

Preface

The medical device and drug industries are consistently among the strongest technological performers. Materials are a key ingredient in their dynamic growth. Development of these materials is in a constant state of activity, with the challenge of replacing old materials that cannot withstand the tests of time, and the new materials' needs coming to the forefront in modern applications. This new reference text, *Biomaterials Engineering and Devices: Human Applications*, focuses on materials used in or on the human body—materials that define the world of “biomaterials.”

Biomaterials Engineering and Devices: Human Applications focuses on materials development and characterization. Chapters deal with issues in the selection of proper biomaterials from biocompatibility to biostability to structure/function relationships. Chapters also focus on the use of specific biomaterials based on their physiochemical and mechanical characterizations. Integral to these chapters are discussions of

standards in analytical methodology and quality control.

The users of *Biomaterials Engineering and Devices: Human Applications* will represent a broad base of backgrounds ranging from the basic sciences (e.g., polymer chemistry and biochemistry) to more applied disciplines (e.g., mechanical/chemical engineering, orthopedics, and pharmaceuticals). To meet varied needs, each chapter provides clear and fully detailed discussions. This in-depth, but practical, coverage should also assist recent inductees to the biomaterials circle. The editors trust that this reference textbook conveys the intensity of this fast moving field in an enthusiastic presentation.

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Polymers in the Oral Environments

Novel Elastomers as Soft Liners

Kalachandra Sid and Tetsuya Takamata

1. Introduction

Glassy polymers are used as dental materials because their rigidity enables them to support loads and to resist forces imposed in service in the oral cavity. Glassy polymers are generally regarded as amorphous and brittle. However, classification of these materials is very much a time-dependent concept, in which a brief experimental time interval generates brittleness, but an extended time-scale can result in viscous flow. This time-dependent behavior of polymers is exemplified in the material known as “bouncing putty,” which flows like a viscous fluid when left under its own weight for extended periods, but shatters like a glass when hit with a hammer. Temperature is another factor that determines whether a polymer is a glassy solid, an elastic rubber, or a viscous liquid.

2. Glass–Rubber Transition Behavior

When cyclic or repetitive motions of stress and strain are involved, it is more convenient to talk about dynamic mechanical moduli. The complex Young’s modulus has the formal definition, $E^* = E' + iE''$. Where E' is the storage modulus and E'' is the loss modulus. The quantity i represents the square root of -1 . The storage modulus is a

measure of energy stored elastically during deformation, and the loss modulus is a measure of the energy converted to heat.

3. Distinct Regions of Viscoelastic Behavior

The states of matter of low-mol-wt compounds are well known: crystalline, liquid, and gaseous. The first-order transitions that separate these states are equally well known: melting and boiling. Another well-known first-order transition is the crystalline–crystalline transition, in which a compound changes from one crystalline form to another.

By contrast, no polymer with high molecular weight vaporizes to gaseous state: All decompose before the boiling point. In addition, no high-molecular-weight polymer attains a totally crystalline structure, except in the single-crystal form.

In fact, many important polymers do not crystallize at all, but form glasses at low temperatures. At higher temperatures, they form viscous liquids. The transition that separates the glassy state from the viscous state is known as the glass–rubber transition, which exhibits the properties of a second-order transition at very slow rates of heating or heating.

In order to provide a broader picture of the

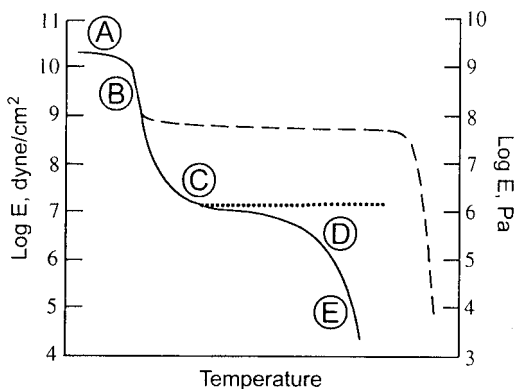


Fig. 1. Five regions of viscoelastic behavior for a linear, amorphous polymer. Also illustrated are effects of crystallinity (dashed line) and crosslinking (dotted line).

temperature dependence of polymer properties, a brief discussion of distinct regions of viscoelastic behavior is presented in the following paragraphs. The five regions of viscoelastic behavior for linear amorphous polymers (1) are shown in Fig. 1.

In region A, the polymer is glassy and frequently brittle. Typical examples at room temperature include polystyrene cups and polymethylmethacrylate (PMMA) (Plexiglas sheets). Young's modulus for glassy polymers has the value of approx 3×10^{10} dyn/cm² (3×10^9 Pa). In the glassy state, molecular motions are largely restricted to vibrations and short-range rotational motions.

The value of the bulk modulus was calculated in terms of the cohesive energy density (CED), which represents the energy theoretically required to move a detached segment into the vapor phase. This, in turn, is related to the square root of the solubility parameter (1). It should be noted that many hydrocarbon and not-too-polar polymers have CED values within a factor of 2 of the values for polystyrene. Region B is the glass transition region. Typically, the modulus drops a factor of approx 1000 in a 20–30°C range. The behavior of polymers in this region is best described as leathery, although a few degrees of temperature change will obviously affect the stiffness of the leather. For quasistatic measurements, the glass transition temperature, T_g , is often taken at the maximum rate of turndown of the modulus at the

elbow, or d^2E/dT^2 is at a maximum. Qualitatively, the glass transition region can be interpreted as the onset of the long-range, coordinated molecular motion. In other words, at low temperatures, polymers become hard and glass-like, because the motion of the polymer chains in relation to each other is slow. The T_g itself varies widely with structure and other parameters.

Region C is the rubbery plateau region. After the sharp drop that the modulus takes in the glass transition region, it becomes almost constant again in the rubbery plateau, with typical values of 2×10^7 dyn/cm² (2×10^6 Pa). In the rubbery plateau region, polymers exhibit long-range rubber elasticity, which means that the elastomer can be stretched, perhaps several hundred percent, and snap back to substantially its original length, on being released.

In this region, two cases need to be discussed. First, if the polymer is linear, the modulus will drop off slowly. The width of the plateau is governed primarily by the mol wt of the polymer: the higher the mol wt, the longer the plateau. Second, if the polymer is crosslinked, the dotted line is followed and improved rubber elasticity is observed, with the creep portion suppressed. An example of a crosslinked polymer above its T_g obeying the equation, $E = 3nRT$ (where n , the number of active chain segments in the network and the term RT represents the gas constant and absolute temperature). An example of a crosslinked polymer above its T_g , which obeys this relationship, is the ordinary rubber band.

The rapid, coordinated molecular motion in this region is governed by the principles of repetition and diffusion. Thus, when the elastomer is stretched, the chains deform with a series of rapid motions of the deGennes type. For crosslinked systems, the motion is thought to become a more complex affair involving the several chain segments that are bound together.

3.1. Region D: The Rubbery Flow Region

As the temperature is raised past the rubbery plateau region for linear amorphous polymers, the rubbery flow region is reached. In this region, the polymer is marked by both rubber elasticity and flow properties, depending on the time-scale of the experiment. For short time-scale experiments, the physical entanglements are not able to relax,

and the material still behaves rubbery. For longer times, the increased molecular motion imparted by the increased temperature permits assemblies of chains to move in a coordinated manner (depending on the molecular weight), and hence to flow.

Region D does not occur for crosslinked polymers. That being the case, region C remains in effect up to the decomposition temperature of the polymer.

3.2. Region E: The Liquid Flow Region

At still higher temperatures, the liquid flow is reached. The polymer flows readily, often behaving like molasses. The increased energy, associated with chains, permits them to reptate out through entanglements rapidly, and to flow as individual molecules.

For semicrystalline polymers, the modulus depends on the degree of crystallinity. The amorphous portions go through the glass transition, but the crystalline portion remains hard. Thus, modulus of a composite is determined. At the melting temperature, which is always above T_g , the modulus drops rapidly to that of the corresponding amorphous material, now in the liquid flow region. Modulus and viscosity are related through the molecular relaxation time.

At a temperature range the phenomenon known as the glass transition (T_g) appears, in which the polymer possesses an intermediate modulus between glassy and rubbery behavior. The resultant viscoelastic response is usually accompanied by the dissipation of energy, which is often expressed as the loss tangent ($\tan \delta$) of the material. Loss tangent is defined as the ratio of imaginary to real moduli. At T_g , there are characteristic changes in both E' and $\tan \delta$. Below T_g , the polymer is in a glassy (rigid) state; just above T_g , it is leathery; above about $T_g + 50^\circ\text{C}$, it is rubber-like. The value of E' in the rubber-like state can be used to calculate the density of elastically effective crosslinks.

Glass transition behavior is important for dental polymers, because a denture base is required to be rigid in the oral environment at temperatures approaching the boiling point of water, in the case of hot drink consumption. The major unfilled glassy polymer for such usage has, for a considerable time, been PMMA. There is also a need for

polymers that exhibit rubber-like characteristics at room temperature through mouth temperature and above, such as methacrylates, into which a plasticizer is incorporated to reduce their T_g to below room temperature. These materials are used as soft liners, which can be attached to the rigid denture base, to form a soft cushion between the soft mucosa and the rigid denture. They are especially applicable to patients suffering effects of trauma or sore mouth conditions. Both the rigid and rubber-like methacrylates are available as heat or use as rigid room-temperature-curing temporary crown and bridge resins and copy dentures. Not only are these monofunctional methacrylate monomers important dental materials, but difunctional methacrylate monomers also form a large and rapidly expanding field as cosmetic composite filling materials. In this situation, the difunctional methacrylate forms the matrix phase of the filled resin. Difunctionally based methacrylate fissure sealants are also available to prevent caries forming in deep occlusal fissures, which are difficult to keep bacteria-free. Oral disease, though not dangerous to human life, affects nearly everybody, certainly in the Western world, where the field of dentistry has been identified as a priority area, in order to overcome oral diseases.

Polymeric materials for denture bases, such as vulcanite (hard rubber), and a form of agar-agar, were used occasionally as soft lining materials and elastic impression material, respectively, before the Second World War. Later, (PMMA) became the chief material of choice for full dentures, albeit with well-known defects.

Fluid room temperature vulcanizing (RTV) rubbers were developed (both silicone and polysulfide types). These were swiftly adapted for dental purposes, changing the dimensional accuracy of impressions; subsequently, other modifications of this principle followed.

4. Soft Lining Materials

There is a great demand for improved elastomeric soft lining materials that will provide longer service life, greater comfort, and improved mechanical properties and dimensional stability in the oral environment. The development of these materials has been difficult and multifactorial, and some of the factors involved in clinical failure are

poorly understood. Compositions of these materials are continually being modified by manufacturers, to improve their properties and service life.

A satisfactory soft lining material is expected to have the following characteristics: It must be compatible with oral tissues; it must be compliant and resilient; it must have dimensional stability; it must adhere to PMMA dentures; it must be resistant to rupture; it must be readily wettable by saliva; it should have low and limited water uptake; and it should not support the growth of *Candida albicans* (2–6).

It is well established that no currently available soft lining material is clinically fully satisfactory (2,7,8). Much of the basic information defining the problems in the design of soft liners for denture bases has been well documented in the literature (4,5,9–12). Until recently, all soft liners fell into two classes: silicone elastomers and plasticized acrylics. Silicone polymers, in general, suffer from poor tear resistance and poor adhesion to PMMA dentures (4). The earliest silicones offered for dental use suffered from several problems. Usually, these silicones were of the condensation type. Some silicone soft liners took up 60% water. Of all elastomeric polymers, silicones have the highest diffusion coefficient for water, and, since water uptake of elastomers is particularly governed by water-soluble impurities, silicones can be worse than any other polymers. There is evidence (13,14) that the presence of organo-tin initiators, used in some condensation silicones, causes degradation in the presence of water. Similarly, the presence of acetate ions, or residual acetic anhydride, promote the growth of *Candida* (3,13).

So-called “soft acrylics” usually owe their compliance to the presence of a plasticizer, commonly a phthalate, although phosphates have been used. Wright (4) has reviewed the composition of a number of such materials. As is well known, loss of plasticizer results in hardening of the liner. At the same time, the presence of a plasticizer increases the tendency of the material to dissolve organic compounds and to discolor. However, the adhesion to PMMA is generally good.

In order to overcome the fundamental problems of hardening, peeling, and discoloration, various alternatives have been developed. Van Handell (14) patented a copolymer system based on an

α - ω -hydroxyl-terminated silicone polymer with methacryloxypropyl trimethoxysilane as cross-linking agent, and at least one commercial product is based on this chemistry. This is not a condensation-type material, and thus avoids many of the problems associated with condensation byproducts. This material must be heat-cured. However, in the uncured state, this polymer becomes partially insoluble in solvents, with time pointing to the development of a crosslinked state. This is clearly a problem, because old batches of the material become difficult to process. Among the existing proprietary soft lining materials, Molloplast B is based on this chemistry. This is probably the best commercial product currently available, even with this shelf life problem.

Another approach is to try to exploit the good adhesion of soft acrylics, but to prevent plasticizer loss. Litchfield and Wood (15) patented a soft acrylic based on poly(ethylmethacrylate) polymer powder, 2-ethoxyethyl methacrylate, and a polymerizable plasticizer, di(2-ethyl hexyl) maleate. Although maleates are not very reactive, sufficient polymerization occurs to suppress leaching. A modified version of this system showed very little leaching after 7 yr (16,17). Parker and Braden also described the use of powdered elastomers, doughed with a higher methacrylate (e.g., tridecyl), to give an elastomeric product with plasticizer, i.e., the problem of plasticizer leaching is largely solved (18).

Gettleman, in a study of polyphosphazene materials, described the use of polyphosphazene polymers, into which methacrylate monomers had been milled to give an elastomer with good bonding, and generally satisfactory results (19). The commercial product based on this approach suffered from excessive water sorption, and is not currently marketed. The use of phosphazene polymers seems very promising, and suggests that other solid industrial polymers should be examined in the same way, i.e., by milling in a suitable monomer, and then curing in the usual way. The choice of a polyphosphazene probably reflects its resistance to aging.

From the clinical point of view, the soft lining materials are shown to be successful (20). Generally between 60 and 100% of patients are satisfied with their soft-lined denture (8). A long-term (9-yr) study shows 12/22 Molloplast B linings still

performing adequately (12), the most common reason for failure being soreness (associated with the wetting characteristics of the material), followed by adhesion to the denture base. The wetting behavior of soft lining materials is a major factor in their performance, because a poorly wetted soft lining material will cause frictional damage to the oral mucosa (8). The plasticized acrylic materials suffer from hardening caused by loss of plasticizer, leading to some concern over the toxicity of the phthalate plasticizer (8).

Comparison of mechanical properties of soft lining materials shows wide variation, with the highest tear and tensile strengths being for the plasticized acrylic materials, and the lowest being for the silicone-based materials (21).

The effect of storage in different solutions has been shown to be important in deterioration, with great reductions being observed in saliva (22). Differences in laboratory and clinical results tend to reflect the inconstant nature of the mouth, with personal habits such as smoking and drinking having a profound effect on some properties, such as viscosity (22) and color (12). The temperature cycling that the denture would be exposed to (from hot and cold drinks, and so on) has also been shown to be detrimental to the compliance of the soft lining (23). The treatment of the denture during cleaning, and so on, effects the longevity of some materials, with some denture cleaning fluids leading to surface degradation (24) or, in the case of bleach, denture discoloration (20). Despite this, the use of *in vitro* testing allows some degree of certainty about the material's behavior in the mouth to be determined.

The bonding of soft lining materials has recently attracted much attention, with numerous studies being conducted on commercial materials. The major factor in determining the strength of the bond is the soft lining material, rather than the type of denture base (25). It is important to realize that there are three possible mechanisms of failure of material: adhesive (along the interface), cohesive (through the soft lining material), or a combination of the two. There is some concern about the testing methodology being used, with two types of tests predominating: a peel test, in which the soft lining material is peeled back on itself; and a tensile test, in which the material is sandwiched between two blocks of PMMA.

Evaluation of these two test methods has shown that both reproduce the same ordering of commercial materials (26). There is, however, cause for concern about the applicability of the peel test to silicone elastomers because the orientation of the loading means the material fails cohesively, reflecting poor tear resistance (26). Geometry of the tensile test makes the reference of its results to the clinical situation questionable (8).

Generally, the plasticized acrylic-based materials (such as Coe Super-Soft and Vertex Soft) have the highest peel strengths, and typically fail at the adhesive joint (25–27). Molloplast B is the best of the silicone-based elastomers, although it tends to fail cohesively, indicating a problem with its tear resistance (27). The peel strength of Novus is between that obtained for acrylic-based materials and silicone materials, but shows a much greater sensitivity to the test method, with values almost equal to acrylic-based materials in peel, but much lower when tested by tension (26). The influence of water storage has been widely investigated, because this represents the clinical situation more accurately. Here the peel strength seems to be generally high at relatively short time intervals (7 d), and lower after a more prolonged adsorption, 3 or 4 mo (27,28). This is attributed to the building up of stresses at the interface and changes in the viscoelastic properties of the material (28).

The water sorption of soft lining materials may explain many factors about the aging process, the plasticized acrylic-based materials (which tend to harden over time) showing a generally high uptake and high solubility, resulting from the leaching of the plasticizer (24). The more durable silicones have a generally smaller uptake and lower solubility (29). As previously stated, Molloplast B is perhaps the best soft lining material currently available, and this reflects its low water sorption and solubility. Thus, consideration and understanding of water uptake characteristics of these materials is of great importance.

The water sorption of PMMA and other rigid polymers is reasonably straightforward: Depending on the geometry of the specimen, a well-defined equilibrium is ultimately reached (2% for PMMA) (21). The kinetics of uptake obey the laws of diffusion, and the D_{eff} can be determined (21,30–35). Extensive studies have been made by Kalachandra and Turner, and Braden, et al. in

predicting the water uptake of polymethacrylate systems (32–41).

With most soft liners, water sorption continues for many years, even for specimens only 1 mm thick, and reaches high levels. In particular, the systems of Parker and Braden (16,17), based on a polymerizable plasticizer, showed continuing uptake after 7 yr, attaining values of >10% water content. It was observed that one silicone elastomer took up more than 50 wt% water (10). These high uptakes cause severe deterioration in mechanical properties. Initially, these results were surprising, because diffusion coefficients of water in elastomers are such that equilibrium should be attained in 1 d. Similar results are also seen with acrylics, even though the soft acrylics based on higher methacrylates should have lower water uptake than PMMA, because they are more hydrophobic.

Muniandy and Thomas (42) working on the application of natural rubber vulcanizates in marine applications, observed similar behavior. They were able to show that the high and prolonged uptake was the result of the presence of water-soluble impurities. When the penetrating water reaches an impurity site, the resultant solution droplet grows until osmotic and elastic pressures balance, i.e., the high compliance of elastomers is the essential feature. Parker and Braden (16,17) have shown that the same phenomenon occurs in acrylic soft lining materials. The slow continued sorption of water over an extended period is controlled by the rate of creep relaxation of the elastic pressure. Desorption, on the other hand, is diffusion-controlled and the desorption is complete in a day or so.

There are further implications in the case of soft lining materials: They are much weaker than natural rubber, and the osmotic pressures may be sufficient to cause rupture; indeed, mechanical failure was how the Parker–Braden materials failed clinically; The uptake should be less in aqueous solutions than in pure water. This was observed by Ellis (43) without realizing the mechanism, and has been demonstrated by Aiken (44). This osmotic process is often transiently obscured by the extraction of plasticizer. In plasticized materials, the loss of plasticizer can give a false equilibrium, which occurs when water uptake is balanced by plasticizer loss.

A number of higher methacrylates have been used in soft lining materials. However, Davy and Braden (45) have shown that the choice is crucial. Going from polymers of n-hexyl to tridecyl methacrylate, strength drops dramatically; hence, the pentyl or hexyl ester should be used.

The following paragraphs succinctly present the findings of the authors' recent studies of soft liners (newly developed experimental and commercial) with reference to water sorption, solubility, and mechanical (dynamic mechanical) properties.

5. Study of Water Sorption of Novel Butadiene/Styrene Elastomers

The water uptake of a commercial powdered butadiene–styrene (BS) elastomer, containing a partitioning agent (i.e., antiblocking agent), was measured and compared to its purified elastomer. The water uptake was 8–12% in 6 mo for the former; the latter had only 0.5–2.5% in 6 mo (43–49). The increased water uptake of BS elastomers was explained as follows: The commercial powdered BS elastomer contained a partitioning agent (talc), to prevent agglomeration on storage. The presence of water-soluble partitioning agent in the elastomers results in the formation of solution droplets at the sites of the partitioning agent. The droplets then grow, the driving force being the chemical potential gradient (osmotic pressure) between the droplet and external solution (water). In fact, the BS samples became cloudy and opaque in water, because the internal droplets scattered the light (45). In order to verify that the osmotic process is indeed responsible for the high water uptake in these systems, water uptake measurements were made with n-hexyl methacrylate (HMA) and 2-ethyl hexyl methacrylate (EHMA)-based BS elastomers in saline and glucose solutions at 37°C. Lower water uptake from saline and glucose solutions was observed, compared to pure water, confirming that the process is osmotically driven. A material that has an uptake of ~6% in water, which is still increasing after 4 mo, has an uptake of only ~1% in 0.9 M saline solution at the same times. The water uptake of most of the materials from artificial saliva is less than from pure water. However, the uptake from saliva is higher than from the other solutions (0.1, 0.3, and

1.0 M NaCl and 0.1, 0.3 and 1.0 M glucose). The lowest uptake is from the saline solutions, because saline solutions of the same concentration have higher osmotic pressures than the saliva and the nonionizing glucose solutions (47,51–53).

Analysis of the data, with reference to a recent study of water uptake of soft lining materials from osmotic solutions, revealed that uptake of the two experimental materials based on 70:30 BS block copolymer, with 1 wt% of lucidol (BS1) and 1 wt% of lauryl peroxide (LP) (BS2) and Novus, was reduced in the saline solutions (0.45 and 0.9 M NaCl) relative to that observed in distilled water (53). This could explain the satisfactory clinical performance of Novus, despite its water uptake from pure water. This finding supports the theory that the high uptake of elastomeric solutions is osmotically driven (48).

In order to study the effect of the nature of the initiator on water sorption, benzoyl peroxide (BP) and lauryl peroxide initiators were used (47,51). Decomposition of BP gives benzoic acid, which is water-soluble at 37°C. However, use of LP instead of BP, in these particular formulations, did not produce any noticeable effect on water sorption, with the effect of the partitioning agent overshadowing that of the benzoic acid. A study of the effect of the extent of crosslinking on water uptake was also undertaken. It was observed that increasing the crosslinking agent (0.5 to 1.0% ethylene glycol dimethacrylate [EGDM]) in systems containing BS (47,51) resulted in a decrease in water uptake (5.4 to 5.0%), indicating that increase in crosslinking density will result in decrease in water uptake. The notable finding is that inclusion of EHMA, instead of HMA, reduced water uptake from 7.1 to 5.4%, because of the more hydrophobic character of the former (47,50), which indicates that the use of EHMA is preferred in the design of soft lining material.

Water uptake of materials prepared using an alternative BS elastomer without a partitioning agent also proved high at ~6% in 4 mo. Similarly, styrene–isoprene (SIS) elastomers produced high-water-uptake materials. These two elastomers are produced by a solution polymerization process, which results in the presence of hydroxyl groups that are hydrophilic, thus increasing the water uptake.

During the course of the water uptake investi-

gation, it was found that some of the materials had sudden increases in water uptake after several weeks in water. This has been attributed to oxidation of the $-C=C-$ bonds producing hydroxyl groups, which account for the increase of water uptake. It has to be noted that these materials discolored and became brittle. The rate at which this happened depended on the composition, water uptake, and immersion solution (48). The BS-based materials showed most tendency to oxidize, the SIS the least tendency. This is thought to result from some steric effect of the methyl group shielding the diene bond. Initial studies have shown that water uptake of the SIS-based materials can be reduced by increasing crosslinking, or by reinforcement with silane-treated silica. The tendency to oxidize is also reduced.

In summary, it was observed that water sorption of the samples is controlled by the nature of the samples, crosslinking density, water-soluble or hydrophilic impurities, and the osmotic pressure of the external solution.

Two types of soft lining materials were developed, based on elastomeric silicones and methacrylates.

5.1. Silicone-based Elastomers

The inherent water adsorption of both peroxy-cured and hydrosilylation-cured silicones were very small (0.5%). However, the introduction of a hydrophilic constituent as a filler increased the adsorption of water, which was attributed to the formation of droplet solutions within the material. The water uptake of the silicone materials is dependent on the filler used and its surface treatment, and on the solubility of components and additives. Use of hydrophilic filler in peroxy-cured silicone did not lead to as much increase in water sorption as anticipated, which was attributed to the siloxane in the silicone bonding or adsorbing onto the surface of the silica, and so covering with a hydrophobic siloxane (54). When calcium stearate was used to increase the wettability in these systems, the water uptake drastically increased to ~8%.

A recent study of the influence of additives in water uptake of hydrosilanized silicone rubbers found that the greater the solubility of the additive, the more prolonged the uptake and the greater the deviation from the classic diffusion theory.

Table 1
Types of Commercial Soft Lining Materials

Product	Material Type	Source
Molloplast B	Heat-cured silicone	Detax/Karl Huber GmbH, KG, Germany
Novus	Polyp-hosphazine	Hygienic, Akron, OH
Kurepeet	Fluoroe-lastomer	Kureha Chemical, Tokyo, Japan
Supersoft	Plasticized acrylic	Coe Laboratories, Chicago, IL

In order to obtain broadly based information on the characteristics of currently available commercial products, four commercial soft liners were selected, each representing a different type of material. These products are listed in Table 1.

6. Dynamic Mechanical Analysis (DMA)

The dynamic mechanical analyses were performed using a Perkin-Elmer (DMA)-7 Thermal Analysis System. This instrument has several design features that make it particularly useful for testing soft liners and other dental products. It is

capable of operating in a compression cycling mode with a wide variety of probe tips, and permits operation with the specimen in air or immersed in water. An attempt was made to adjust the conditions of the test, to approximate, when possible, the normal conditions of use. The specimens were prepared in accordance with the manufacturer's processing instructions, and in the form of a flat sheet, 1.5-mm thick and 15-mm square. They were supported on a rigid plate and loaded with a flat-ended probe 3 mm in diameter. The probe was adjusted to maintain a static stress of 5×10^4 Pa, with a superimposed dynamic stress of 5×10^3 Pa, at a frequency of 1.0 Hz, (*see* Fig. 2).

Specimens were tested in both wet and dry conditions. The wet specimens had been preconditioned in 37°C water to constant weight, or for a minimum of 100 d for those specimens that failed to equilibrate. Dry specimens were tested in air; wet specimens were tested in distilled water. Each test run consisted of measurements made while heating the specimen from 5 to 95°C at 2.5°C/min. A schematic drawing showing the arrangement of the test apparatus is shown in Fig. 2; the test conditions are summarized in Table 2.

The results are obtained in the form of graphs of storage modulus (E') and $\tan \delta$ vs temperature for each run. It is possible to superimpose the results from separate runs on the same graph, thus

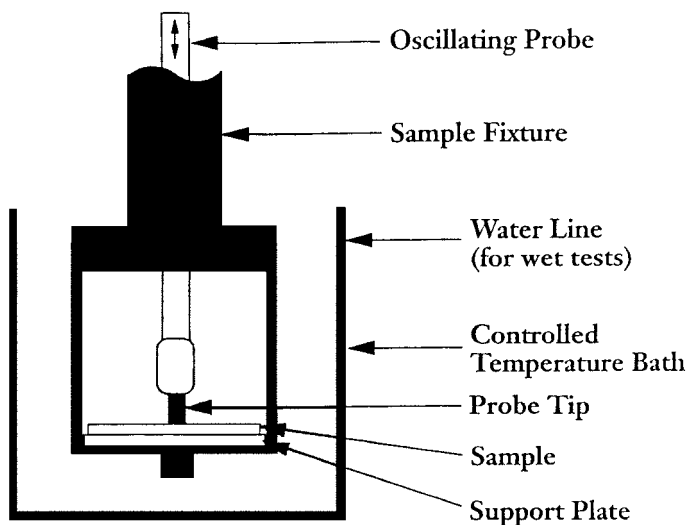


Fig. 2. A specially designed, flat-tip 3-mm diameter probe used in conjunction with Perkin-Elmer DMA-7 System.

Table 2
Dynamic Mechanical Analysis Test Conditions

Equipment	Perkin-Elmer DMA-7 Thermal Analysis System
Probe	3 mm diameter, flat tip
Specimen	Flat sheet-15 mm/square, 1.5 mm thick
Conditions	Wet and dry
	Temperature range: 5–95°C
	Temperature rate: 2.5°C min
	Static stress: 5×10^4 Pa
	Dynamic stress: 5×10^3 Pa
	Frequency: 1.0 Hz

facilitating direct comparison of different materials or test conditions. An example of such a comparison is shown in Fig. 3, in which the results for wet and dry Supersoft are compared. These results are characteristic of the plasticized acrylic materials. A vertical line has been inserted at 37°C as an aid in evaluating the properties of the material under the condition of use. The corresponding results for Moloplast B are shown in Fig. 4. Such results are characteristic of most silicone-based soft liners.

The differences between these two sets of curves, particularly in their response to changes in temperature, can provide significant information

about the structure and likely behavior of the materials. However, when comparisons are to be made among several products, it is often more convenient to tabulate the properties under the expected conditions of use. Table 3 is such a tabulation of the properties of the four materials evaluated in this study at body temperature (37°C).

Figure 5 presents the E' and $\tan \delta$ measurements from an independent test of an additional dry Supersoft specimen, tested over an extended temperature range from -30°C to 150°C. Such tests can provide supplemental information to distinguish between curve deflection caused by glass transitions and melting.

The water sorption measurements (5) for commercial samples indicated that Mollosil and Eva-touch had high % solubility in water (8.7 and 4.56, respectively). Novus was found to exhibit the highest water uptake (34%). The other samples with high water uptake values were Evatouch and Supersoft (6.2 and 7.35%, respectively). Moloplast B had both a low % solubility (0.37) and a low water uptake (0.4%), compared to other samples.

The DMA measurements (54) of the commercial samples indicated that changes in E' between the wet and dry samples of Moloplast B, Kurepeet, and Supersoft were insignificant. The E' of

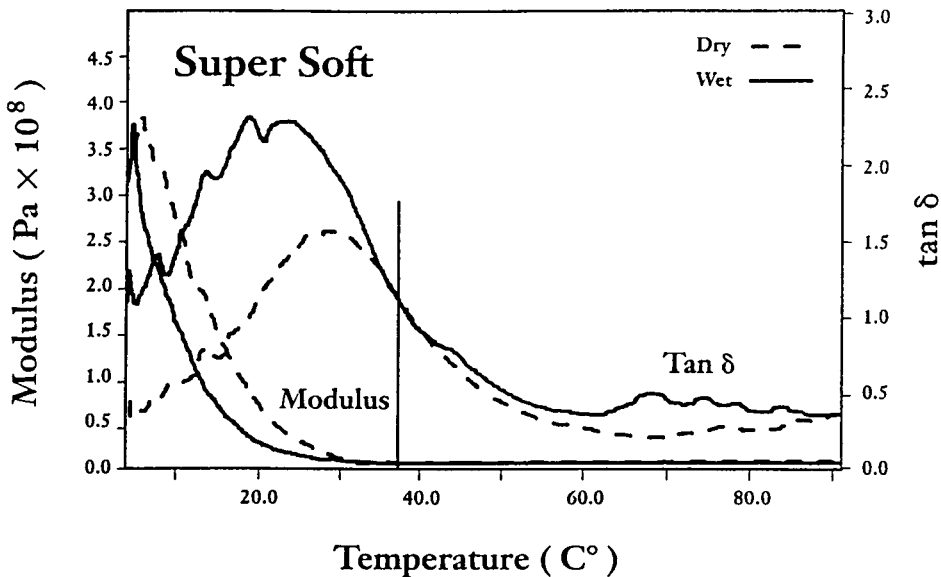


Fig. 3. DMA traces from 0 to 100°C for Supersoft in dry (---) and wet (—) conditions.

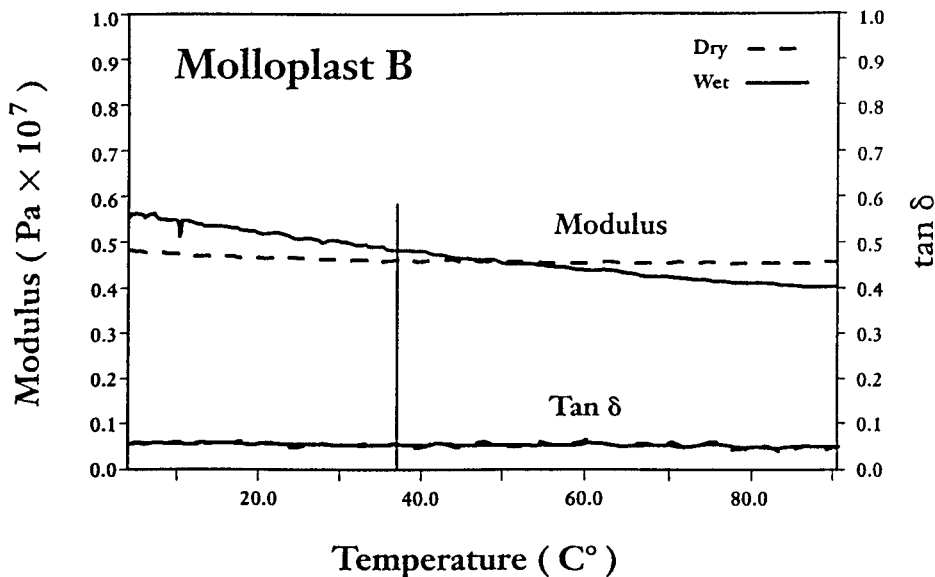


Fig. 4. DMA traces from 0 to 100°C for Molloplast B.

the wet samples of Novus, on the other hand, was about 42% lower than the dry samples, because the sorbed water (~ 34%) presumably acted as a plasticizer in the wet samples. A significant increase in $\tan \delta$ of the Novus wet sample suggested that the material is capable of dissipating more energy.

No detectable correlation between tensile strengths, elongation, and the Shore durometer hardness could be found for these samples (54). Silicones and fluoroelastomer-based soft liners exhibited low tear strengths. Acrylic- and polyphosphazene-based materials had tear energies 5–10× higher. The wet samples of Molloplast B and Novus did not show any significant difference from dry samples; the acrylic Supersoft doubled

in strength in the wet condition, because of stress relaxation by water.

The adhesion of these commercial soft liners were studied by measuring their peel strength (54). Molloplast B and Supersoft failed in cohesive mode; the silicones had little or no bond strength, and failed in adhesion. Novus and Kurepeet showed mixed adhesive/cohesive failure. The peel strength of Novus was found to be the greatest among all materials investigated.

6.1. Novel Silicone Materials

Although it was intended to develop silicone materials to replicate Molloplast B, this could not be achieved because of analysis and identification problems. However, alternative materials were

Table 3
DMA Properties at 37°C

Material	Chemical type	Modulus E' Dry	(Mpa), wet	Damping, dry	Tan δ , wet	Water sorption
Molloplast B	Silicone	4.8	5.1	0.005	0.005	0.5
Novus	Polyphosphazine	6.2	3.5	0.12	0.10	34.0
Kurepeet	Fluoroelastomer	5.0	5.0	0.5	0.75	2.0
Super-Soft	Plasticized acrylic	10.0	8.0	1.25	1.25	5.0

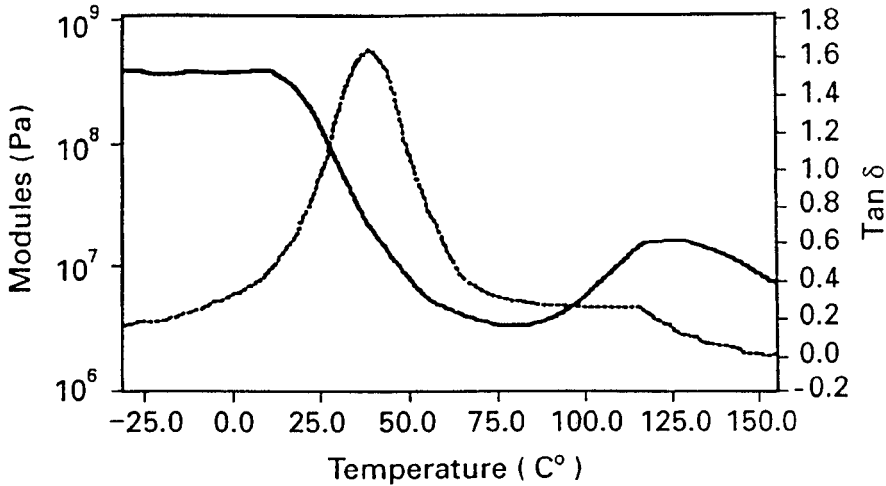


Fig. 5. DMA traces from -25 to 150°C for Supersoft.

developed that exhibited superior properties to Molloplast B. Silicone elastomers can be prepared by three different curing reactions, i.e., acetoxy, condensation, and addition. During curing, the first two processes liberate byproducts, resulting in curing shrinkage, more water sorption, and support of the colonization of the liner by *C. albicans*. Hence, it was decided to follow the addition cure method for the preparation of the silicone materials, in which both peroxy and hydrosilylation polymerization mechanisms were followed (55). The properties of materials produced by both mechanisms were dependent on filler and filler surface treatment (55).

6.2. Novel Elastomeric Methacrylate Systems

Systems based on the elastomers of BS copolymers, polyisoprene, and SIS copolymers have been developed. A higher alkyl methacrylate monomer (HMA or EHMA), a crosslinking agent (EGDM) and an initiator (BP or LP) were gelled with the elastomer. Then the resulting gel was reasonably stable at room temperature, so that it could be molded to the required shape, and polymerized as required. The choice of the monomers was based on their desired mechanical properties. The variations in the monomer, the elastomer:methacrylate monomer ratio, amount of crosslinking agent, and the nature of the initiator,

provided adequate information about the effect of these variables on water sorption and mechanical properties (46–50,53).

6.3. Viscoelastic and Mechanical Measurements

DMA measurements were made on five BS methacrylic elastomeric systems, using identical conditions (the same instrument and same technique) used for the analysis of commercial materials, in order to compare the properties (51,52,54).

Increasing the amount of the crosslinking agent (from 0.5 to 1.0% EGDM) resulted in an increase in the modulus (from 15.9 to 20.9 MPa) in systems investigated with BS elastomer, EHMA monomer, and 1% LP initiator. This is apparently the effect of an increase in crosslinking density in the range studied. The incorporation of EHMA, instead of HMA, in BS elastomer-based materials resulted in reduction in dry modulus (from 19.2 to 15.9 Mpa). It also resulted in a reduction in the decrease in the modulus caused by water sorption in wet samples. This is the result of the hydrophobic nature of the EHMA monomer, which reduces the water sorption, as mentioned earlier. The developed soft liners based on BS elastomers with EHMA monomers exhibited large improvements in ultimate tensile strengths, compared to the corresponding HMA monomer systems; both systems had comparable strains (12). Although

Table 4
DMA Properties and Water Sorption for
SIS 5+ Experimental Materials

	E' (MPa)	Tan δ	% water
Dry	7.4	0.39	0
Immersed in water for 4 wk DMA measurements were made	7.1	0.53	1.8

the change of initiator from BP to LP led to no apparent change in water sorption of the BS-based elastomers, a slight increase in modulus was observed with LP-initiated systems, compared to BP-initiated systems (14.0 vs 19.2 for 0.5% and 19.2 vs 20.0 Mpa for 1.0% initiator compositions). This may be attributed to the less-reactive nature of the LP, resulting in increased molecular weights. The tan δ values of these experimental materials lie within the range of accepted commercial materials. The glass transition temperatures of all the materials were observed to be below body temperature.

DMA measurements were performed for both dry and wet samples for the elastomeric materials developed (51,52). Water absorption in the wet samples may act as plasticizers for these samples, reducing the I_g , E', and compliance of the material. The use of DMA over a wide range of temperatures (0–95°C) provided ideas about the changes in viscoelastic properties of these experimental materials at various intervals of time (by preimmersing the samples from 1 wk to at least 6 mo).

Analysis of the following preliminary data (Table 4), obtained from DMA measurements on the elastomer based on SIS copolymer (SIS 5+), confirmed that the sorbed water (after 4 wk immersion) acted as a plasticizer, reducing E' and increasing tan δ , which is consistent with expectations (47,53).

Tensile strength of the elastomer-based materials was 12 MPa, with elongation to break of 800% for SIS 5+ and 400% for SBS 5+. Tear strengths were in the range 10–12 kJ/m² for both elastomers. All are well above values obtained for commercial materials (51). Tear energy for peroxide-cured silicone materials were as high as 5.5 kJ/m²; the hydrosilylation-cured silicones had tensile

strengths over 7 MPa and elongation to break of 400%.

6.4. Microbiology

A serious clinical concern is the propensity for some soft lining materials to become colonized by growth of indigenous oral *C. albicans* yeasts, causing allergic irritation and inflammation of the palate. In vitro microbiological tests of soft liners were performed to evaluate their interactions with *Candida* yeasts in vitro, using various growth media. When examined by scanning electron microscopy, previous exposure of soft liner materials to *Candida* species in a suitable liquid growth medium suggested that surfaces of at least one polymer were invaded by yeast cells. The following study was undertaken to repeat the tests, using two soft liner materials to explore various parameters of the study for reproducibility. The test yeasts used were American Type Culture Collection (ATCC) strains of *Candida krusei* and *C. albicans*.

A commercial brand of silicone polymer soft liner material, Molloplast B, was chosen as a representative with no acetate content, and appeared not to be attacked by yeasts. Another commercial brand of soft liner, Supersoft, was chosen as a representative of a plasticized acrylic soft liner material of liner that appeared to be attacked by yeasts, with the formation of yeast-shaped holes.

Analysis of the test results revealed the following (55). The silicone polymer soft liner material, Molloplast B, and a plasticized acrylic soft liner material, Supersoft, did not appear to appreciably soften nutrients in order to support growth of the *Candida* species of yeasts; the yeasts had some ability to cling to the liner materials in a rich culture medium, but not to penetrate them; there was no indication that the yeasts could invade or digest either of the liner materials; and there was no indication that the liner materials did or could inhibit growth of the yeasts.

6.5. Relationship Between Soft Lining Materials and Yeasts

Colonization by *C. albicans* or other *Candida* strains results in poor denture hygiene, and may prevent the soft-lined denture from fulfilling the requirement of durability in the oral environment. Consequently, the evaluation of new materials

should include appropriate tests of the relationship between lining materials and yeasts. This relationship may include both inhibitory effects or support of the growth of yeasts (55).

This brief report outlines the method and results of the relationship between two commercial (Coe Supersoft, Novus) and three experimental (BS5+, DH5, RTV) soft lining materials and three strains of *Candida* (*C. albicans* [ATCC 24433], *Candida tropicalis* (ATCC 750), and *C. krusei* [ATCC 6258]). Tests of yeast inhibition by soft liners were performed, and the ability of soft liners to imbibe nutrients was studied (58).

6.5.1. Tests of Yeast Inhibition by Soft Lining

At 24 h, inhibition was seen to occur with all *Candida* strains for RTV, and with *C. tropicalis* for BS5+. At 7 d, no further soft lining strips inhibited any *Candida* strains, and examination of the surface of the plates under the strips demonstrated some growth in every case. Even when inhibition was observed, growth of small colonies still persisted within the inhibition zones and underneath the strips. All cultures were pure. The examination of the undersurface of the strips under the dissecting microscope demonstrated heavy contamination of the lining surface via yeasts on RTV and DH5, and sparse contamination on Coe Super-Soft, Novus, and BS5+. The surface of the lining was either smooth (Novus and BS5+), smooth with some wrinkles (Coe Supersoft), smooth with small air bubbles (DH5), or rough with numerous pimples (RTV) (55).

The examination of the undersurface of the strips under the scanning electron microscope is incomplete, but BS5+ with *C. albicans* demonstrated a smooth surface between the pimples and yeast cells only, and DH5 with *C. krusei* demonstrated a rough surface, but no yeast cells.

6.5.2. Ability of Soft Lining to Imbibe Nutrients

As indicated above, the results from the initial protocol showed a consistent and large increases in colony-forming units (CFU)/mL between the initial load of yeasts and the 3-d results, for both the test and control strips. Following the modification of the protocol to include washing of the yeast cells to avoid carryover of nutrient, little or no increase in CFU/mL occurred. In some cases, a reduction was found.

Analysis of the data revealed that the majority of soft lining materials neither inhibit or promote the growth of yeasts, and the materials tested here are no exception. The inhibition of growth of all *Candida* strains tested by RTV is similar to the literature data, since these are all RTV silicone rubber materials, and it is likely that the catalyst is responsible. In this case, the inhibition is not complete, and it has not been established how long this effect will last in the oral environment. No obvious relationship between the surface characteristics of the soft lining material and the contamination by yeasts can be demonstrated by these methods.

Although soft lining materials have a tendency to imbibe water, they do not appear to imbibe sufficient nutrient to encourage the growth of yeasts under the conditions of this experiment. Consequently, if good denture hygiene can be established, there is no reason for increased incidence of yeasts associated with the use of these materials (55).

6.5.3. Investigation of Ability of Solid-state Nuclear Magnetic Resonance to Characterize Dental Polymers

An attempt has been made to evaluate the ability of solid-state nuclear magnetic resonance (NMR) measurements to characterize soft liners, in terms of residual monomer, water content, and the associated molecular motion as functions of chemical structure. A study of the effect of water content on the molecular motion was performed on commercial samples. Because Molloplast B absorbs little water, it was anticipated that it would not exhibit many changes in molecular motions. Hence, the study was limited to two other popular soft liners, namely, Supersoft and Novus.

The cross-polarization/magic-angle-spinning Carbon 13 (^{13}C CP/MAS) spectra did not exhibit any changes associated with water sorption for these samples. The $T_{1\rho}(\text{H})$ and $T_{1\rho}(\text{C})$ measurements also did not give any fruitful results. A limitation of this technique may be that the sample must be spun at more than 3 kHz; this restricted the experiments to be performed for samples with high water uptakes (>10%), because the sorbed water centrifuged out of the systems during the measurements. The fact that no changes were seen in the relaxation spectra is not necessarily a limita-

tion of the technique: It may result from the nature of the systems. There are several plausible reasons why no changes were seen in relaxation times: The water did not affect the molecular motion at these water uptakes; the water affected the motion of the molecules, but it was at a frequency that does not affect the rotating frame relaxation rate, $T_{1\rho}$ (this is typically in the tens of kHz); and the water formed pools, so that it did not affect the bulk motion, but only a very small percentage of the molecules. The Novus samples are probably particularly prone to this phenomenon, because they have a highly hydrophobic portion, the polyphosphazene and more hydrophilic regions, such as the barium sulfate.

In order to detect low levels of residual monomer in a commonly used PMMA dental polymer, use of ^{13}C CP/MAS NMR technique has been made. In radiation-polymerized PMMA, amounts of methyl methacrylate (MMA) as low as 0.05%, were detected using this technique (56,57).

PMMA is an extensively studied linear polymer in dental materials, particularly with reference to networks with increasing amounts of crosslinking, e.g., made by copolymerization of ethylene glycol dimethacrylate with PMMA and softliners, in which plasticized PMMA is used in order to soften the material, i.e., lower the T_g .

The following paragraphs deal with influence of mol wt and plasticizers on the sorption of water by glassy PMMA (58–70).

6.6. Effect of Mol Wt on Water Sorption by PMMA

Relatively little work has been done on the influence of mol wt on the water sorption of polymers (58–61). Sheppard and Newsome noted that “there is some evidence . . . that the moisture regain, or water absorption, of cellulose is progressively lowered by treatments which degrade the cellulose.” Degradation was monitored by measurements of solution viscosity (65,66). Independently, Kargin pointed out that a decrease in mol wt may result in closer molecular packing in the glassy state, and hence in a lower sorptive capacity (67). As an extreme case, he contrasted the sorption of water vapor by glasses of cellulose and by crystalline glucose. At low vapor pressures, the polysaccharide takes up water into pores, but the close-packed monosaccharide does

not. Such a difference in sorptive capacity is not limited to water as penetrant, and a similar contrast was demonstrated on contacting ethyl benzene vapor with high polymers and with oligomers of styrene.

With respect to the kinetics of sorption, Rogers cited data showing that, generally, “the molecular weight of a polymer has been found to have little effect on the rates of diffusional permeation (71–73).

The following paragraphs briefly describe the study of the influence of molecular weight on the sorption of water by glassy PMMA. Previously, Brauer and Sweeney (30) found water sorption to be little influenced by molecular weight in the range of $0.18\text{--}1.56 \times 10^6$ Daltons, at temperatures from 4 to 60°C. Bueche (71) found water diffusion to be independent of molecular weight in the range investigated, from $0.2\text{--}1.0 \times 10^6$ Daltons. In order to extend this work to much lower molecular weights, samples of high-molecular weight PMMA were exposed to γ -rays, which results in random fracture of the macromolecular backbone, yet with negligible concurrent crosslinking (64). Previously, this technique had been used in studies of the influence of molecular weight of PMMA on fracture surface energy (58), fracture morphology (58), T_g , (59), and tensile strength (60).

A PMMA powder, described as of average mol wt 12,000 (Aldrich, Milwaukee, WI), was heated at 65°C for several weeks, in vacuum. After this treatment, the powder no longer smelled of residual monomer or transfer agent. T_g s were determined by differential scanning calorimetry (DSC), at 20°C/min, using a DuPont 990 Thermal Analyzer: before heating, $T_g = 80^\circ\text{C}$; after heating, $T_g = 82^\circ\text{C}$.

Another PMMA powder from Aldrich, provided as a secondary mol wt standard of M_w (weight average molecular weight) = 60,600 and M_n (number average molecular weight) = 33,200, was heated at 75°C for 6 h in vacuum.

The thinnest available sheets of PMMA were used, in order to reduce the time to water saturation to a few weeks (one-thirty-second in. Plexiglas, Rohm and Haas, Philadelphia, PA). Subsequently, this material was withdrawn from the market, and further experiments had to be curtailed. An approximate value of $M_n = 6 \times 10^5$ was calculated from solution viscosity data, assuming

Table 5
Approximate Values of M_n and T_g for Irradiated Samples of PMMA

Dose (Mrad)	0	5.7	17.7	36.6	55.5	74.7	93.9
M_n (D)	6×10^5	8.4×10^4	3.0×10^4	1.5×10^4	9.8×10^3	7.3×10^3	5.9×10^3
T_g (C)	103	—	94	87	81	75	70

a random molecular weight distribution: $T_g = 103^\circ\text{C}$. Sample dimensions $7.5 \times 2.5 \times 0.07$ cm were machined and exposed in air to γ -rays from a cesium 137 (^{137}Cs) source: The dose rate was 0.8 Mrad/h; ambient temperature = 35°C . After irradiation, samples were degassed at room temperature, in vacuum, for 1 wk. Approximate values of M_n were calculated assuming 1.7 random main-chain fractures/100 eV energy deposition ($1 \text{ Mrad} = 6 \times 10^{19} \text{ eV/g}$) (11). Approximate values of T_g were estimated from a pertinent experimental relationship between T_g and radiation dose, in the range that allows interpolation (Table 5).

6.7. Water Sorption Measurements

All samples were dried to constant weight (W_0) over anhydrous calcium sulphate (Drierite, W. R. Hammond) in air. The thickness was taken as the mean of 8- μm readings. Dried samples were immersed in distilled water at $24.2 \pm 0.7^\circ\text{C}$. They were periodically removed, mopped dry, and weighed (W_t), using a Mettler Digital Balance of precision ± 0.05 mg, up to a limiting value (W_∞). A few samples were studied further in a desorption cycle over the same desiccant.

A diffusion coefficient (D) was obtained by reference to Stefan's approximation of the appropriate solution of Ficks' law (71–76) for plane sheet geometry (Eq. 1):

$$M_t = W_t - W_0; M_\infty = W_\infty - W_0,$$

$$M_t/M_\infty = -8/\pi^2 \sum_{n=0}^{n=\infty} 1/(2n+1)^2 \exp[-(2n+1)^2\pi^2Dt/\pi l^2] \quad (1)$$

$$M_t/M_\infty = 2(Dt/\pi l^2)^{1/2} \quad (2)$$

where M_t and M_∞ are the masses of water sorbed, or desorbed, at times t and ∞ , respectively; and $2l$ is the thickness of the specimen.

Density measurements were made by Archimedes' method. Sorption data for molded samples

of low molecular weight (12,000 Daltons) conform approximately to eq. 1. One sample, designated by the open circles, departed from the expected linearity of Stefan's approximation, which holds up to values of M_t/M_∞ of about 0.5. It is believed that this was caused by initiation and growth of a crack, which eventually caused separation of the sample into two fragments. The initial slope selected to represent both sets of data, is shown by the full line, and corresponds to a value of $D = 0.82 \times 10^{-8} \text{ cm}^2/\text{s}$. Values obtained for water uptake, referred to initial dry wt, of the two samples were 1.88 and 1.83 wt%. The density of the wet sample (1.1852 g/cm^3) was only slightly greater than that of the dry sample (1.1803 g/cm^3). It is difficult to interpret the water sorption of samples of PMMA of low molecular weight, because volumetric changes, though small, can cause microcracking or void formation. Such changes might increase both diffusion and uptake of water. Nevertheless, there are observations from uptake data that are consistent with the occurrence of closer molecular packing. First, samples of low molecular weight ($M_w = 60,600$, $M_n = 33,200$) take up only 1.2% water, compared with samples of high molecular weight ($M_w > 10^6$) which take up to 2.0% (61).

Second, although the other sample of low-molecular-weight (12,000) took up as much as 1.8–1.9% water, yet it differs from high-molecular-weight PMMA in increasing only slightly in density on saturation. In the case of high-molecular-weight PMMA, it was calculated, from changes in density, that the increase in volume accounted for only about one-half the uptake of water. The discrepancy was attributed to accommodation of about 50% of the water uptake in microvoids (58). The same line of reasoning suggests that only 15% water is accommodated in microvoids in the low-molecular-weight sample. A decreased microvoid volume would be consistent with lower molecular packing. For an

explicit example of the way in which a penetrant molecule might be accommodated in a microvoid, the reader is referred to the work of Barrier et al. on gas sorption by glassy ethyl cellulose, which, like PMMA, has stiff and bulky macromolecules (73). Their depiction of a penetrant accommodation site (73) can be regarded as one example of an entanglement site, mentioned in subheading 5.1. It has been concluded from the foregoing discussions that samples of PMMA of low molecular weight (110^4 Daltons) may take up less water (1.2%) than samples of normally high molecular weight (10^6 Daltons: 2.0 wt%); from density changes accompanying water sorption, it is estimated that a low-molecular-weight sample accommodated only 15% water in microvoids, compared with 50% for samples of high mol wt: Those first two conclusions are consistent with the hypothesis that, in glassy polymers, closer molecular packing may be effected in samples of low mol wt.

6.8. Effects of Plasticizers on Water Sorption of PMMA

In this subheading, some important findings made with reference to the influence of plasticizers on the water sorption of PMMA are presented. Relatively little work has been done on the influence of plasticizers on the water sorption of glassy polymers, and such work has been concentrated mostly on copolymers of vinyl chloride. Doty studied the permeation of water vapor through a copolymer of vinyl chloride and vinyl acetate containing 25% plasticizer. He was able to draw interesting conclusions from conventional analyses of temperature dependence (75). This approach, at a single plasticizer content, was pursued by Kumins et al. (76), who expected that plasticizer would cause a physical loosening of bonds and thereby result in a decrease in activation energy, followed by a rapid increase in diffusion above T_g . A decrease in activation energy was observed, but a rapid increase in diffusion was obtained at a much higher temperature than expected. It was suggested that the copolymer had a second higher value of T_g at which the change occurred, but, in retrospect, this suggestion seems unlikely.

No systematic studies have been reported of the influence of variations in plasticizer content

on the water sorption of a glass polymer. However, such studies have been reported regarding the permeability of poly(vinyl chloride) (PVC) to gases. It has been reported that plasticization of PVC results in an increase in permeability; antiplasticization results in a decrease (63,75,77). In an extension of this work, Raucher and Sefcik (78) reported that the apparent diffusion coefficient for CO in plasticized PVC reached a minimum value, with about 10% tricresyl phosphate. The main-chain relaxation rate, determined from ^{13}C NMR spectra, reached a minimum value, with about 15% tricresyl phosphate. This correlation was interpreted as evidence for a rate-determining step, in which the jumping of CO molecules is determined by cooperative motions of the polymer main chains (78), as had been described in detail by Pace and Datyner (79).

Use was made of a technique in which specimens were made by high-energy irradiation of mixtures of MMA and plasticizer. Previously, this technique was found to give specimens with values of T_g that conformed to theoretical predictions of the Kelley–Bueche free-volume theory (80). Also, it has been reported that inclusion of up to approx 10% dioctyl phthalate (DOP) resulted in a pronounced decrease in water uptake, which was attributed to the filling of microvoids, which, otherwise, in the absence of the plasticizer, would be available to water (62–64). The chief objective of this study is to investigate whether, consistent with a physical loosening of bonds, there would be simple increases in the rate of water diffusion in the glassy state, i.e., up to T_g . An alternative possibility is that more complex behavior might be observed that would parallel antiplasticization effects, as inferred from measurements of tensile properties of PMMA plasticized with phthalates (62,77).

In studies of proprietary plasticized acrylic polymers, estimation of values of diffusion coefficients was complicated by leaching out of plasticizer (63,74). Plasticized PMMA was made by γ -irradiation of mixtures of monomer and various phthalates. Samples were immersed in water and uptake, and diffusion coefficients determined. More reliance was placed on determinations made in desorption, because these did not involve complications caused by loss of components of dissolution, i.e., mixtures were made of MMA (Ald-

rich) with both diethyl phthalate (DEP) (Aldrich) and DOP, i.e., di(2-ethylhexyl) phthalate. Mixtures of MMA and plasticizer in various proportions were polymerized by 6-h exposure to a ^{137}Cs γ -ray source (dose rate = 0.8 Mrad/h; ambient temperature = 35°C) in a nitrogen atmosphere. The plasticizer content was calculated as a volume percent, as described in previous work (62). The polymerized products, cylindrical in shape, were cut under a stream of water with a high-speed diamond band saw, to provide samples with a diameter of 1.4 cm and thickness of 0.1 cm. With up to 25% plasticizer, the products that generally were transparent appeared to be homogeneous. However, with 30% or more of DOP, products were slightly turbid. Samples were immersed in distilled water, usually at 50°C, until equilibrated with water: They were dried at room temperature over anhydrous calcium chloride, and weighed periodically. The water uptake was determined relative to the dry wt of the sample (64).

Values of T_g were estimated by DSC, as described in subheading 6.7.

The rates of desorption and sorption was analyzed by reference to conventional solutions by Fick's laws of diffusion for plane sheet geometry (Eq. 1) (68,71).

Data both in sorption and desorption conformed experimentally to Eq. 2 (Figs. 3–5). A higher rate of desorption is similar to that reported previously in studies of PMMA alone, at room temperature, and interpreted as the result of a dependence of the diffusion coefficient on water content (62,71,76). This same complexity is recognized for values of De_{eff} obtained in the present work.

Furthermore, there is a tendency for plots to remain linear beyond the validity of the approximation in Eq. 2, i.e., at $M_t/M_\infty > 0.5$, which may indicate a time dependence of swelling on uptake of water (62). In view of these departures from ideal behavior, use of Eq. 2 provides apparent values of the diffusion coefficient, but these suffice to give a preliminary overview of trends. More reliance is placed on values of De_{eff} calculated from desorption data up to 37°C, for which duplicate runs agreed within a few percent, but, at higher temperature, results were less reproducible (Table 6). Nevertheless, most measurements were made at 50°C, to reduce testing time.

Table 6 summarizes the data, with reference to the effect of temperature on the uptake of water and diffusion coefficient of PMMA specimens with 20% DOP.

Samples immersed in water increased in weight and reached values that are stationary, in the sense that apparently constant values were attained over a period of several days. Such stationary values are used in the present work, but it should be noted that, on prolonged immersion, a slow decrement in weight was detected, presumably caused by leaching out of plasticizer. This effect may also be a factor in accounting for the observation that estimates of water uptake by desorption are generally greater than values estimated by sorption. In the present work, uptake of water is estimated, more reliably, from desorption data.

The water uptake decreased markedly with increasing plasticizer content, up to about 10% (Fig. 6). At higher plasticizer contents, decreases were less marked, presumably because of replacement of PMMA by the more hydrophobic plasticizer. Decreases were greater for DOP than for DEP, which is consistent with a difference in water uptake: DOP, 0.18 wt%; DEP, 0.92 wt%. Water uptake increases with temperature, up to about 50°C (Fig. 6).

The influence of plasticizer on the uptake of water may be analyzed with respect to two regions, i.e., one below 10 vol% and the other above 10 vol% of the plasticizer content (Fig. 6). Above approx 10%, the influence is small and consistent with the replacement of polymer by the more hydrophobic plasticizer. Previously, the unexpected efficacy of smaller proportions of DOP was attributed to microvoid filling. This interpretation was based on evidence that PMMA, without plasticizer, takes up about 2 wt% water, but swells by only 1%. It was suggested that about one-half of the water is accommodated in microvoids. It was further suggested that DOP could also fill microvoids, and thereby exclude uptake of water. This explanation is now extended to include DEP, which is judged to be less effective as a microvoid filler. Perhaps DEP is more soluble in PMMA, and its partition into microvoids less favored. In broader perspective, similar ideas about the influence of liquid in reducing water sorption by rigid polymers can be traced back to

Table 6
Influence of Temperature on Uptake of Water and Deff of PMMA Specimens with 20% DOP

	Temperature (°C)			
	26	37	50	60
Uptake by desorption (%)	0.71	0.83	1.05	1.04
	0.60	0.84	1.08	1.07
Uptake by sorption (%)	0.71	0.53	0.91	1.04
	0.61	0.63	0.87	1.00
Diffusion coefficient, by desorption, $Deff_d$, ($\text{cm}^2/\text{s} \times 10^8$)	4.90	6.5	11.1	23.8
	5.1	6.5	9.0	19.7
Diffusion coefficient, by sorption, $Deff_s$, ($\text{cm}^2/\text{s} \times 10^8$)	5.6	7.7	9.6	20.6
	4.5	5.9	9.4	26.0

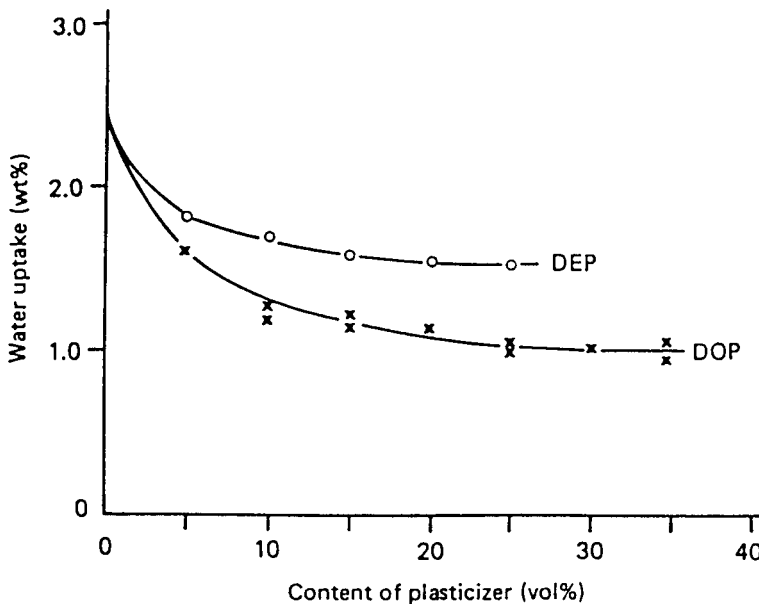


Fig. 6. Effect of plasticizers, DEP and DOP on the uptake of water by PMMA at 50°C.

Sheppard's work on cellulose and its derivatives (62,65,66).

The uptake of water in one plasticized composition (20% DOP) was found to increase with temperature (Fig. 6). It has been reported that water uptake by unplasticized PMMA ($T_g = 100^\circ\text{C}$) increases above 70°C , but quantitative data are not available for comparison. In the present work, the water uptake appears to level off in the temperature range of 50 – 60°C (Fig. 7). For the binary composition under consideration, $T_g = 66^\circ\text{C}$ (Fig. 8), but this would be depressed by 1% water ($T_g = -140^\circ\text{C}$) to $T_g = 61^\circ\text{C}$, according to

the Fox equation (65). Thus, it appears that the leveling off occurs near the T_g .

A number of factors might be expected to complicate the influence of plasticizer content on the diffusion of water through PMMA. First, differences in microvoid filling might affect results up to approx 10%. Second, antiplasticization might affect results at higher contents. In this latter respect, it has been reported that the tensile strength of PMMA at 26°C exhibits minimum and maximum values with 7 and 26% dibutyl phthalate, respectively. Notwithstanding such potential complexities, there is a relatively simple

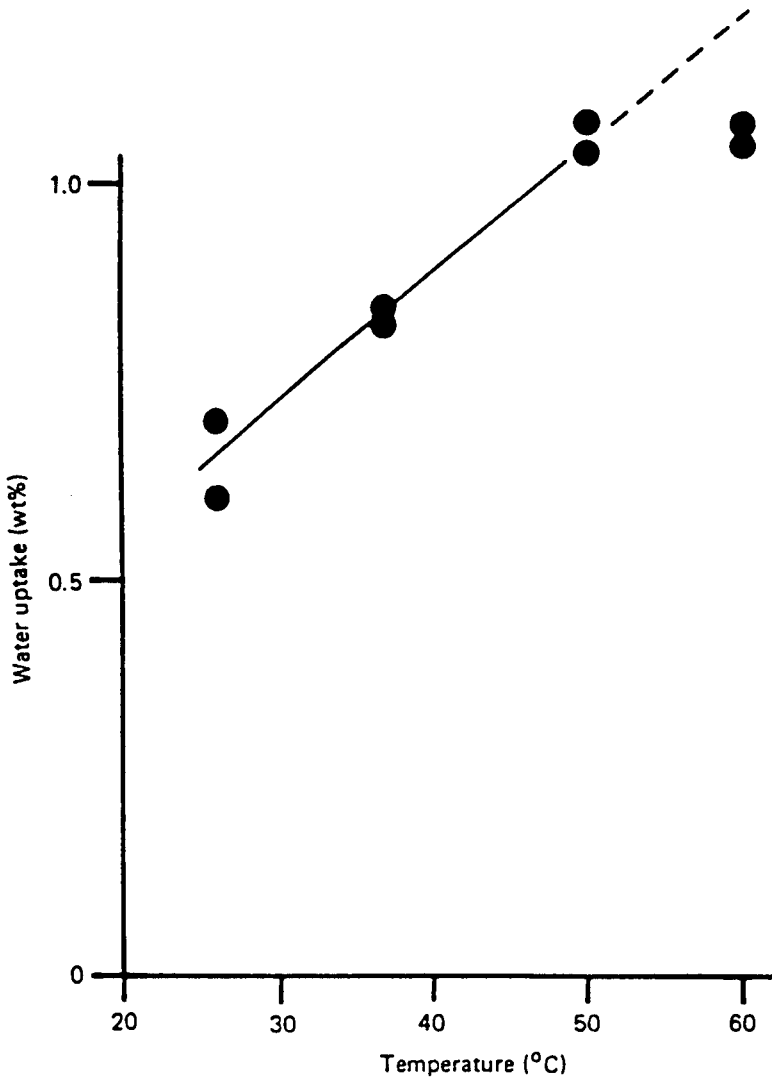


Fig. 7. Influence of temperature on water uptake: DOP 20%; PMMA, 80%.

monotonic increase in the D_{eff} with increasing plasticizer content (Fig. 8). In the absence of any theoretical guidance, a least-squares straight line was drawn through diffusion values for all plasticized compositions judged to be in the glassy state by reference to values of T_g , i.e., with $\leq 20\%$ plasticizer (Fig. 9). On this basis, it appears that the value of D_{eff} increases more rapidly above T_g . This upturn is less marked in the case of DOP, but additional evidence of a change in mechanism was obtained in experiments on temperature dependence (Fig. 9). These indicate a higher rate of diffusion at temperatures above 50–60°C,

which is near the T_g value for this composition, i.e., 61°C. The activation energy for diffusion in the glassy state is 20.5 kJ/mol. This is lower than the value reported for unplasticized PMMA (43.5 kJ/mol) (65,66).

There are several factors that might influence the way in which a plasticizer affects water transport in a glassy polymer. One factor is that the plasticizer molecules might increase transport by decreasing the attractive forces between segments of the macromolecules. This would have the effect of decreasing the activation energy for diffusion, as observed in the present work. Such an effort

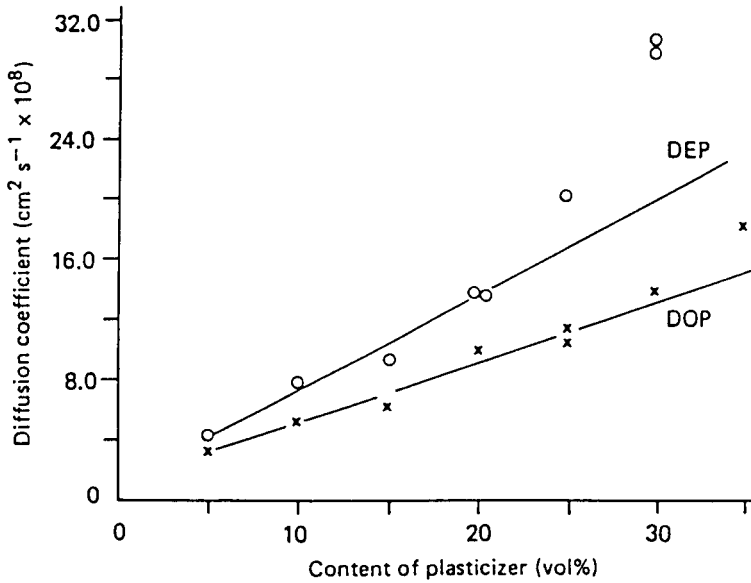


Fig. 8. Influence of plasticizer content on D_{eff} , in desorption at 50°C .

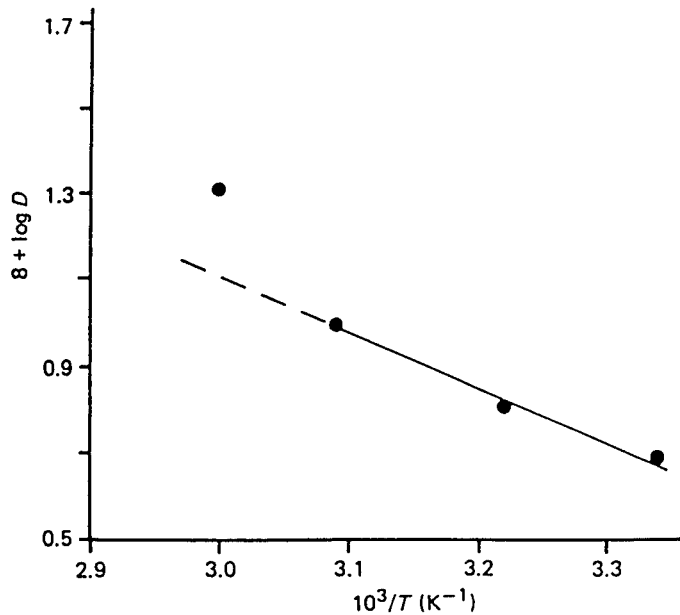


Fig. 9. Influence of temperature on D_{eff} , in desorption: DOP, 20%; PMMA, 80%.

would also be consistent with the observed monotonic increase in the D_{eff} up to T_g . The more marked increase in the diffusion coefficient above T_g would be consistent with transport into holes formed by main-chain motions, of the kind gener-

ally adduced to account for glass transport in glassy polymers (62). A second factor is that transport might be affected by plasticizer molecules occupying space, here termed "microvoids." Evidence for such occupancy has been presented, but

any affect on transport does not complicate the simple picture as presented above.

7. Conclusions

1. Two experimental materials, based on 70:30 BS block copolymer, with 1 wt% of lucidol (BS1) and 1 wt% LP (BS2), and the commercial material, Novus (based on polyphosphazine chemistry), reduced the water uptake from osmotic solutions. This could explain its good clinical performance, despite its excessive water uptake from pure water. This finding supports the theory that the high uptake of elastomeric solutions is osmotically driven.
2. It has been concluded, from the study of the relationship between soft lining materials (experimental and commercial), that these materials, studied under experimental conditions, did not support the growth of yeasts. This has been attributed to the inability of the materials to imbibe sufficient nutrients to encourage the growth of yeasts.
3. Use of CP/MAS ^{13}C NMR technique permitted detection of low levels of residual monomers (as low as 0.05%) in a commonly used PMMA dental polymer.
4. The uptake of water by PMMA is reduced by inclusion of either DOP or DEP in a way that has been interpreted to involve the filling of microvoids, which, in the absence of such additives, can accommodate water.
5. The diffusion coefficient of water in PMMA increases monotonically with increasing contents of either DOP or DEP. The diffusion coefficient increases less markedly when the plasticized polymers are in the glassy state.

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