

Mechanical Properties of Polyurethane Film Exposed to Solutions of Nonoxynol-9 Surfactant and Poly(Ethylene Glycol)

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ABSTRACT: Mechanical properties of two polyether urethane films (Estane and Tecoflex) were studied after exposure to solutions of nonoxynol 9 (N9) surfactant and poly(ethylene glycol) 400 (PEG) for various times. Large amounts of N9 were absorbed from N9/PEG solutions, resulting in soft-segment plasticization and lower mechanical properties. As the N9 concentration increased, Estane absorbed more liquid and its mechanical properties decreased more compared to Tecoflex, although the mechanical properties of Estane were higher than Tecoflex at low concentrations of N9. Hard-segment domain disruption is probably not occurring because the relationship between the elastic modulus and polymer volume fraction followed Flory's theory for swollen elastic rubber networks and the liquids do

not fully dissolve the polymers. The diffusion behavior of N9 and PEG was observed to follow Fickian behavior. Most of the absorption and decrease in mechanical properties occurred within the first 20 h after soaking, implying that additional loss in strength over longer times would be minimal. Mechanical property anisotropy suggests that condoms should be cut from Estane film in an orientation that optimizes the property–orientation relationship for specific end uses. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1086–1096, 2004

Key words: polyurethanes; mechanical properties; surfactants; swelling; thermal properties

INTRODUCTION

Recently, polyurethane condoms have been introduced as an alternative to natural rubber latex condoms.^{1,2} Although most condoms are made from natural rubber, condoms made from other materials (polyurethane, polyethylene, and styrene-butadiene rubber) have been considered because of disadvantages with natural rubber (viz., oxidative degradation,³ decreased strength when exposed to oil-based lubricants,⁴ and the fact that 3% of the population are allergic to proteins found in natural rubber^{5–7}). Of the nonlatex rubber condoms, only polyurethane condoms have been cleared for marketing in the United States by the Food and Drug Administration (FDA).

A major problem for both rubber latex and polyurethane condoms is condom breakage. In a review of the literature, Stratton and Alexander⁸ reported rates of male condom breakage that ranged between 0.5 and

7%. Liskin⁹ reported breakage rates of new condoms ranging from <1% up to 12%. Rosenberg et al.¹ reported clinical breakage rates of 0.3 to 2.1% for Avanti polyurethane condoms and 2.1% for latex condoms on the basis of data from four clinical studies. For covalently crosslinked rubber latex condoms, oxidation commonly lowers mechanical properties, which results in condom breakage. Although certain lubricants have also been suspected of lowering mechanical properties of latex rubber,^{4,10} silicone lubricant was shown in one article to have the opposite effect because silicone lubricant lowered oxygen penetration into latex rubber.¹¹

Lubricants may affect the mechanical properties of latex rubber and polyurethane differently because the crosslinking, chemistry, and morphology of these materials are different. The polyurethanes used in condoms (Fig. 1) are thermoplastic elastomers formed from block copolymers consisting of two different types of blocks (also called segments) in the chain: a stiff or “hard” block and a flexible or “soft” block. The hard and soft blocks are chemically dissimilar and thermodynamically incompatible, which drives them

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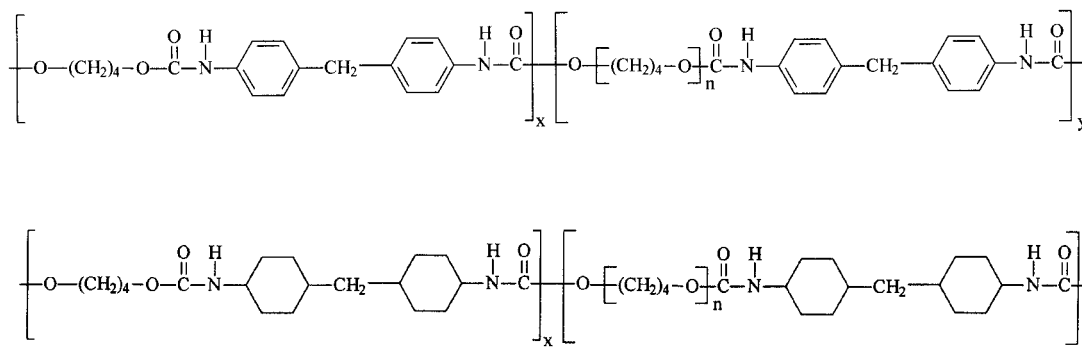


Figure 1 Chemical formulas of Estane 5714 (top) and Tecoflex SG 80A (bottom).

to phase separate into microdomains consisting of a uniformly dispersed phase in a matrix. Because the hard and soft segments are covalently bonded together to form a linear copolymer chain, the physical distance that soft blocks can separate from the hard blocks to form microdomains is limited to about 5 nm.¹² This is referred to as microphase separation.¹³ Polyurethane elastomers have low-weight fractions of hard segment, so their morphology consists of hard-segment domains embedded in a matrix of (mainly) soft segments with some hard segments mixed in. Because of either kinetic restraints or partial miscibility, there is often some mixing of the hard and soft segments at the microdomain boundaries. In the case of polyurethane elastomers, short hard-segment sequences may be dissolved in soft-segment domains.

Hard segments are strongly bound together in hard-segment microdomains by inter- and intramolecular hydrogen bonding and crystallization (depending on the specific hard segment chemical structure).^{14–17} The rigid hard-segment domains give polyurethanes their superior rubbery properties by acting as filler particles and/or physical crosslinks of the soft-segment matrix.^{18,19} Hydrogen bonding and crystallization are disrupted when heated and reform when cooled, allowing thermal and solution processing of polyurethane, which cannot be performed on covalently crosslinked elastomers such as latex rubber.^{20,21}

However, unlike covalently crosslinked latex rubber which has no microphase structure, the physical crosslinking of the soft segment matrix by the hard domains may be disrupted by certain lubricants. Many condoms are coated with lubricants containing the spermicide nonoxynol 9 (N9) mixed with poly(ethylene glycol) 400 (referred to henceforth as PEG) (chemical formulas in Fig. 2, molecular weight 400 g/mol)²² because *in vitro* tests have shown N9 to be effective at killing both sperm and human immunodeficiency virus (HIV) in the event of condom failure.²³ PEG acts as a lubricant and as a carrier of N9. The condom may also be exposed by condom users to products that contain N9 such as other lubricants and

contraceptives. N9 is a nonionic surfactant with a polar hydrophilic end [$-O(C_2H_4O)_n$] and a hydrophobic hydrocarbon end ($-C_9H_{19}$). The chemical similarity of the hydrophilic part of N9 and polyurethane suggests that N9 may be absorbed by polyurethane and interact with the hard and/or soft segments. Solvation of the soft segment should swell the polymer, whereas solvation of the hard segment,^{24,25} and plasticization of the soft segment,²⁶ would likely lower the mechanical properties.

There are no articles in the literature known to us which specifically address N9/polyurethane interactions, but there is literature about N9 interactions with polymers other than polyurethanes. N9 diffuses through polymers such as ethylene-vinyl acetate copolymer and silicone elastomer.²⁷ Trap et al.²⁸ reported that 50% of N9 on the surface of rubber latex condoms was absorbed into the polymer, diminishing the N9 concentration on the surface to the extent that it may not inhibit HIV. N9 was also found to extract protein from rubber latex condoms.²³ Brown et al.²⁹ reported a decrease in the resistance to slow crack growth of polyethylene gas pipe with greater N9 concentration.

The effect of surfactants or external plasticizers other than N9 on microphase-separated polymers is reported in the literature. Fatigue resistance of a poly(urethane-urea) composed of MDI-PTMO soft segment and MDI-EDA or MDI-DAM hard segment was reduced because of plasticization by the surfactants cholesterol and lecithin lipid³⁰ (MDI, diphenylmeth-

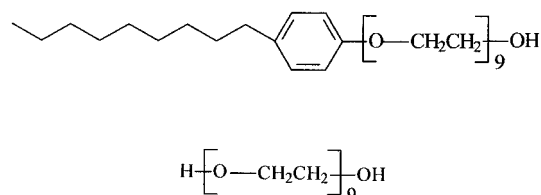


Figure 2 Chemical formulas of nonoxynol 9 (N9) (top) and polyethylene glycol 400 (PEG) (bottom).

ane diisocyanate; PTMO, polytetramethylene oxide; EDA, ethylenediamine; DAM, 4,4'-diaminodiphenylmethane). Oberth and Bruenner³¹ reported that plasticization of polyurethane rubber resulted in the formation of micelle-like structures consisting of domains of plasticizer and polymer. This caused some chains to bear a higher portion of the load than others, resulting in a nonuniform distribution of load over the network, which lowered the mechanical properties. Mandal et al.³² studied the absorption of two plasticizers into an ionic polymer composed of carboxylated nitrile rubber containing about 10% ZnO. The ZnO formed ionic clusters with the rubber to create a hard phase within a soft rubber-phase matrix. Mixing in plasticizers [up to 15% dioctylphthalate (DOP) or up to 8% dimethylsulfoxide (DMSO)] resulted in preferential absorption and plasticization of the soft phase by DOP and of the hard phase by DMSO.

Structural changes in polyurethane have been observed following absorption of small molecules. For example, Grigoriew et al.³³ studied morphological changes after swelling poly(urea-urethanes) in ethanol. The polymers contained 22 or 39% hard segment and were composed of TDI-PTMO soft segment and TDI-HQE or TDI-PP hard segment (TDI, 2,4-toluene diisocyanate; HQE, bis(2-hydroxyethyl)ether; PP, 4,4'-diaminodiphenylmethane). Small-angle X-ray scattering (SAXS) showed that after soaking in ethanol, the hard-segment domain size decreased from about 16 to 14 nm and a previously absent 4 nm aggregate with a low size dispersion appeared. The authors suggested the small aggregates may be made up of hard segments originating from the diminished larger hard segment domains. Nierzwicki and Majewska³⁴ determined that the degree of swelling of MDI/BD/PEA [PEA, poly(ethylene adipate) diol, molecular weight, 2000] films by various solvents is affected by the degree of microphase separation. Cooper reported the solvation of the soft and hard segments of a polyester urethane (Estane 5740-100) by various concentrations of benzene-methanol mixtures.²⁵ Soaking Pellethane 2363 in acetone 24 h increased phase separation and interdomain spacing dramatically as observed by SAXS.³⁵

There are three polyurethane condoms currently marketed in the United States. The Reality female condom made from Estane 5714 (an aromatic polyether polyurethane), the Trojan male condom made from Tecoflex SG 80A (an aliphatic polyether polyurethane), and the Durex (also known as Avanti) male condom made from Estane 5767 (a polyester polyurethane). Although N9 is not currently included in the lubricant on the female condom, there is literature that recommends the use of N9 with this particular condom³⁶ and there have been recommendations for increasing the concentration of N9 used on condoms in general.²⁸ This study examines the change in proper-

ties of Estane 5714 with time of exposure to various mixtures of N9 and PEG to address how the properties are affected by the composition of solutions to which it might be exposed. The Trojan male condom, which is made of Tecoflex SG 80A, was used as a negative test control because this is the only condom coated with N9 at manufacture on the U.S. market (8% N9 concentration in PEG) and so may be considered as an acceptable standard for evaluating the effect of PEG and N9 on other types of polyurethanes.

METHODS

Directional variations (anisotropy) in swelling, annealing shrinkage, tensile strength, strain to failure, and creep of polyurethane film were measured to determine the appropriate orientation of the film tensile direction for all subsequent tests in this study. The tensile strength, strain to failure, elastic modulus, diffusion kinetics, and soft-segment glass transition temperature (T_g) were then measured after soaking film in mixtures of N9 in PEG with a molecular weight of 400 g/mol for either 20 h or 18 days. Percentages of N9 in PEG that were studied included 0, 4, 8, 16, 32, 50, 64, 80, and 100% (all percentages of N9 in PEG in this article are in volume percentages). N9 was provided by Rhodia, Inc. (Cranbury, NJ). PEG was bought from Sigma-Aldrich (Milwaukee, WI). Polyurethane films that were tested included Estane 5714 (B.F. Goodrich, Brecksville, OH) and Tecoflex SG 80A (Thermedics, Inc., Chelmsford, MA). Estane 5714 contains MDI, whereas Tecoflex SG 80A (solution grade) is made from 4,4'-dicyclohexyl methane diisocyanate (HMDI). Both have the same soft-segment (PTMO) and chain extender (butane diol). The molecular weight of PTMO and molar ratios of the three monomers are not published and are unavailable.

Estane 5714 (referred to as Estane henceforth) is used in the Reality female condom manufactured by Chartex International (London, UK). The 40- μ m-thick film is made by blow molding (Deerfield Urethane, Deerfield, MA). Silicone lubricant is added during condom manufacturing before the condom is packaged, so Estane film from which the Reality female condom is made was tested in this study rather than the condom itself to avoid the effects of lubricant absorbed by the condom. Samples tested in this study were cut from a large roll of Estane provided by Deerfield Urethane and stored in nitrogen in a heat-sealed PE-coated foil bag made from Marvelseal 470 (Ludlow Laminating and Coating Corp., Homer, LA).

The Trojan male condom (also about 40 μ m thick) is made by solution dipping at Carter Wallace, Inc. (Frazer, PA; now owned by ArmKel, LLC, an affiliate of Church and Dwight Co., Inc., Princeton, NJ). Trojan condoms were not available without lubricant. Another form of Tecoflex SG-80A was not tested in this

study in place of the Trojan condom because of the possible differences in processing on the results. The condoms were removed from their packages; their rings were cut off the open end, and they were then slit lengthwise and soaked in water 1 month to extract absorbed N9/PEG with which they were coated before packaging by the manufacturer. The water was changed three times a week. N9, PEG, and water are miscible at all concentrations in one another.

After soaking one sample (10 × 17 cm) per soak-time interval in any given solution composition, liquid coating the surface was thoroughly blotted off before samples were cut and/or tested. This was done by placing a specimen on virgin Kimwipes EX-L (Kimberly-Clark, Roswell, GA) free of lint and foreign material. The sample was flipped over and moved to a dry area of the wipe numerous times until no wet spots were visible on the wipe. This process was repeated by using the same methods except weighing paper (VWR Scientific Products, West Chester, PA) was substituted for the Kimwipes. The weighing paper was flatter and clung to the film better than the Kimwipe, resulting in greater contact and additional removal of liquid from the film surface. The film weight (M) was then measured and the fractional change in weight

$$|M_{\text{final}} - M_{\text{initial}}|/M_{\text{initial}} \quad (1)$$

was calculated.

Anisotropy in swelling, annealing shrinkage, and tensile strength, strain to failure, and creep were measured in two directions. For Estane, this was longitudinally along the length of the roll (i.e., the machine direction) and transversely (i.e., normal) to the edge of the roll of film. For Tecoflex SG 80A cut from the Trojan condom, this was along the length and along the circumference of the condom. The methods of measuring strength, strain to failure, and creep are described below. Dimensional changes were measured in the two orthogonal directions after swelling in pure N9 for 3 h, 2 days, and 15 days or after annealing 66, 90, or 113°C for 24 h (times and temperatures were selected arbitrarily). The percentage of change in each property P (where P is the weight, dimension, or mechanical property) was calculated as:

$$|P_{\text{final}} - P_{\text{initial}}|/P_{\text{initial}} \quad (2)$$

For tensile strength and strain to failure measurements, dumbbell samples were cut from the film with an ASTM D 412 Type D die (reduced zone 3.6 cm long, 0.64 cm wide). For soaked samples, dumbbell specimens were cut out of film after the film had been soaked. The thickness of the two ends of each dumbbell were averaged and eight samples were tested as described in test method ASTM D412³⁷ by using an

Instron model 4465 machine at room temperature at a crosshead deflection rate of 500 mm/min.

Creep, elastic modulus, and dynamic properties were measured by using a dynamic mechanical thermal analyzer (DMTA) model V (Rheometric Scientific, Inc., Piscataway, NJ). A DMTA test specimen was made by cutting a strip from film by using parallel razor blades set 8 mm apart. A 1-inch-long sample was cut from the strip and the center thickness was measured. Specimens were examined under a stereomicroscope and rejected if the edges were not straight and the width was not uniform. For soaked samples, DMTA specimens were cut out of film after the film had been soaked.

The elastic modulus of DMTA specimens was measured prior to all creep and dynamic property measurements. The DMTA specimen was aligned in the DMTA with the sample grips set about 10 mm apart and tightened to 0.02 N·m to securely hold the film with minimal sample deformation. The film was stretched at a strain rate of 0.001/s to a maximum elongation of less than 1.0 mm. A data point was taken every 10 s. The modulus was calculated from the slope of a linear regression line through at least four of the most collinear points on the stress-strain plot. After the test, the distance between grips was quickly returned to their initial positions prior to starting a creep test or dynamic property measurement that immediately followed, as described below.

Creep samples were enclosed in the DMTA oven and held at 25.0 ± 0.05°C during the test. A 3-MPa tensile stress was applied for at least 5.5 × 10⁴ s. A data point was taken every 60 s. After each test, the slope of a linear regression line through points between 4.5 × 10⁴ and 5.5 × 10⁴ s was measured as well as the change in sample length (ΔL) between 10⁴ and 5 × 10⁴ s.

Dynamic properties [storage modulus E' , loss modulus E'' , and $\tan \delta (E''/E')$] were measured by using the DMTA at 1 rad/s and 1 Hz. Measurements were made at room temperature for about 1 min. The sample was then cooled in the DMTA with liquid nitrogen at the maximum rate and heated from about -80 to 0°C at 2°C/min by methods described in ASTM D5026.³⁸ Samples (10–15 μg) were also cooled and then heated, both at a rate of 10°C/min in a differential scanning

TABLE I
Tensile Strength and Strain to Failure of As Received Estane Measured in the Machine (Longitudinal and Transverse Directions)

Tension	Transverse	Machine	Probability (t -test)
Strength (MPa)	67 ± 3	71 ± 3	0.33
Failure Strain (%)	615 ± 22	536 ± 17	10 ⁻⁴
No. of samples	8	8	—

TABLE II
Creep of As Received Estane Measured in the Machine
(Longitudinal) and Transverse Directions

Creep	Transverse	Machine	Probability (<i>t</i> -test)
Rate ($\mu\text{m}/\text{min}$)	2.35 ± 0.10	0.79 ± 0.27	0.06
Δ Length (mm)	4.09 ± 3.7	0.99 ± 0.38	0.20
No. of samples	4	3	—

calorimeter (DSC model SP, Rheometric Scientific). Soft segment T_g was measured by ASTM method E-1356³⁹ and taken as the inflection point in DSC plots of heat flow versus temperature and by ASTM method D-5026 as the $\tan \delta$ peak temperature in DMTA plots of $\tan \delta$ versus temperature.

RESULTS AND DISCUSSION

Compared to the transverse direction, the machine direction of as-received Estane film had a significantly lower tensile strain to failure, creep, and lower swelling in solution, and greater thermal annealing shrinkage. For example, the probability (P) that there was no difference in the mechanical properties of Estane in the two directions by using the t -test (Tables I and II) was low for values of the strain to failure and for the slope of the creep curve (change in length between 10,000 and 50,000 s). A greater orientation of molecules in the machine direction (i.e., direction of take up onto rolls) probably resulted in the observed differences in properties between the machine and transverse directions.

Estane film immersed in pure N9 swelled in the transverse direction nearly twice as much as it swelled in the machine direction. Annealing caused as-received Estane film to shrink in all directions, probably

due to relaxation of the molecules oriented during blow molding. The higher the annealing temperature, the greater the shrinkage (e.g., shrinkage was 12% in the machine direction compared to 3.3% in the transverse direction for film annealed at 113°C). These results suggest that the effect of anisotropy on condom properties should be monitored. In this study, the tensile direction of all test specimens were oriented in the transverse direction unless otherwise noted.

Estane film was soaked in mixtures of N9 and PEG (0, 4, 8, 16, 32, 50, 64, 80, and 100% N9 in PEG) until absorption of the liquid by the film reached equilibrium. The final weight of the soaked film as a fraction of its initial weight (in percentage) was proportional to the PEG : N9 solution concentration (Fig. 3). Estane absorbed large amounts of the liquid, especially N9. The weight increase of film soaked in pure N9 (134%) was about 19 times greater than the weight increase of film soaked in pure PEG (7%). The liquid absorption at 23°C was about 5–10% higher than at 21°C. Estane condoms stored at a higher temperature or coated with a higher N9 concentration will absorb more of the liquid. This is important for N9 efficacy because the total volume of solution placed on a condom must equal the amount absorbed in addition to the amount necessary for its effectiveness against microbes.²⁸

The N9 fraction could be determined by using radiolabeled N9 or by extraction and HPLC or if the relationship between the liquid fraction (absorbed liquid weight divided by swollen film weight) and PEG : N9 solution concentration followed a simple rule of mixtures [i.e., a linear relationship between weight gain and liquid composition (dashed lines in Fig. 4)]. However, the actual absorption of mixtures of N9 and PEG (solid line in Fig. 4) was greater than the rule of mixtures, probably because the N9–PEG molecular interaction was weaker than polyurethane–N9 or

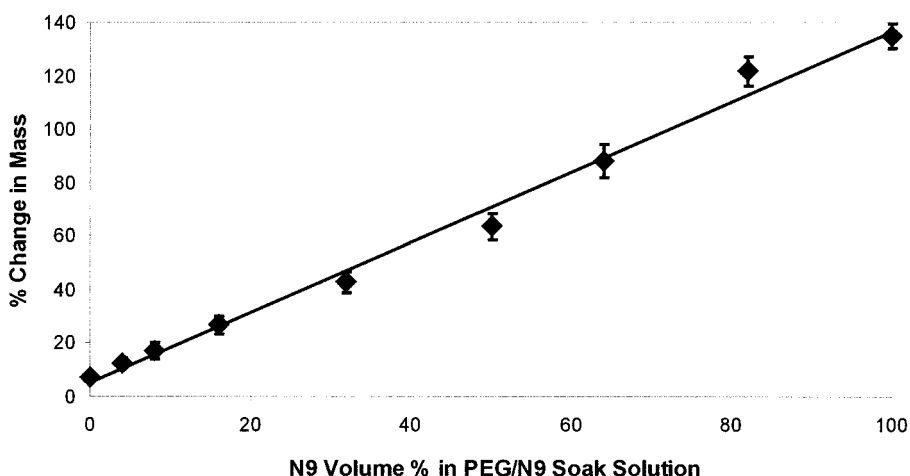


Figure 3 Percentage of change in weight with respect to initial weight of Estane soaked in various concentrations of N9 (three samples per data point).

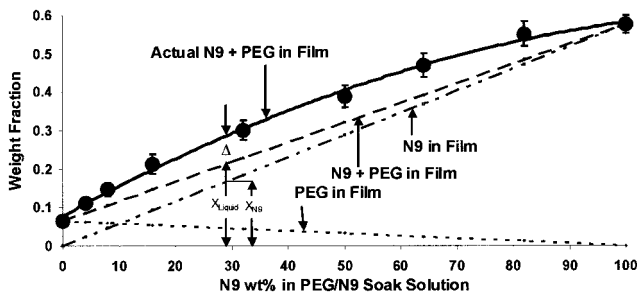


Figure 4 The actual absorption of mixtures of N9 and PEG (solid line, three samples per data point) compared to that which would be calculated by a linear rule of mixtures (dashed lines).

polyurethane-PEG interaction.^{40,41} This may be due to the surfactant properties of N9. The N9 fraction versus solution concentration was estimated by assuming that plots of the N9 and PEG fractions versus solution concentration deviated from linearity in the same positive direction as the liquid fraction did. This assumption is valid because the liquid weight fraction at all soak solution compositions were intermediate between that of the pure components and there were no maxima⁴² or inflection points⁴³ as observed in other systems of polymers soaked in two solvents. A second assumption was that the magnitude of the deviations from linearity of plots of the N9 and PEG fractions were proportional to the amount of N9 and PEG that would have been absorbed for a linear rule of mixtures relationship (dashed lines in Fig. 4). This assumption is valid for an elastomer such as Estane, which is above its T_g and is plasticized by both fluids. For glassy polymers exposed to a mixture of a plasticizer and nonplasticizer, this assumption would not hold because small amounts of the plasticizer lowers the T_g enough to allow large amounts of the nonplasticizer to be absorbed.⁴⁴⁻⁴⁷

By applying these two assumptions, the N9 fraction was plotted (Fig. 5) as

$$L_{N9} + \Delta(L_{N9}/L_{(N9 + PEG)}) \tag{3}$$

where L is the weight fraction of N9 or PEG or both when plotted linearly versus solution concentration (dashed plots in Fig. 4) and Δ is the difference between the solid and dashed liquid fraction plots in Figure 4. The resulting plot in Figure 5 suggests that N9 is absorbed much more than PEG and has no effect on the amount of PEG absorption.

The diffusion rates of the penetrant molecules N9 and PEG are dependent on their size, concentration in the polymer, and interactions with the polymer (e.g., hydrogen bonding⁴⁸) as well as on the intermolecular forces in the polymer.⁴⁹ The diffusion coefficient D is the proportionality constant between the chemical concentration gradient of the penetrant in the polymer and the rate of transport or flux of the liquid through the material, so a measure of D can be related to material properties for a given temperature and penetrant molecule.⁵⁰

Effective diffusion coefficients were measured by the sorption method. The sorption curve (Fig. 6) was obtained by plotting the weight of liquid (i.e., $m_t - m_0$, where m_t is the film weight at time t and m_0 is the initial film weight prior to soaking) sorbed into Estane film versus the square root of time. The weight increase asymptotically approached a limiting value (i.e., $m_{\infty} - m_0$, where m_{∞} is the film weight at equilibrium saturation of the film) where the system was at thermodynamic equilibrium and there was no longer an increase in absorption with time. D was calculated from the reduced sorption curve (Fig. 7), which is $(m_t - m_0)/(m_{\infty} - m_0)$ versus $(t^{1/2}/\text{thickness})$, based on the following equation^{51,52}:

$$\frac{m_t - m_0}{m_{\infty} - m_0} = \sqrt{\frac{D}{\pi}} \sqrt{\frac{\text{time}}{\text{thickness}^2}} \tag{4}$$

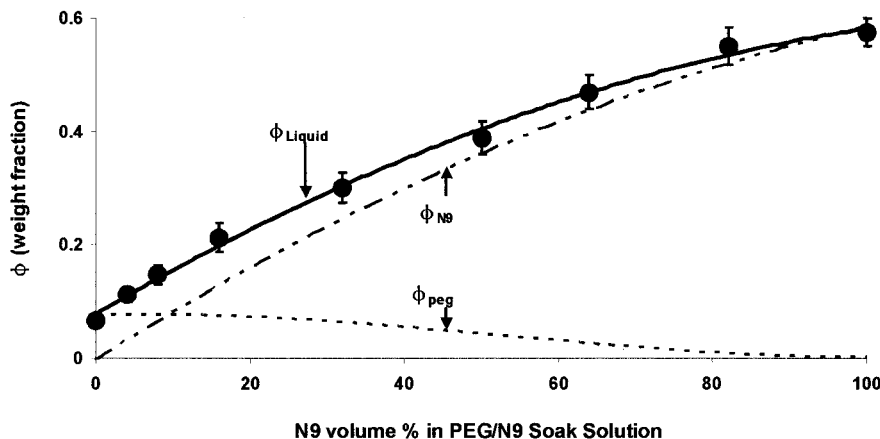


Figure 5 Calculated N9 and PEG weight fractions in the film.

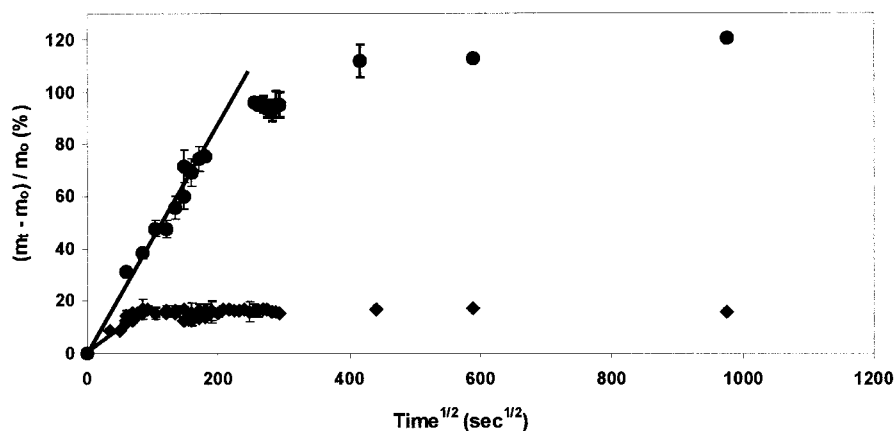


Figure 6 Change in weight of Estane film soaked in pure N9 and pure PEG (three samples per data point).

The D that is supposedly measured by the experiment results from the diffusion down the concentration gradient formed inside the solid after the liquid has adsorbed and then dissolved into the surface layer of the specimen. D for PEG was 40 times larger than D for N9 (D was 1.5×10^{-9} and 0.038×10^{-9} cm^2/s for PEG and N9, respectively) because of the greater size of N9 compared to PEG. By using a two-chamber diffusion cell, Saltzman²⁷ measured similar diffusion coefficients for N9 (between 5×10^{-10} and 4×10^{-9} cm^2/s) in a 100- μm -thick silicone elastomer. These values are higher than D for smaller molecules diffusing through elastomers (e.g., 60×10^{-9} cm^2/s for decane into Vibrathane B600 polyurethane membrane at 25°C⁵³ or 70×10^{-9} cm^2/s for methyl salicylate into epichlorohydrin membrane at 25°C).⁵⁴ Increased thickness of the film because of swelling by N9 can affect the value of D ,⁵⁵ but this was not the case here because the sample thickness was much less than the sample radius.

Liquid uptake and mechanical property changes of Estane film soaked in pure N9 and pure PEG ap-

proached equilibrium within about 20–40 h and 2–3 h, respectively (Fig. 6). N9 absorbance was not measured between 25 and 30 $\text{min}^{1/2}$. Khinnavar⁵³ measured diffusion and sorption into 1.5-mm-thick polyurethane sheets for a series of n -alkanes ($n = 6$ –10). For example, decane uptake was found to reach a plateau at 430% of the original sample weight in less than 1 h. Harogopad⁵⁶ reported diffusion and sorption of hydrocarbons ranging from C_8 to C_{16} into four different nonurethane polymers (also 1.5 mm thick). All reached maximum absorption in less than 1 h. These and other studies⁵⁷ showed that the higher the molecular weight of the absorbed molecule, the less that was absorbed and the longer it took for maximum absorption. Because the molecular weight of N9 (617 g/mol) and PEG (400 g/mol) are significantly higher than the molecular weight of absorbed molecules reported in these articles and because N9 contains a bulky ring structure, it is not surprising that a much smaller percentage of N9 and PEG are absorbed by the Estane in the present study over a much longer time, consistent with the lower entropy of mixing and slower diffusion rates for these molecules. However, time to film saturation by N9 and PEG is much less than the shelf-life, which would be at least 1 month, suggesting that shelf life is probably not an issue if property changes are as rapid.

Strain to failure, strength, elastic modulus (E), storage modulus (E'), loss modulus (E''), and T_g were measured before and after soaking Estane film in various mixtures of PEG : N9 for 20 h or 18 days (approaching equilibrium). Strain to failure tended to be slightly greater after soaking 18 days compared to results after soaking 20 h except for samples aged in 100% N9. Strain to failure (Fig. 8 shows 18 days data) increased initially because of plasticization and then decreased slightly at higher N9 fractions, perhaps because of excessive dilution of polymer chains and crosslinks in the swollen film so that the material broke before larger strains could be achieved.⁵⁸

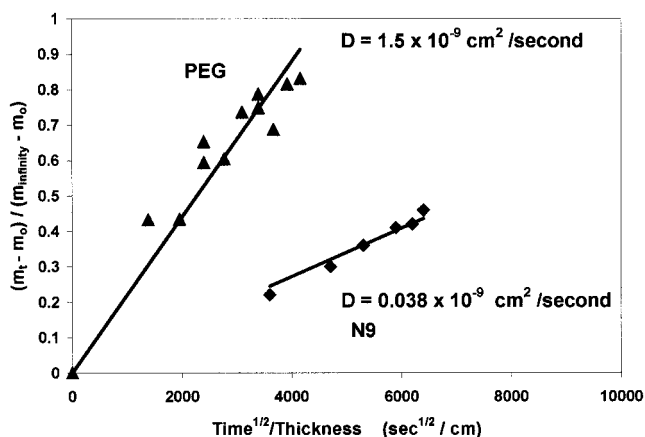


Figure 7 Weight gain versus time (three samples per data point).

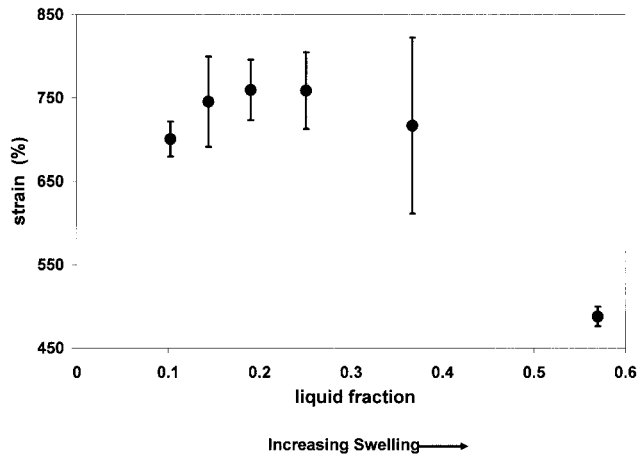


Figure 8 Maximum strain to failure versus liquid fraction for samples soaked 18 days (eight samples per data point).

Strength and moduli were divided by the polymer fraction based on the mixture rule

$$X_{\text{swollen}} = f_{\text{polymer}}X_{\text{polymer}} + f_{\text{N9}}X_{\text{N9}} \quad (5)$$

where X is the strength or modulus and f is weight fraction. $X_{\text{N9}} = 0$, so

$$X_{\text{swollen}} = f_{\text{polymer}}X_{\text{polymer}} \quad (6)$$

This compensates for the increase in the cross section of the soaked sample because of absorbed N9 by factoring out the increase in dimensions because of the presence of N9, which carried no load. However, plots of N9 fraction versus $X_{\text{swollen}}/f_{\text{polymer}}$ and N9 fraction versus X had the same general shape and were only shifted along the y -axis relative to one another. All the plots decreased asymptotically with increased N9 fraction. The plots of E , E' , and E'' were similar (e.g., Fig. 9 shows E) and were not as linear as the plot of strength (Fig. 10). E , E' , and E'' for samples soaked 18 days were slightly lower compared to the values of samples soaked 20 h, although most of the change in properties occurred in the first 20 h.

Soft-segment T_g was measured by ASTM method E-1356 at the inflection point in the DSC scan and by ASTM method D-5026 (1 rad/s oscillation frequency) at the $\tan \delta$ peak temperature of the DMTA scan. Soft-segment T_g of swollen film decreased with liquid fraction up to a liquid fraction of 0.5 (64% N9 soaking solution concentration) (Fig. 11). For phase-mixed polyurethane, T_g may also be lowered because of phase separation as a result of greater plastication, although this is unlikely for the materials under study here. N9 is more likely to dissolve the hard phase, resulting in phase mixing, which tends to raise T_g . The average of the E'' and $\tan \delta$ peak temperatures ($T_{g\text{ave}}$) was compared to DSC T_g values. $T_{g\text{ave}}$ and DSC T_g

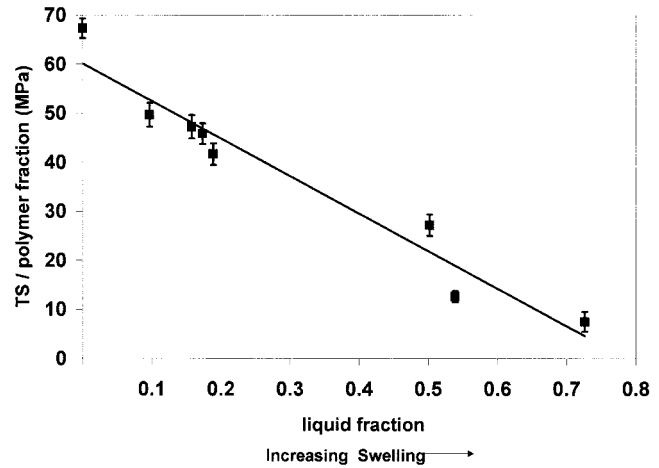


Figure 9 Tensile strength (TS) divided by polymer fraction plotted against liquid fraction (eight samples per data point).

were within 4°C of one another ($T_{g\text{ave}}$ was always greater than DSC T_g) over most of the N9 fractions. For DMTA scans run at 1 rad/s oscillation frequency, DSC T_g and $T_{g\text{ave}}$ differ by $\pm 4^\circ\text{C}$ for a wide variety of commercially available polymers⁵⁹ and $\pm 2^\circ\text{C}$ for crosslinked acrylic polyurethane films.⁶⁰

The effect of N9 concentration on T_g above a polymer fraction of 0.5 was similar to results in other studies.^{46,61} For example, Cooper and Tobolsky⁶¹ plotted the decrease in elastic modulus and T_g with increased PEG 200 plasticizer concentration mixed in during solution casting of Estane and reported a slope of $2.2 \times 10^5 \text{ Pa}/^\circ\text{C}$. The same result was obtained in this study except the slope of elastic modulus versus plasticizer concentration ($6.8 \times 10^5 \text{ Pa}/^\circ\text{C}$) was three times greater in the Cooper and Tobolsky study, probably due to the large absorption of N9 in our study. The original (nonsoaked) elastic modulus of Estane

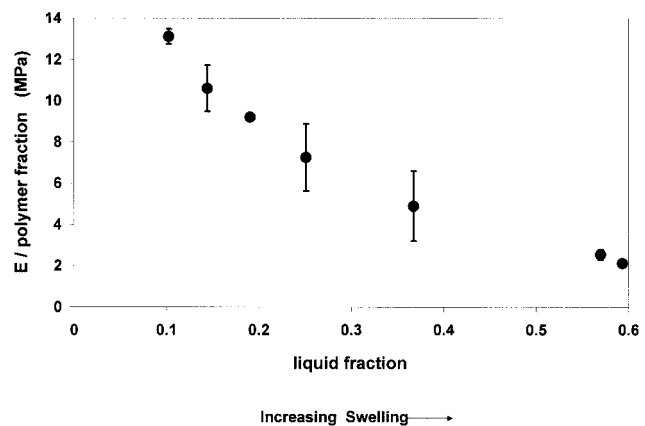


Figure 10 Elastic modulus divided by polymer fraction plotted against liquid fraction (eight samples per data point).

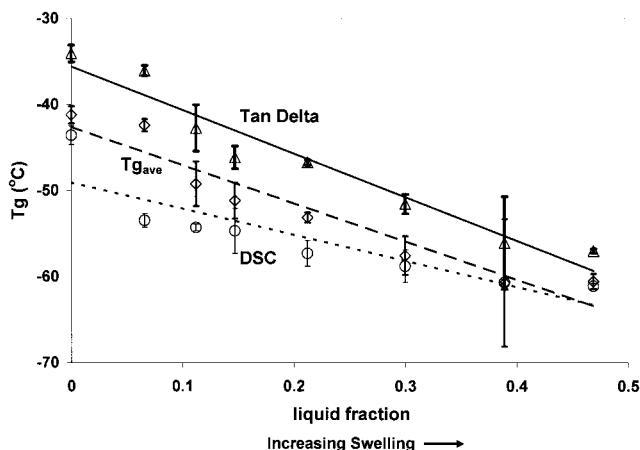


Figure 11 The average of the E'' and $\tan \delta$ peak temperatures compared to DSC T_g values (three samples per $\tan \delta$ data point, two samples per DSC data point).

was about 1.7×10^6 Pa in both studies. T_g versus liquid composition for the Estane/N9/PEG system did not follow the Fox relationship,^{62–64} or free volume theory for plasticizers.⁶⁵

The opposite trend has also been observed in the literature (i.e., increased soft-segment T_g of polyurethane with absorption of solvent⁶⁶). T_g of Pellethane 2363-55D increased 11°C because of absorption of 1.6% water (equilibrium amount) because water promoted hydrogen bonding between hard and soft segments and between ether oxygens of soft segments. T_g also increased with cortisone absorption, but then suddenly dropped when the absorption rate suddenly

increased at 36 h (0.25% absorption) because cortisone's three carbonyl groups (good hydrogen bond acceptors) may have interacted with the N—H groups of Pellethane (good hydrogen bond donors) to disrupt hydrogen bonds between the hard and soft segments, thus increasing the mobility of the soft segments, and therefore, lowering T_g .

It is unlikely that absorbed N9 disrupted the hard-segment domains in our study because the Fickian diffusion behavior observed suggests that hard domains generally maintain their structure in the swollen state as a result of strong attractions between parallel hard segments.¹⁸ Schneider et al.⁶⁷ found that *n*-heptane follows Fickian diffusion in Estane 2714 (which has a PTMO : MDI : BD ratio of 3 : 2 : 1 and a PTMO molecular weight of 1000) and so concluded that the solvent does not affect the hard-segment structure. Chloroalkanes of increasing polarity caused greater swelling and deviation from Fickian behavior, suggesting solvent interaction with and relaxation of the hard phase. In polyester urethane based Estane, Cooper²⁴ reported that solvents with greater polarity associate with aromatic urethane linkages, causing a greater solvation of the reinforcing tie points.

The loss of mechanical properties with increased N9 concentration was likely due to plasticization of the soft-segment domains. Hard-segment domain disruption was probably not occurring because the relationship between the elastic modulus and polymer volume fraction followed the Flory–Rehner relationship for swollen elastic rubber networks (Fig. 12) (the elastic modulus after swelling is proportional to the recip-

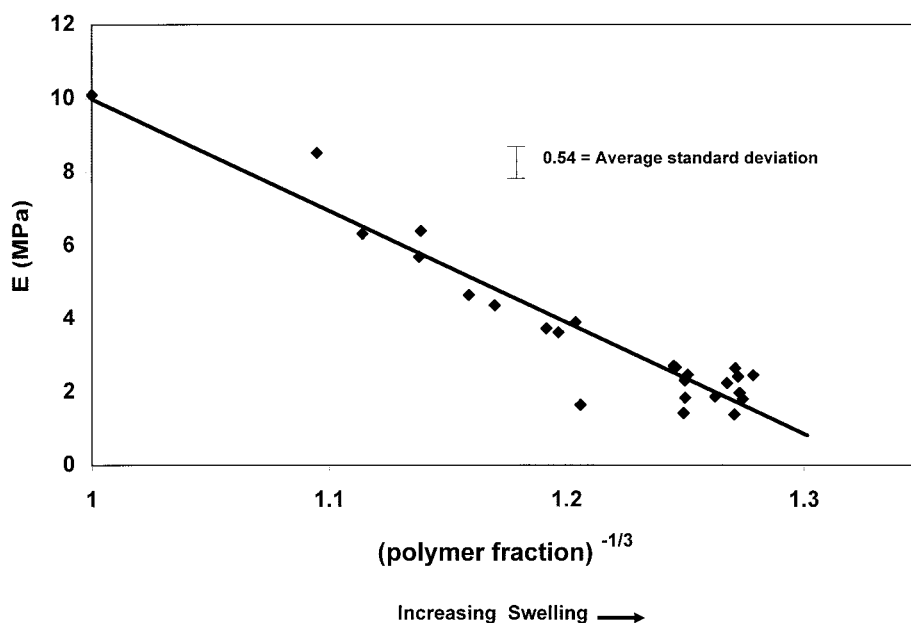


Figure 12 The elastic modulus versus the reciprocal cube root of the polymer volume fraction for Estane swollen in pure PEG or pure N9.

rocal cube root of the polymer volume fraction^{68–70}) and diffusion of neat N9 and neat PEG followed a Fickian behavior. This is expected because hard domains are much more difficult to disrupt because of strong hydrogen bonding and/or crystallization.

The properties of Estane were compared to Tecoflex because Tecoflex is used in the only polyurethane condom packaged with a coating of an N9 solution (8% N9 in PEG). Tecoflex contains HMDI, whereas Estane contains MDI, and Tecoflex probably has more soft segment than Estane based on the fact that Estane has a higher modulus (Table III). The equilibrium weight uptake of Estane and Tecoflex as a fraction of the initial weight was proportional to the PEG/N9 solution composition (Fig. 13). Estane absorbed 15 times more N9 than PEG (150% in pure N9 compared to only 10% in pure PEG), whereas Tecoflex absorbed about 10 times more N9 than PEG (35% in pure N9 compared to only 3.5% in pure PEG).

Tecoflex Trojan condoms and Estane film presoaked in 8% N9 solution were both washed in water. These films, as well as neat Estane film, were then soaked in either water, PEG, or N9 and the elastic modulus, E' , E'' , and T_g were measured by DMTA. These properties were highest for film soaked in water, followed by PEG, and then by N9 (Table III). Beksinska et al.⁷¹ reported that washing, drying, and relubricating of the female condom up to eight times does not affect the burst and seam strengths. Tecoflex presoaked in 8% N9 (i.e., the Trojan condom) and then washed had lower properties than Estane presoaked in 8% N9 and then washed (Table III). However, the opposite was true if the second soaking was in pure N9, so the impact of N9 on Estane was greater than on Tecoflex.

CONCLUSION

Properties of Estane film were reduced more than those of Tecoflex film when soaked in various mixtures of N9 and PEG. This may not matter for low concentrations of N9 because the initial, nonsoaked

TABLE III
Properties of Estane and Tecoflex, Both Soaked in 8% N9 Then Washed in Water, Followed by Soaking in Water, PEG, or N9

Parameter	Material	Properties after 2 nd soaking		
		Water	PEG	N9
T_g (°C)	Estane	−31	−40	−48
	Tecoflex	−52	−54	−58
E (MPa)	Estane	11	10	1
	Tecoflex	5.5	5.1	3.9
E' (MPa)	Estane	15	12	0.97
	Tecoflex	6.2	5.1	3.7
E'' (MPa)	Estane	13	8.6	1.0
	Tecoflex	4.8	4.0	2.4

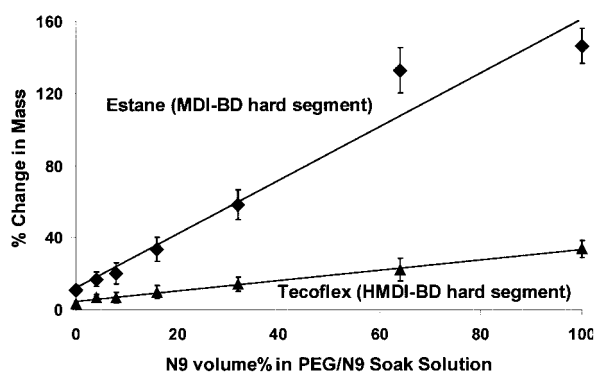


Figure 13 The equilibrium percentage of change in weight as a fraction of initial weight of Estane and Tecoflex soaked in various PEG/N9 solutions (three samples per data point).

properties of Estane were higher than those of Tecoflex. The reduction in properties should be weighed against the benefit provided by an increase in concentration of N9 in solutions coating condoms made out of either material. A smaller reduction in mechanical properties may be achieved by reducing N9 absorption, perhaps by adjusting the polymer chemistry or processing, or via an additive in the lubricant (e.g., macrogels minimize migration of N9 into latex rubber²⁸). Loss in properties with increased N9 concentration is likely due to plasticization of the soft-segment domains. Hard-domain disruption is less likely because the relationship between the elastic modulus and polymer volume fraction followed Flory's theory for swollen elastic rubber networks and diffusion of neat N9 and neat PEG followed a Fickian behavior. As most of the absorption and decrease in properties occurred in the first 20 h after soaking, the long-term shelf life may not be an issue, although this inference has yet to be confirmed. The condom user might store the condom at temperatures greater than 23°C, which would increase the equilibrium absorption, lower properties, and further reduce the amount of N9 available at the surface to neutralize microbes. Estane film anisotropy suggests that the condom should be cut in an orientation that optimizes this property–orientation relationship.

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