

Influence of a Novel Castor-Oil-Derived Additive on the Mechanical Properties and Oxygen Diffusivity of Polystyrene

Markus Klinger, Lars Poulsen Tolbod, Peter R. Ogilby

Center for Oxygen Microscopy and Imaging, Department of Chemistry, Aarhus University, Århus DK-8000, Denmark

Received 3 November 2009; accepted 1 April 2010

DOI 10.1002/app.32548

Published online 3 June 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Mechanical properties, densities, and oxygen diffusion coefficients have been measured in polystyrene samples (PS) as a function of additive loading. The additive employed is based on castor oil, and is a desirable alternative to phthalates. Tensile strength measurements indicate the additive renders PS stronger at low loadings, i.e. it antiplasticizes the material. In contrast, the additive plasticizes PS at high loadings. Specific volumes and oxygen diffusion coefficients do not show this dual behavior. Rather, one observes a monotonic decrease in density and oxygen diffusivity with an increase in additive loading. This suggests that the larger segmental motions

responsible for the macroscopic properties of the polymer are influenced by the additive in a different manner than the local motions and confined changes in free volume that govern the mobility of oxygen. These data indicate that antiplasticization cannot be predicted solely from diffusivity and density measurements and, vice versa, trends in diffusivity cannot be deduced from mechanical measurements alone. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1643–1650, 2010

Key words: plasticizer; polystyrene; oxygen diffusion; barrier

INTRODUCTION

Monitoring, quantifying, and understanding oxygen diffusion in polymers is critical in the characterization, development, and application of many materials and polymer-based devices. On one hand, many polymers are routinely exposed to oxygen-containing environments, and it is well-known that oxygen plays a key role in mechanisms of polymer degradation.^{1,2} On the other hand, oxygen is a molecule whose presence in a polymer can be used to probe a variety of the polymer's properties, even though the polymer may be designed to work in oxygen deficient applications.^{3–6} Finally, oxygen itself has many unique properties, and it is of interest to develop oxygen sensors. These sensors often rely on a key polymer-based component in which oxygen transport is important.^{7,8}

Plasticizers are widely used to ease the processing or change physical properties of a given polymer. Indeed, the effects that a given additive can have on a given polymer have been so well studied over the

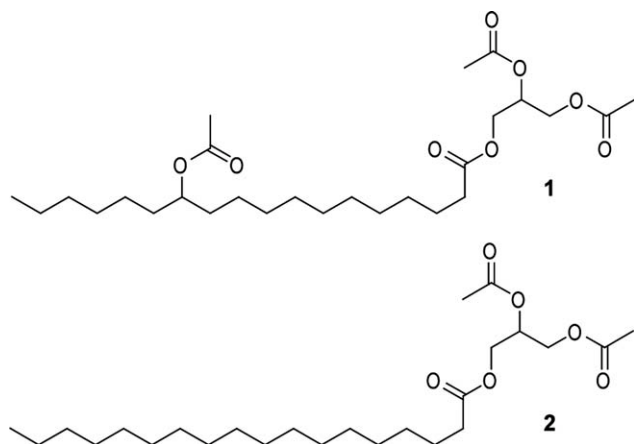
years for a wide range of materials that one can use plasticizers to selectively and accurately tune the properties of a polymer to suit a specific application.^{9–11} One important property of a polymer that can be influenced by the presence of a plasticizer is oxygen diffusion.^{12,13} The diffusion of oxygen has also been used to characterize antiplasticization, a phenomenon often associated with a decrease in the macroscopic flexibility of the material, among other things.^{12,14–16}

Phthalates are arguably the most commonly utilized plasticizers (e.g., di-(2-ethyl hexyl) phthalate).¹¹ They are readily available, and a given phthalate can be used in a wide range of different polymers. However, among other things, phthalates are suspected to be hazardous to human health.¹⁷ As such, their use has been discouraged or banned for certain applications (e.g., toys, medical products, food packaging).¹⁸ In response, other compounds have been developed and used as plasticizers for specific applications where humans could be particularly influenced. Such plasticizers include alkyl sulphonates, benzoates, citrate esters, or core-hydrogenated phthalates.¹⁹ Other alternatives include molecules derived from hydrogenated castor oil. Of specific interest in this regard are materials produced by Danisco A/S in Denmark with the trade name Grinsted® Soft-N-Safe (SNS).²⁰

Given that SNS has a number of desirable features, we set out to investigate the extent to which, when added in small amounts, it will influence

Correspondence to: P. R. Ogilby (progilby@chem.au.dk).

Contract grant sponsor: Danish National Research Foundation (block grant for the Center for Oxygen Microscopy and Imaging).



Scheme 1 Chemical structures of the main components in the Grinsted[®] Soft-N-Safe (SNS) plasticizer: fully acetylated 12-hydroxy stearic acid monoglyceride (1) and stearic acid monoglyceride (2).

selected properties of glassy polystyrene. We were particularly interested in quantifying the effect of added SNS on the oxygen diffusion coefficient, D , and ascertaining whether or not SNS-dependent changes in D correlated with SNS-dependent changes in other properties of the polymer.

EXPERIMENTAL SECTION

Materials

The plasticizer Grinsted[®] Soft-N-Safe (SNS) was obtained from Danisco A/S, Denmark. SNS is a blend of molecules made from fully hardened castor oil and acetic acid.²⁰ The main components are the fully acetylated monoglycerides of 12-hydroxy stearic acid (84 mol %, $M_w = 500,665 \text{ g mol}^{-1}$) and stearic acid (10 mol %, $M_w = 442,629 \text{ g mol}^{-1}$), see Scheme 1. The density of SNS is 1.014 g cm^{-3} at 23°C and the boiling point is $> 300^\circ\text{C}$ (1 mm Hg).

Spectroscopic grade benzene (Sigma-Aldrich) and 5,10,15,20-Tetrakis-(2,3,4,5,6-pentafluorophenyl)-porphyrin-Pd(II), denoted with the acronym PdTFPP (Porphyrin Systems, Germany), were used as received. Polystyrene (PS) was obtained in the form of pellets from either Sigma-Aldrich ($M_w = 280,000$) or Polimeri Europa (Edistir N1840) and was used as received.

Compounding

Samples used for tensile measurements were prepared from pellets that had been compounded. SNS was mixed with 600 g of PS pellets (Edistir N1840) to yield respectively 0.0, 2.5, 4.2, 6.3, and 8.9 weight percent of added SNS (the actual amount of SNS in the polymer was quantified using gas chromatography, see below). Hereafter, the material was extruded at 215°C (extruder 832401, plastograph 815060, Brabender) and pelletized (881202, Brabender).

Dumbbell preparation

Standard dumbbell-shaped samples used for the tensile measurements were obtained by first preparing polymer plates, 1.1 mm thick, $7.6 \times 7.6 \text{ cm}$ area, from compounded pellets using an injection molder (BOY 25M, Dr. Boy). The plates were molded at 220°C and cooled at 35°C . The injection time was 0.2 s and the total cycle time was 18 s. M-II dumbbell shapes were then cut out of the plates using a pressing tool (DP6-B2, Compac).

Gas chromatography

To determine the actual SNS content in the polymers, both the compounded pellets and the injection molded samples were analyzed.

To this end, 0.4 g polymer was dissolved in 10 mL heptane and pyridine (50 : 50 v/v) overnight. Thereafter, 500 μL of the heptane phase were transferred to a crimp vial, 100 μL *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) were added to enhance the GC separation, and the vial was placed in a heating cabinet at 60°C for 15 min. Finally, the sample was injected into the chromatograph (Autosystem XL, PerkinElmer).

Heptadecane was added to the polymer solution as an internal reference to calculate the response factor of a known amount of SNS. The latter was obtained from the same batch as the one used for compounding.

Tensile properties

After equilibrating for 72 h at 23°C and 55% relative humidity, tensile properties were measured using a universal testing machine (4301, Instron). Specimens of neat polystyrene and the SNS-containing polymer were examined at a pull-rate of 5 mm/min. The gauge length was 25 mm and the ATSM D638M method was followed. The thickness and width of the specimen were measured using a micrometer screw (293-521-30, Mitutoyo).

Glass transition temperature

The glass transition temperatures of the samples were determined using differential scanning calorimetry performed at a rate of $10^\circ\text{C min}^{-1}$ (DSC822e, Mettler Toledo or STA 449 C, Netzsch). Transition temperatures were obtained from the midpoint of the heat capacity step change during the second heating cycle.

Size exclusion chromatography

Size exclusion chromatography (SEC) was used to characterize the molecular weight and molecular

weight distributions of the PS samples. The SEC system was composed of three columns: a 50 mm × 7.5 mm PLgel 5 μm guard, a 300 mm × 7.5 mm PLgel 5 μm mixed-C, and a 300 mm × 7.5 mm PLgel 5 μm mixed-D.

A differential refractometer/viscometer (200, Viscotek) was used to monitor the material eluted. The columns and the detectors were maintained at 20°C. THF was used as the eluent and was pumped through the system at a rate of 0.5 mL/min (LC-10AD HPLC pump, Shimadzu).

The refractometer signals were calibrated using a series of 11 PS standards with M_w ranging from 1,250 to 1,900,000 g mol⁻¹ and having a polydispersity of less than 1.09.

Density measurements

Densities were determined using an analytical balance (AE-100, Mettler) equipped with a density determination kit (ME-33360, Mettler). For these measurements, cylindrical samples with dimensions of ~ 0.5 cm (diam) × 1.1 mm were cut from the “dumbbells” (vide supra), and the reference liquid was 99.9% methanol.

Film preparation

PS films used in oxygen sorption experiments were prepared by spin-casting using a photoresist spinner (EC101DT-R790, Headway Research). In a typical procedure, PS from Sigma-Aldrich, the luminescent probe and a varying amount of SNS (0–10 wt % relative to the amount of polymer) were dissolved in benzene. The amount of polymer used was 22 wt % relative to the amount of benzene. The polymer solutions were maintained at ambient temperature and pressure for 4 h on a shaking table (Vibrax VXR basic, IKA) to achieve homogeneity and then were spin-cast onto borosilicate glass plates. The typical spinning speed was 2500 rpm. After standing for 24 h at ambient temperature and pressure, the spin-cast films were then placed under vacuum for 24 h. Finally, the films were annealed 35°C below their respective T_g , vide infra, for 24 h under vacuum using a vacuum oven (3620-ST-1, Lab-Line Duo-Vac). Under these conditions, films with a thickness in the range 12–14 μm were generally produced. The film thickness was quantified using a profilometer (DEK-TAK 3030, Veeco Instruments).

Absorption measurements

Absorption spectra were recorded using a diode array spectrometer (8453, Hewlett-Packard/Agilent Technologies).

Oxygen diffusion measurements

Oxygen diffusion coefficients were obtained using an approach wherein one monitors the rate at which oxygen quenches the luminescence of a dye added to the polymer sample.^{21–23} PdTFPP was used as the luminescent dye. It has an absorption band with a maximum at 410 nm and a phosphorescence band with a maximum at 670 nm. In PS samples that contain dissolved oxygen, PdTFPP phosphorescence is efficiently quenched.

When preparing the polymer samples, the amount of PdTFPP used was adjusted to yield an absorbance at 410 nm of ~ 0.6–0.7 in the final film. This corresponds to a PdTFPP concentration of ~ 2×10^{-3} M in the film. At such concentrations, the presence of the phosphorescent probe does not perturb oxygen diffusion in the polymer.²⁴

During an experiment, PdTFPP was irradiated using a steady state 150W horizontal-burn Xe lamp (horizontal burn, PTI) whose output was passed through the following optical elements in succession: (1) a 3 cm water filter, (2) KG filters (Schott), (3) a monochromator (FWHM 20 nm, model 77250, Oriel), (4) and a 400 nm bandpass filter (60% transmittance, FWHM = 70 nm, Thorlabs). The resulting light, chosen to match the maximum absorption of the sensitizer, was focused into a temperature and pressure-controlled sample chamber (model 21000, Specac). The area illuminated, and hence the area in which oxygen diffusion was monitored, was typically 0.25 cm².

PS films were mounted in a chamber where both the ambient temperature and oxygen partial pressure could be readily controlled.²⁴ This chamber was evacuated to obtain an oxygen-free sample. Oxygen was then rapidly introduced into the environment surrounding the polymer sample using a quick response toggle valve.²⁴ The resultant decrease in PdTFPP phosphorescence intensity was detected through a 675 nm bandpass filter (70% transmittance, FWHM = 40 nm, Spectrogon) using a fiber optic spectrometer (USB2000, Ocean Optics) in combination with an optical fiber (M29L02, Thorlabs). The observed signal was integrated in the wavelength range 655–690 nm with a sampling time of 30–50 ms. The experiment could be readily repeated simply by degassing the sample and reintroducing an ambient atmosphere of oxygen.

RESULTS

Molecular weights and SNS loading

For the optically-based oxygen diffusion experiments, we opted to use laboratory grade PS (Sigma-Aldrich). The intent in using this material was to

TABLE I
Mechanical Properties of PS at Different SNS loadings^a

SNS content (%)	Stress-at-break (MPa)	Strain-at-break (%)	Modulus ^b (GPa)
0.0	29.8 ± 1.2	3.3 ± 0.2	1.02 ± 0.06
2.0	31.8 ± 1.2	3.5 ± 0.2	1.01 ± 0.05
4.2	30.8 ± 0.8	3.4 ± 0.1	0.98 ± 0.06
6.3	27.9 ± 0.4	3.3 ± 0.2	0.93 ± 0.04
8.9	24.6 ± 0.7	3.4 ± 0.2	0.85 ± 0.04

^a A commercial grade of PS was used ($M_w = 212,000 \text{ g mol}^{-1}$). Errors represent the standard deviation of the experiment obtained from measurements made on multiple samples.

^b Obtained from the slope of the stress:strain plot (i.e., Fig. 2).

minimize the effect that adventitious impurities would have on our luminescent probe. Samples prepared from this material were also of better optical quality than samples prepared from compounded commercial grade PS. We ascertained that this laboratory grade PS had a weight average molecular weight (M_w) of $279,000 \text{ g mol}^{-1}$ and a polydispersity of 3.1. Commercial grade polystyrene was used for the mechanical tests (Polimeri Europa). The molecular weight of the latter was found to be $212,000 \text{ g mol}^{-1}$ with a polydispersity of 2.4. These experimentally determined molecular weights correspond to the manufacturers' specifications. SNS loading was determined by gas chromatography and is summarized in Table I.

Glass transition temperatures

As shown in Figure 1, the T_g of both the laboratory and commercial grades of PS decreased with an

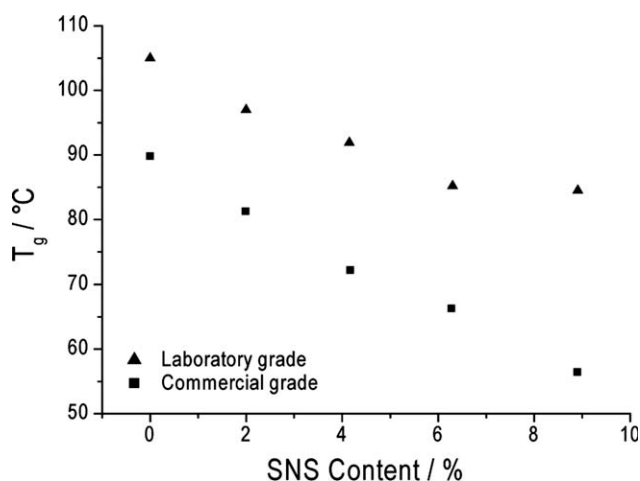


Figure 1 Glass transition temperatures for two different PS samples as a function of SNS loading. Laboratory Grade = Sigma-Aldrich (films) and Commercial Grade = Polimeri Europa (dumbbells).

increase in the amount of added SNS. The systematic observation that, at any given SNS loading, the T_g of the commercial material was lower than that of the laboratory grade material likely reflects the combination of a number of different phenomena (e.g., molecular weights of the respective materials, stabilizers and other additives in the commercial material). In any event, because we are principally interested in making comparative SNS-dependent observations in this study, this systematic sample-dependent difference in T_g should be of minor consequence.

Tensile properties

Values of tensile strength were obtained from the stress-at-break point (Fig. 2). The data indicated that the samples with 2.0 and 4.2% added SNS had slightly larger tensile strengths than that observed from the SNS-free PS. With larger amounts of added SNS, however, the tensile strength ultimately decreased to a value significantly lower than that of the neat PS (Fig. 3 and Table I). This additive-dependent increase in tensile strength is characteristic of "antiplasticization", where low loadings of plasticizer lead to a stronger material.^{9,14,15} This phenomenon is generally reversed with higher loadings of the additive where a plasticization threshold is ultimately reached and the material is softened.

Density measurements

The reciprocal density (i.e., the specific volume, ρ^{-1}) decreases as the amount of added SNS increases (Table II). Moreover, all SNS-containing PS samples have a specific volume that is less than the specific

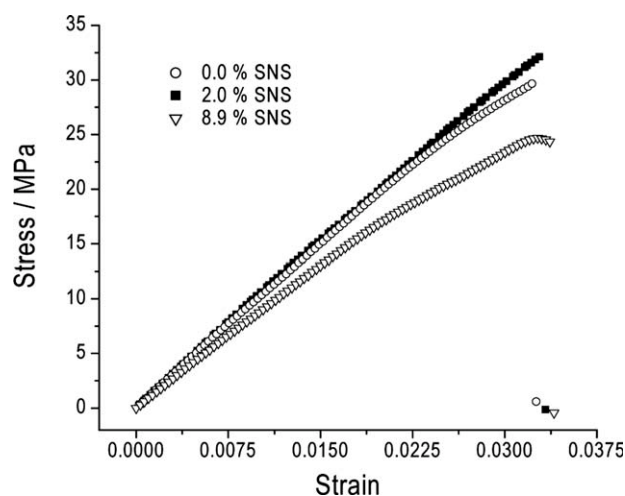


Figure 2 Representative stress–strain curves for different SNS loadings in PS. For the sample with 8.9% added SNS, the curve indicates a yield point.

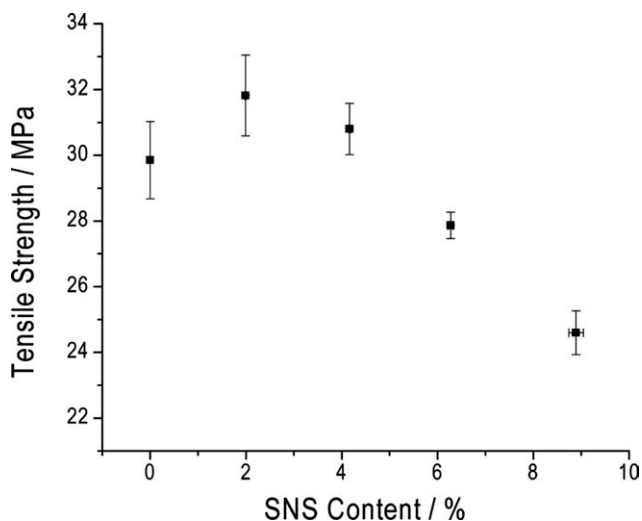


Figure 3 Tensile strength of PS as a function of SNS loading. Initially, the polymer tensile strength increases, which is characteristic of antiplasticization. At higher levels of added SNS, the polymer is plasticized.

volumes of PS and SNS themselves, $0.9583 \text{ cm}^3 \text{ g}^{-1}$ and $0.986 \text{ cm}^3 \text{ g}^{-1}$, respectively.

Oxygen diffusion

Oxygen sorption into a degassed polymer film can be monitored using the phosphorescence decay of a molecule incorporated into the film as a spectroscopic probe.^{7,21,23,25} For the work reported herein, we used a fluorinated porphyrin, PdTFPP, as the luminescent probe.

The ratio of the PdTFPP phosphorescence intensity in the absence of oxygen (I_0) to the phosphorescence intensity in the presence of oxygen (I) should depend on the oxygen concentration in the polymer film as described by the Stern-Volmer equation [eq. (1)]. In Equation 1, the bimolecular rate constant for oxygen quenching of the phosphorescent state is denoted k_q , and the lifetime of this state in the absence of oxygen is denoted τ .

$$\frac{I_0}{I} = 1 + k_q\tau[\text{O}_2] = 1 + K_{SV}[\text{O}_2] \quad (1)$$

TABLE II
Oxygen Diffusion Coefficients, D , and Specific Volumes Obtained for SNS-Containing PS Samples

SNS content (%)	Specific volume $\text{cm}^3 \text{ g}^{-1}$	$D(\text{O}_2) 10^{-7} \text{ cm}^2 \text{ s}^{-1}$
0.0	0.9583 ± 0.0003	1.38 ± 0.07
2.0	0.9574 ± 0.0003	1.20 ± 0.06
4.2	0.9551 ± 0.0003	1.10 ± 0.06
6.3	0.9527 ± 0.0003	0.99 ± 0.04
8.9	0.9520 ± 0.0002	0.98 ± 0.07

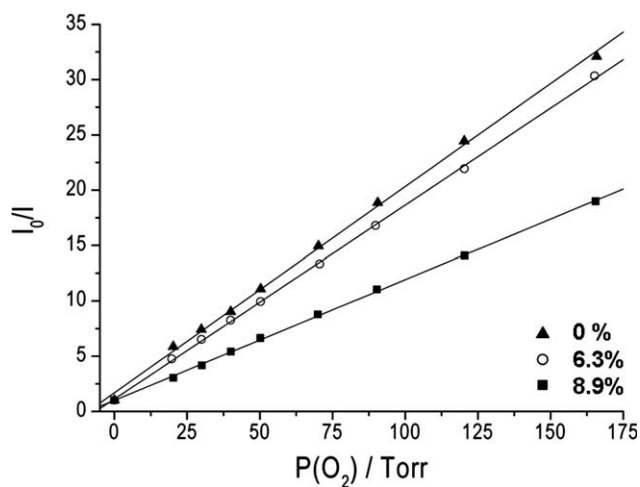


Figure 4 Stern-Volmer plots for the quenching of PdTFPP phosphorescence in films of PS and PS with SNS. Instead of plotting the concentration of sorbed oxygen on the x-axis, the partial pressure of oxygen in the atmosphere surrounding the polymer sample is plotted (see discussion in text). The solid lines are the result of linear fits to the data. Data are shown for 0, 6.3, and 8.9% added SNS.

As shown in Figure 4, we observe that this ratio of phosphorescence intensities depends linearly on the ambient oxygen partial pressure for both neat PS and PS containing SNS over the pressure range 0–175 Torr. This is in agreement with previous findings for neat PS,²⁶ and indicates that over this pressure range (1) the solubility of oxygen in PS is linearly dependent on the ambient partial pressure and follows Henry's law behavior, and (2) PdTFPP appears to be distributed homogeneously throughout the polymer in sites that are equally accessible to oxygen.

However, the data in Figure 4 clearly indicate that, for these SNS-containing PS films, the slope of the Stern-Volmer plot for oxygen quenching of PdTFPP depends on the sample. This observation is entirely reasonable on the basis of the following points: (1) Because the solubility of oxygen in the different SNS-containing films may not be the same, one may, in turn, see different Stern-Volmer slopes. (2) Both the bimolecular rate constant for quenching by oxygen, k_q , and the PdTFPP phosphorescent state lifetime, τ , may likewise depend on the sample.

Although we observe different, sample-dependent Stern-Volmer slopes, the key feature is that, for a given sample, the ratio of phosphorescence intensities, I_0/I , always depends linearly on the ambient oxygen pressure over the range used in our studies (20–175 torr). Thus, in all cases, the change in PdTFPP phosphorescence intensity observed upon exposure of a previously degassed PS film to an oxygen atmosphere in this pressure range can be used to quantify the rate of oxygen sorption by the polymer film.

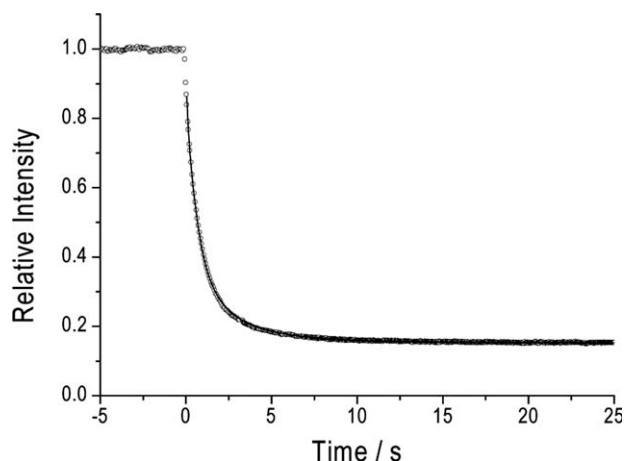


Figure 5 PdTFPP phosphorescence intensity recorded as oxygen is sorbed into a 12 μm thick PS film cast onto a borosilicate substrate. These data were recorded upon exposure, at time = 0, of a degassed film to 30 Torr of oxygen. In these experiments, the rate at which oxygen enters the sample chamber and surrounds the film is much faster than the rate of oxygen sorption by the film. The line is the result of a fit of eq. (3) to the data.

Upon exposure of a degassed film containing PdTFPP to an ambient atmosphere containing oxygen, the time-dependent process of oxygen sorption by the film can be followed by monitoring changes in the intensity of the PdTFPP phosphorescence signal (Fig. 5).

Data such as those shown in Figure 5 can be quantified to yield the diffusion coefficient for oxygen in that given film.^{21,27} Specifically, using Fick's second law for one-dimensional diffusion, the oxygen concentration in the film (C) at a given penetration depth, x , and at a given time, t , is given as shown in eq. (2).²⁸

$$\frac{C(x, t) - C_0}{C_1 - C_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \left(\frac{(-1)^n}{2n+1} \right) \times \exp\left(\frac{-D(2n+1)^2 \pi^2 t}{4\ell^2} \right) \cos\left(\frac{(2n+1)\pi x}{2\ell} \right) \quad (2)$$

Using conditions where the initial oxygen concentration (C_0) is zero and the concentration at the film surface (C_1) is normalized to one, the equation simplifies and can be incorporated into eq. (1). D is the oxygen diffusion coefficient and ℓ is the film thickness. Upon integration over the limits 0 to ℓ , one obtains an expression for the time-dependent intensity of PdTFPP phosphorescence [eq. (3)].

$$I(t) = \int_0^{\ell} \frac{I_0}{1 + K_{\text{SV}}[\text{O}_2(x, t)]} dx \quad (3)$$

A numerical solution to eq. (3) can be used in a standard least-squares fitting routine to obtain an

oxygen diffusion coefficient from phosphorescence data such as those shown in Figure 5. Built into this procedure is a convergence check; eq. (2) typically converges after 5–10 terms in the summation.

Oxygen diffusion coefficients obtained for the various SNS-containing films are listed in Table II. Data obtained from SNS-free samples compare favorably with data previously obtained from PS films.^{12,23,24,29} Although the SNS-dependent changes in D are subtle, there is nevertheless a clear trend showing that the magnitude of D systematically decreases as the amount of SNS in the PS sample is increased. This change in D correlates well with the corresponding SNS-dependent change in the specific volume of the polymer sample (Table II).

It has been shown for a variety of materials that the oxygen diffusion coefficient, obtained as a function of the temperature of the polymer film, exhibits Arrhenius behavior.¹² Indeed, reasonably linear Arrhenius plots [eq. (4)] can be obtained over comparatively large temperature ranges below T_g .^{12,29,30} In this way, one can obtain an apparent activation energy, E_{act} , that can be useful in characterizing features and properties of the polymer that influence oxygen diffusion.^{12,29–31}

$$D = D_0 \exp\left(\frac{-E_{\text{act}}}{RT} \right) \quad (4)$$

Temperature-dependent diffusion coefficients were recorded for a sample of neat PS and a PS sample containing 2.0% SNS (Fig. 6). The data obtained indicate an indiscernible SNS-dependent change in E_{act} : E_{act} (2% SNS) = $31.3 \pm 0.7 \text{ kJ mol}^{-1}$, E_{act} (neat PS) = $30 \pm 1 \text{ kJ mol}^{-1}$. The values of E_{act} obtained in this work from SNS-free samples likewise compare favorably with those previously obtained from PS films.^{12,29}

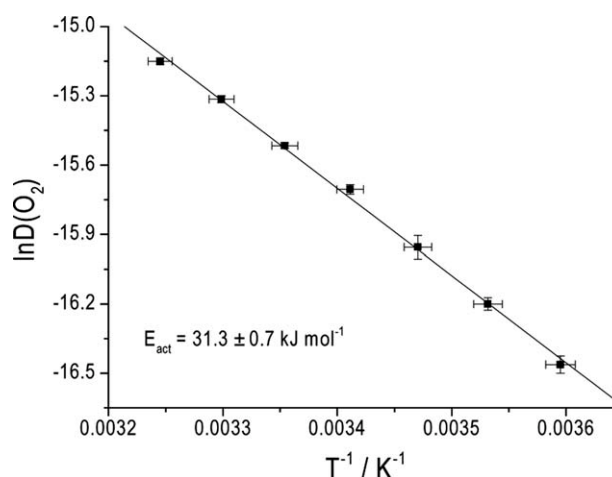


Figure 6 Arrhenius plot of the oxygen diffusion coefficient in polystyrene with 2.0% added SNS.

DISCUSSION

Of all the SNS-dependent properties quantified in this study, the tensile strength data stand apart. In this case, instead of seeing a systematic and incremental (or decremental) change in a given parameter with an increase in the amount of added SNS, we observe an initial increase in tensile strength followed by a decrease at higher SNS loadings. Numerous studies have reported that small amounts of a given additive (e.g. up to 20% by weight or volume) can increase the hardness and the tensile strength of the polymer.^{9,32,33} This effect has been termed antiplasticization.⁹ Dynamic mechanical studies have shown that antiplasticization can be accompanied by the additive-dependent suppression of secondary relaxations,³⁴ and density measurements have shown that this change can be accompanied by a decrease in the specific volume of the polymer.³⁵

Maeda and Paul³⁵ and Vrentas et al.³⁶ have proposed mathematical models that describe the negative departure from ideal volume (i.e. decrease in specific volume), which can be observed when mixing glassy polymers with low molecular weight additives. In these models, the volume contraction is seen as a consequence of a decrease in the unrelaxed volume of the mixture relative to the pure polymer. In accordance hereto, the suppression of secondary relaxations is to some degree merely a consequence of the loss of free volume. These models thus equate the antiplasticization phenomenon to a decrease in specific volume and, correspondingly, the plasticization phenomenon to an increase in specific volume. However, as shown in this work, plasticization can occur even if the specific volume is decreasing. The additive-dependent change we observe in the oxygen diffusion coefficient correlates with the additive-dependent change in specific volume and, as such, our diffusion data are consistent with accepted free volume-based theories for small molecule transport in a polymer.^{37,38}

Based on the results described here, it seems that antiplasticization cannot be predicted from sole diffusivity and density measurements. Likewise, trends in diffusivity cannot be deduced from mechanical measurements. Indeed, in a separate study, Andersen et al.¹⁶ have shown that high molecular weight PS is plasticized even though there is a slight decrease in free volume. Moreover, previous studies from our laboratory have shown that high loads of dimethyl phthalate (up to 25 %) in PS were, as described here, also accompanied by a decrease in the oxygen diffusion coefficient.¹²

These findings indicate that the interaction of an additive with the macromolecule can influence polymer properties in seemingly unpredictable ways. Specifically, larger segmental motions that are gener-

ally responsible for the macroscopic mechanical properties of the polymer can be influenced in a different manner than the local motions and confined changes in free volume that govern the mobility of small gases such as oxygen.

In the context of this latter statement, it is interesting to note that, within the errors of our measurements, we are unable to discern a significant difference in the values of E_{act} for samples containing 0 and 2% added SNS. It is generally assumed that the value of E_{act} derived from an oxygen diffusion experiment reflects an activation barrier for polymer motions that influence translation of oxygen through the polymer matrix.^{12,29} Admittedly, there is also a noticeable amount of curvature in the Arrhenius plots recorded (Fig. 6), indicating that one must proceed with caution when interpreting these temperature-dependent data; this is a complex multivariate system.

CONCLUSIONS

In PS, the castor-oil-derived additive Grindsted[®] Soft-N-Safe (SNS), acts as an antiplasticizer at low loadings, leading to an increase in the tensile strength of the polymer. At higher loadings, this additive acts as a plasticizer in PS in that the tensile strength of the polymer decreases with an increase in the amount of added SNS. However, both the specific volume and oxygen diffusivity of the polymer systematically decrease with an increase in the amount of added SNS. Our data demonstrate that a direct correlation does not necessarily exist between the mechanical properties of a polymer and the properties that influence gas diffusion in the polymer. Indeed, the phenomenon of antiplasticization appears to be a complex phenomenon that can depend on a number of different variables.³⁹

We thank (1) Lotte Nielsen, Technical University of Denmark, for SEC measurements, and (2) The Laboratory of Inorganic Chemistry, Aarhus University for the use of their DSC calorimeter. We are grateful for the assistance and cooperation of Danisco A/S during the course of this project. Specifically, we thank (1) Bjarne Nielsen for supplying Grindsted[®] Soft-N-Safe and discussions at the early stages of this study, (2) Anna-Malin Bouwens for discussions of the tensile property measurements, (3) Lis Lund Knudsen for assistance in compounding, (4) Thomas Schjødt Thomsen for assistance in injection molding, (5) Ina Paaske for the GC-analysis, and (6) Sally Bording Pedersen for DSC-measurements on the Polimeri Europa samples.

References

1. Grassie, N.; Scott, G. *Polymer Degradation and Stabilisation*; Cambridge University Press: Cambridge, 1985.
2. Schnabel, W. *Polymer Degradation*; Macmillan/Hanser: New York, 1981.

3. Hiltner, A.; Liu, R. Y. F.; Hu, Y. S.; Baer, E. *J Polym Sci Part B: Polym Phys* 2005, 43, 1047.
4. Yampolskii, Y. P.; Pinnau, I.; Freeman, B. D. *Materials Science of Membranes for Gas and Vapor Separation*; Wiley: Hoboken, 2006.
5. Paul, D. R.; Yampol'skii, Y. P., Eds. *Polymeric Gas Separation Membranes*; CRC Press: Boca Raton, 1994.
6. Ogilby, P. R.; Dillon, M. P.; Gao, Y.; Iu, K.-K.; Kristiansen, M.; Taylor, V. L.; Clough, R. L. *Adv Chem Ser* 1993, 236, 573.
7. Kose, M. E.; Crutchley, R. J.; DeRosa, M. C.; Ananthakrishnan, N.; Reynolds, J. R.; Schanze, K. S. *Langmuir* 2005, 21, 8255.
8. Demas, J. N.; Degraff, B. A.; Coleman, P. B. *Anal Chem* 1999, 71, 793A.
9. Sears, J. K.; Darby, J. R. *The Technology of Plasticizers*; John Wiley and Sons.: New York, 1982.
10. Zweifel, H. *Plastics Additives Handbook*; Hanser: Munich, 2000.
11. Krauskopf, L. G.; Godwin, A. In *PVC Handbook*; Wilkes, C. E., Summers, J. W., Daniels, C. A., Eds. Carl Hanser: Munich, 2005.
12. Gao, Y.; Baca, A. M.; Wang, B.; Ogilby, P. R. *Macromolecules* 1994, 27, 7041.
13. Maeda, Y.; Paul, D. R. *J Membr Sci* 1987, 30, 1.
14. Jackson, W. J.; Caldwell, J. R. *J Appl Polym Sci* 1967, 11, 227.
15. Jackson, W. J.; Caldwell, J. R. *J Appl Polym Sci* 1967, 11, 211.
16. Anderson, S. L.; Grulke, E. A.; Delassus, P. T.; Smith, P. B.; Kocher, C. W.; Landes, B. G. *Macromolecules* 1995, 28, 2944.
17. Heudorf, U.; Mersh-Sundermann, V.; Angerer, E. *Int J Hyg Environ Health* 2007, 210, 623.
18. Hileman, B. *Chem Eng News* 2005, 83, 11.
19. *Plast Addit Compound* 2002, 4, 30.
20. Danisco. SoftNSafe, July 2009, Available at <http://www.danisco-softnsafe.com>; Accessed on 26 April 2010.
21. Yekta, A.; Masoumi, Z.; Winnik, M. A. *Can J Chem* 1995, 73, 2021.
22. Xu, W. Y.; Kneas, K. A.; Demas, J. N.; Degraff, B. A. *Anal Chem* 1996, 68, 2605.
23. Rharbi, Y.; Yekta, A.; Winnik, M. A. *Anal Chem* 1999, 71, 5045.
24. Gao, Y.; Ogilby, P. R. *Macromolecules* 1992, 25, 4962.
25. Lu, X.; Manners, I.; Winnik, M. A. *Macromolecules* 2001, 34, 1917.
26. Demas, J. N.; Degraff, B. A.; Xu, W. Y. *Anal Chem* 1995, 67, 1377.
27. Kneas, K. A.; Demas, J. N.; Nguyen, B.; Lockhart, A.; Xu, W. Y.; DeGraff, B. A. *Anal Chem* 2002, 74, 1111.
28. Crank, J. *The Mathematics of Diffusion*; Oxford Press: Oxford, 1975.
29. Wang, B.; Ogilby, P. R. *Can J Chem* 1995, 73, 1831.
30. Poulsen, L.; Zebger, I.; Klinger, M.; Eldrup, M.; Sommer-Larsen, P.; Ogilby, P. R. *Macromolecules* 2003, 36, 7189.
31. Klinger, M.; Tolbod, L. P.; Gothelf, K. V.; Ogilby, P. R. *ACS Appl Mater Interface* 2009, 1, 661.
32. Ruiz-Trevino, F. A.; Paul, D. R. *J Appl Polym Sci* 1997, 66, 1925.
33. Ruiz-Trevino, F. A.; Paul, D. R. *J Appl Polym Sci* 1998, 68, 403.
34. Ngai, K. L.; Rendell, R. W.; Yee, A. F.; Plazek, D. J. *Macromolecules* 1991, 24, 61.
35. Maeda, Y.; Paul, D. R. *J Polym Sci Part B: Polym Phys* 1987, 25, 1005.
36. Vrentas, J. S.; Duda, J. L.; Ling, H. C. *Macromolecules* 1988, 21, 1470.
37. Duda, J. L.; Zielinski, J. M. In *Diffusion in Polymers*; Neogi, P., Ed.; Marcel Dekker: New York, 1996.
38. Ritums, J. E.; Neway, B.; Doghieri, F.; Bergman, G.; Gedde, U. W.; Hedenqvist, M. S. *J Polym Sci B: Polym Phys* 2007, 45, 723.
39. Pittia, P.; Sacchetti, G. *Food Chem* 2008, 106, 1417.