$  value of Suc reflects the excellent oxygen barrier of Suc-plasticized  $\beta$ -Lg films. The lower OP value of Suc suggests that the bulky ring structure and low water-attracting ability of Suc limit its ability to reduce protein chain hydrogen bonding compared to the straight-chain PEGs of similar MW. The structure of Suc and interactions among Suc molecules may also obstruct oxygen transmission through Suc-plasticized films. These results with OP correspond to the effect of Suc on the mechanical properties of  $\beta$ -Lg films. Suc-plasticized  $\beta$ -Lg films were stiffer and stronger than both PEG 200- and PEG 400-plasticized films (Sothornvit and Krochta, 2000).

(3) *Number of Plasticizer O Atoms.* The OP and resulting  $k_{OP}$  of Sor-plasticized films were lower than those of PEG 200, even though Sor has one more O atom than PEG 200. This might be due to the availability of O atoms to interact with  $\beta$ -Lg. The spacing of O atoms in PEG 200 may have allowed more room for the formation of H-bonding with  $\beta$ -Lg (Table 1) and thus provided more flexible films. These OP results are consistent with film mechanical properties. It was shown earlier that PEG 200-plasticized films were more flexible, that is, provided more free volume in the  $\beta$ -Lg matrix compared to the Sor-plasticized films (Sothornvit and Krochta, 2000). Greater free volume in the  $\beta$ -Lg matrix also allows easier transmission of oxygen through the films.

Sor-plasticized  $\beta$ -Lg films also had lower OP and resulting lower  $k_{OP}$  values than films plasticized with Gly, even though Sor has a higher number of O atoms.

**Table 3. Plasticizer Efficiency Ratios between Mechanical Properties and OP of Various Plasticizers with  $\beta$ -Lg Films**

property (Y) (MPa)	plasticizer	$k_{MO}$ value <sup>a</sup>
EM	Gly	0.050
	Sor	0.392
	PEG 200	0.006
	Suc	17.16 <sup>b</sup>
	PEG 400	0.002
TS	Gly	0.048
	Sor	0.378
	PEG 200	0.006
	Suc	15.7 <sup>b</sup>
	PEG 400	0.002

<sup>a</sup>  $k_{MO} = k_{EM}/k_{OP}$  or  $k_{TS}/k_{OP}$  based on type of mechanical properties on all bases. <sup>b</sup> Estimated from OP value at detection limit and the highest sucrose content studied.

Similar results occurred with whey protein films (McHugh et al., 1994) and casein films (Chick and Ustunol, 1998). Thus, for milk proteins, size of plasticizer appears to have greater importance than number of O atoms for plasticizers with similar chemical compositions. Arvanitoyannis et al. (1997) found for Sor-plasticized gelatin/soluble starch films slightly greater OP than in Gly-plasticized films.

Another comparison is Suc (number of O atoms = 11) and PEG 400 (number of O atoms = 9). Suc-plasticized  $\beta$ -Lg films had significantly greater oxygen barrier, and they were stiffer and stronger. In this comparison, plasticizer shape and the lower hygroscopicity of Suc compared to PEG 400 appear to have greater importance than number of O atoms.

*Correlation between Mechanical Properties and OP.* As shown above, film OP seems to have an important relationship to film mechanical properties. From our previous study, elastic modulus (EM) and tensile strength (TS) had the following exponential relationships with plasticizer content:

$$EM = 1500 e^{-k_{EM}x} \quad (2)$$

$$TS = 37.28 e^{-k_{TS}x} \quad (3)$$

$$\text{from eq 1, } x = OP/k_{OP} \quad (4)$$

Substituting eq 4 into eqs 2 and 3, we get

$$EM = 1500 e^{-(k_{EM}/k_{OP})OP} \quad (5)$$

$$TS = 37.28 e^{-(k_{TS}/k_{OP})OP} \quad (6)$$

Thus, mechanical properties and OP of  $\beta$ -Lg films have a negative exponential relationship. Therefore, higher film EM or TS reflects lower film OP. The plasticizer efficiency ratios between mechanical properties and OP ( $k_{MO} = k_{EM}/k_{OP}$  or  $k_{TS}/k_{OP}$ ) are shown in Table 3. All three bases showed similar efficiency ratios. Five plasticizers, Gly, Sor, PEG 200, Suc, and PEG 400, were analyzed. The plasticizers with higher  $k_{MO}$  values have greater efficiency for modifying mechanical properties than for modifying OP. This is a desirable attribute because plasticizers are normally added to improve film flexibility, and little or no effect on increasing OP is desirable. For example, at similar mechanical properties Sor-plasticized films have much lower OP than PEG-plasticized  $\beta$ -Lg films.

**Conclusions.** Generally, plasticizer effect on  $\beta$ -Lg film OP has a negative exponential relationship to film

mechanical properties. Suc- and Sor-plasticized  $\beta$ -Lg films are the best oxygen barriers, followed by Gly- and PG-plasticized films. PEG 200- and PEG 400-plasticized  $\beta$ -Lg films are poor oxygen barriers. Plasticizer efficiency ratios between mechanical properties and OP relate plasticizer efficiency for modifying mechanical properties to efficiency for modifying OP. High plasticizer efficiency ratios are desirable, because they reflect a plasticizer's ability to improve film flexibility while having little effect on OP.

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