

EFFECT OF GLAZE COATINGS AND PRESSURE-HEAT PROCESSING ON  
SHORT-TERM SOFT DENTURE LINERS

BY

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To my father, Te The Luu, who passed away on August 9, 1999, in Jackson, LA, while I was busy writing this thesis. Although he was by necessity often an absent father, he was very active in shaping the person I have become today. He will always be remembered by his sagacity, fortitude, and devotion in ensuring the well being as well as the intellectual and moral development of his children.

## ACKNOWLEDGMENTS

This study started out from the desire to verify if an unsubstantiated idea promulgated in a professional journal has any merit. It has many adherents in the prosthodontic specialty as well as non-believers with little more to back up their belief than their clinical experience. From the outset, it seemed to be a short, easy study to conduct until questions from my mentor, Dr. Chiayi Shen, could not be answered satisfactorily. As usual in any research, the answers to one question lead to more questions until the scope of the study has reached seemingly unending proportions.

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## TABLE OF CONTENTS

	<u>page</u>
ACKNOWLEDGMENTS .....	iii
LIST OF TABLES .....	vi
LIST OF FIGURES .....	viii
CHAPTERS	
1 BACKGROUND .....	1
Temporary Soft Denture Liners.....	1
Extending Service Life of Temporary Soft Denture Liners .....	6
Proposed Study.....	9
2 HYPOTHESES .....	10
3 MATERIAL AND METHODS .....	13
Material Selection .....	13
Methods.....	21
Instruments for Data Collection.....	26
Data Collection and Statistical Analysis .....	32
4 RESULTS .....	34
Surface Resilience by Shore A Hardness .....	34
Dynamic Mechanical Test of the Specimen.....	38
Release of Plasticizer in the Immersion Solution by UV/VIS Spectrophotometer .....	41
Weight Changes of the Specimen .....	44
pH of the Solution .....	49
Statistical Correlation between Parameters.....	51
Macro Photography and Micro Photography.....	53
5 DISCUSSION.....	57
Effect of Surface Treatment on the Appearance of the Specimen .....	57
Plasticizer Leaching, Weight Loss, and pH of Storage Medium .....	61

Powder-to-liquid Ratio Influence on weight change.....	67
Leachants in Extruded Acrylic (Lucite-ES) Substrate .....	68
Mechanical Properties as Influenced by the Coating .....	69
6 SUMMARY AND CONCLUSIONS .....	77
APPENDIX	
POLYMERIZATION IN A METHACRYLATE PREPARATION WITH EXCESS MONOMER - MONO-POLY .....	81
REFERENCES .....	90
BIOGRAPHICAL SKETCH .....	94

## LIST OF TABLES

<u>Table</u>	<u>page</u>
1. Chemical composition of soft liners.....	19
2. Batch numbers.....	19
3. Powder to liquid ratio.....	23
4. Times needed prior to manipulation.....	24
5. Shore A hardness values 30- sec after indentation.....	35
6. Shore A values measured 2-min after indentation .....	36
7. Tukey's grouping of the surface treatment on Shore A hardness .....	37
8. Elastic modulus of soft liners as result of surface treatment and time .....	39
9. Rate of recovery .....	40
10. Tukey's grouping of the surface treatment on dynamic tests.....	41
11. Estimated leachant loss by UV absorbance at higher wavelength.....	42
12. Estimated leachant loss by UV absorbance at lower wavelength.....	43
13. Tukey's grouping of the effect of treatment on the leaching by UV .....	44
14. Weight change of soft-liners in water with time as influenced by treatment.....	45
15. Weight loss in air.....	47
16. Tukey's grouping of the effect of surface treatment on the weight change.....	49
17. pH values of storage solutions at the time of replacement.....	50
18. Tukey's grouping of the effect of surface treatment on the pH of storage solutions.....	51

19.	Coefficient of determination ( $r^2$ ) of linear regression between leaching by UV at high and low wavelength .....	51
20.	Coefficient of determination ( $r^2$ ) of linear regression between leaching at high wavelength and weight loss by balance.....	52
21.	Coefficient of determination of Linear regression between weight change in water vs. Modulus of Elasticity .....	52
22.	Coefficient of determination of linear regression between weight loss in water and rate of recovery .....	52
23.	Coefficient of determination of linear regression between modulus of elasticity and leachant by UV absorbance at high wavelength.....	52
24.	Coefficient of determination of linear regression between rate of recovery and leachant by UV absorbance at high wavelength.....	53
25.	Coefficient of determination of linear regression between modulus of elasticity and rate of recovery.....	53

## LIST OF FIGURES

<u>Figure</u>	<u>page</u>
1. Molds used in specimen forming .....	25
2. Shore A Durometer .....	28
3. Typical UV absorption curve .....	30
4. Hardness values 30 seconds post indentation of Flexacryl-Soft .....	37
5. Hardness values 30 seconds post indentation of Lynal .....	38
6. Weight loss with time for Lynal.....	46
7. Weight loss with time for Tempo.....	46
8. Weight loss with time for the control specimens . .....	48
9. Weight loss with time for the mono-poly coated specimens .....	48
10. Specimen coated with mono-poly.....	54
11. Microscopic view of specimens coated with Jet Seal .....	55
12. Microscopic view of sections of Tempo and Coe-Soft samples. ....	56
13. Shore Hardness indentors.....	70
14. Shore A Durometer readings.....	70

Abstract of Thesis Presented to the Graduate School  
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EFFECT OF GLAZE COATINGS AND PRESSURE-HEAT PROCESSING ON  
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Purpose: Post-process treatments of temporary soft denture liners, such as heat and pressure or sealing with a glaze coat, were reputed to extend service-life of these materials. This investigation was to examine how these surface treatments may affect relevant properties and correlations among changes of these properties.

Materials and Methods: Four treatment modalities were used, namely as-prepared by the manufacturer's instructions, with subsequent exposure either to heat and pressure; or coating with mono-poly, a solution of ten parts autopolymerizing methacrylate monomer to one part heat-cured methacrylate polymer; or with Jet Seal, a commercial glaze coat. These treatments were applied to five materials: Lynal, Coe-Comfort, Coe-Soft, Tempo and Flexacryl-Soft. Six samples were prepared for each treatment/material combination. Six more samples were prepared for those with a coating for Shore A hardness testing; it damaged the coating and necessitated resealing. At baseline, 2, 7, 14, 28, 42, 63 and 84 days after immersion in distilled water, weight changes, Shore A hardness, modulus of

elasticity, recovery rate, plasticizer leaching, pH of storage water, and surface texture for the 180 samples were collected. The water was renewed at each data collection.

Results: Flexacryl-Soft behaved differently from the other four materials. Both surface treatment and storage time showed statistical significant influence on the six physical parameters measured. In general, significant changes occurred within first two weeks of storage. There is no change in surface appearance for as-prepared and pressure/heat groups, while there were blister formations with mono-poly and cracks and wrinkles with Jet Seal. Only Lynal and Flexacryl-Soft show reliable Shore A hardness values.

Nonetheless, mono-poly and pressure/heat yielded higher values. All materials lost weight in water and air, mainly due to loss of volatile alcohol. Mono-poly consistently reduced weight loss in water while Jet Seal had no effect. Tempo lost the most both in air and water due to high alcohol content. Lynal lost more in air than in water, indicating significant water absorbance. UV absorbance data indicated that leaching of plasticizer was small; some of which might be due to monomers in coatings. The coating yielded lower pH values of storage water because of monomer leaching. Mono-poly coating often resulted in higher modulus of elasticity, except for Tempo, and lowest rate of recovery. Jet Seal coating often is in the next ranking group.

Conclusion: Pressure/heat does not significantly improve the quality of temporary soft denture liners. Mono-poly coating is semi-permeable to water and generally minimizes deterioration of some of the physical properties of the material. This effect is not consistent across all materials tested or all the parameters tested. Both coatings developed surface defects with time in storage, which puts in question their benefits versus the cost of applying them.

## CHAPTER 1 BACKGROUND

### Temporary Soft Denture Liners

#### History of Development

Resilient dental materials used to interface a hard prosthesis surface and the oral tissues that it contacts are generally divided into permanent soft lining materials and temporary soft liners. Permanent soft lining materials are resilient polymers used to replace the fitting surface of a hard plastic denture while temporary soft liners and functional impression materials are used for their viscoelastic properties, specifically, their ability to flow under masticatory and linguistic forces, spreading the load evenly.

Temporary Soft Denture Liners are also referred to as short-term soft liners, tissue conditioners and functional impression materials.<sup>1</sup> Their use in dentistry goes back a long time and they provide the clinician with expanded scope for short-term resolution of patient problems.<sup>2-6</sup> They are generally used for tissue conditioning, lining surgical splints and stents,<sup>6</sup> lining implant interim prostheses, and for stabilizing trial denture bases, determining optimal arch form, or neutral zone.

Temporary soft liners are used for their viscoelastic properties. Viscoelastic behavior is an intermediate between elastic solid and viscous solid. By virtue of its elasticity, it will deform when under load and recover when the load is removed. Because it is viscous, this recovery is not instantaneous. Furthermore, when the load is

applied over time, it will exhibit permanent deformation and will not recover by itself.<sup>7</sup> In other terms, viscoelasticity is the ability of a material to flow and adapt under function to continuous tissue changes, yet provide some degree of cushioning under load. For some applications it is desirable to have a longer service life while retaining these properties, which the long-term soft liners do not possess. This is because long-term soft liners are used for their elasticity, meaning the ability of the material to instantly recover its original shape. Therefore, an important factor in temporary soft denture liners is the time factor, more specifically the time interval required for the material to recover its initial shape. Ideally, the tissue conditioner should mimic the properties of a viscous fluid confined within an envelope or a pouch fixed to the borders of the prosthesis so as to constrain its deformation to a very narrow range while interfacing the mucosa and the hard prosthesis surface.<sup>6</sup>

### General Composition

Temporary soft liners or tissue conditioners generally consist of a polyethyl methacrylate powder mixed with copolymers, which when mixed with ethanol and plasticizers, typically dibutyl phthalate, in the liquid<sup>6</sup>, would be uniformly dispersed.

The alcohol is reported to vary from 6 to 40 %<sup>8</sup> by volume. Ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ , pKa 16.0) is reportedly the most common alcohol used in the liquid component. It has a low boiling point ( $78^\circ\text{C}$ ) and therefore a high propensity to evaporate. However, one of the materials included in the study does not contain ethanol, namely Flexacryl-Soft.

Alcohol is used mainly to facilitate the penetration of plasticizers into the polymer by swelling the polymer beads.<sup>6,9,10</sup> The lower the molecular weight of the polymer and the smaller the particle size, the greater the alcohol penetration, the faster its rate of adsorption within the polymer.<sup>11</sup> In contrary, within a single polymer chain, the larger the meric weight (the weight of each repeating unit in the polymer), the speedier the alcohol penetration. A longer side chain group is one way to obtain larger meric weight. It should be noted that longer side chain decreases the density of the polymer chain, therefore lowering molecular weight. Increasing the number of carbon groups would also increase the meric weight, decreasing the quantity of alcohol needed to achieve a reasonable plasticization of the polymer beads. For practical purposes, the methyl methacrylate rate of adsorption of alcohol is too slow and while that of higher groups than ethyl methacrylate is too fast. Although a benefit of ethanol in the plastic composition is its antimicrobial properties, the benefit is of short duration because it diffuses completely from the gel within 24 hours.<sup>12</sup> This is why the majority of the soft denture liners have ethyl methacrylate as the main ingredient in the powder.

Jones *et al.*,<sup>12</sup> in analyzing the plasticizer content of eight dental soft polymers, found that ester (a reaction product of an alcohol and an acid) contents of the liquid portion varied from to 52% with the balance being ethyl alcohol. The authors stated that it is misleading to think that dibutyl phthalate (DBP) is the most common ester compound because it does not compose the major proportion of the liquids and in fact is an impurity associated with butyl phthalyl butyl glycolate (BPBG) standards. They concluded that on the basis of plasticizer found in appreciable proportion in the liquid component, BPBG is the most common ester constituent. All the esters have a boiling

point higher than 300°C and are therefore relatively non volatile. Phthalate esters have a low water solubility, which increases with lower the molecular weight. They stated that benzyl salicylate and benzyl benzoate are in this later category and have a cumulative leached amount after 14 days of 8.3-8.7 mg/g and 5.7 mg/g respectively. However, they also stated that this higher rate of loss represents less than 2% of the ester originally present. These authors also found that there is no significant change in the rate of loss when the specimens were subjected to cyclic loading. Therefore, the need to simulate the masticatory cycles when conducting in vitro leakage tests is questionable.

Two of the materials included in this study, Coe-Comfort and Coe-Soft, according to the manufacturer, were covered by US patents #3,476,854 Nov 4,1969 and #3,558,540 Jan 25, 1971 and are summarized below.

Patent #3,476,854 covers the use of zinc undercylenate, an antimycotic that could be combined into soft, pliable plastic compositions in sufficient concentration to be effective without adversely affecting its physical properties. This heavy salt of monocarboxylic fatty acids needs to be present in a minimum of 1 wt % concentration to be effective, whereas concentration above 5 wt % do not further retard fungal growth. It is claimed that this fungal inhibitor is hydrophobic and does not leach out of the plastic composition under the effect of saliva or other aqueous solutions. As stated earlier, although alcohol in the plastic composition inhibits microorganism growth, it diffuses completely within 24 hours. It is interesting to note that the patent states in the different examples of tissue conditioner formulations that benzyl benzoate, besides being a non-toxic solvent/plasticizer, also has fungicidal properties.

Patent #3,558,540 details the range of chemicals that could be used to manufacture tissue conditioners. One starts with a room temperature soluble resin, meaning a resin that can be effectively gelatinized by a solvent at ambient temperature. This resin is preferred to be of the low molecular weight methacrylate polymer or copolymer in small bead or granular form. For ease of manipulation, a small amount of anti-tack solid or powder such as calcium carbonate, ultra fine silica, or zinc stearate is added. Additives such as coloring, fillers and modifiers are then added to the solid component. The liquid solvent is composed of primary plasticizer, such as DBP or BPBG, from 5 to 30% by volume, to which extenders such as vegetable oils are added to control setting time and non-tackiness. Added to the liquid are gel formers containing alcohol and other groups, slow evaporating esters, higher molecular weight glycols, and benzyl radical containing plasticizer. In particular, benzoic acids and salicylic acids have been found to be efficient solvent gel formers. Benzyl alcohol is also added to the liquid to operate as a coupling agent. Benzyl alcohol has the added advantage of behaving as a solvent, gel former and flexibilizer while other higher alcohols such as hexadecyl alcohol behave only as coupling agents. The disadvantage of benzyl alcohol is that it adds tackiness. Secondary plasticizers, that is extenders for primary plasticizers, of the alkyl aryl hydrocarbons group may also be added to the liquids. They typically include paraffin and its derivatives, toluene, which is also an aromatic, and propylene, which is alkylated with an aliphatic compound.

### Existing Problems

Both short-term and medium-term acrylate-based soft liners suffer plasticizer and alcohol leakage and in time become progressively more rigid.<sup>12-17</sup> In our experience,

relying on the medium-term soft liner for longer service is not always possible because although it is resilient, it has a high proportional limit and does not maintain a plastic phase during service, which means that it would not adapt easily to changing tissue conditions as inflammation subsides. Because of this lack of adaptation to tissue changes, the short-term resilient liner is favored as a treatment liner (tissue conditioner) although replacement linings are required more frequently.

Speculation regarding plasticizer leakage has been described by several authors.<sup>14,18,19</sup> However, Braden and Causton,<sup>13</sup> and Ellis *et al.*<sup>14</sup> suggested that phthalate esters could not leach out in water at 37°C and weight loss is due to alcohol diffusion. This suggestion was not supported by chemical analysis and was based completely on weight changes. Because of the complex two-way exchange of alcohol/plasticizer loss and water uptake in the plastic composition, using weight change alone for quantification of plasticizer loss would not provide an accurate picture. Although Gas Chromatography would be the instrument of choice for identification and quantification of leachants, within the confines of this study, UV Spectrophotometry was selected because of availability.

#### Extending Service Life of Temporary Soft Denture Liners

The expressions short-term soft denture liners and long-term soft denture liners are misnomers because they are used for their respective specific physical properties. The limited service life of the former is a limitation of the available chemistry to achieve those properties. Therefore, many authors have suggested ways to improve on the service life of short-term soft denture liners.

### Reported Methods for Extending Service Life

Corwin and Saunders<sup>20</sup> described a curing technique aimed at extending liner longevity. The procedure requires the denture with soft liner be placed in a pressure pot with water at 110 to 115 °F and allowed to cure for an additional 20 to 30 minutes under 25 to 30 psi. They did not present any data to substantiate their claim of an extended service life.

Gardner and Parr<sup>21</sup> described the use of a coating to extend the longevity of temporary soft liners. They used a syrup-like mixture that was coined mono-poly, consisting of one part heat-cured clear polymethyl methacrylate beads and 10 parts of autopolymerizing methyl-methacrylate monomer to seal the porous surface of the soft liner and form a smooth surface. It was believed that a smooth surface could reduce fungal and bacterial growth that is often cited as the cause of discoloration and eventual breakdown of liners.

Vacuum mixing of tissue conditioner was reported by Nimmo *et al.*<sup>22</sup> to reduce the presence of voids, hence producing a denser material, but did not reduce bacterial adhesion. This method would not be used by majority clinicians as it is rarely recommended in the manufacturer's instructions, requires additional equipment and clean-up time, it was not included in our study.

### Effectiveness of Coatings

Aslan and Avci<sup>23</sup> observed in their in vitro experiment that autopolymerizing acrylic resin samples covered with mono-poly evidenced a significant reduction in *E. coli*

colonies compared to the uncoated group, supporting the contention that mono-poly coating provides a smooth surface that reduce fungal and bacterial growth.

Casey and Scheer<sup>24</sup> showed by Scanning Electron Microscope that Coe-Soft protected with either mono-poly glaze or Minute-Stain glaze in different areas of the palatal intaglia of an upper complete denture worn by a patient for 30 days retained the glasslike appearance that it had immediately after coating. The uncoated area under the same condition had shown severe degradation as evidenced by the exposure of subsurface air bubbles incorporated during mixing. Home care instructions included brushing the denture base with a denture brush twice daily and soaking it overnight in dish washing liquid. The smooth surface that Gardner and Parr<sup>21</sup> had predicted was not affected by the normal use. However, no information was provided on whether there is a marked change in the physical properties of the tissue conditioner. This in vivo study included only one patient and one material with three parameters. No statistical studies were available.

Dominguez *et al.*<sup>25</sup> found that the mono-poly coating reduced water absorption, weight and plasticizer loss from Visco-gel, a tissue conditioner, which was immersed in water over a one-month period. They concluded that the mono-poly coating acted as a barrier in preventing water absorption and loss of plasticizer. Gronet *et al.*<sup>26</sup> hypothesized that surface sealing of the temporary soft liner may enhance the life of these liners and extend their period of resilience. They used mono-poly and Palaseal, a light cured glaze, to seal the surfaces of the soft liners, thermocycled them 500 times and measured the resilience of the material as influenced by the coating. Their results showed that soft liners coated with surface sealers exhibited higher resilience than

uncoated samples. They interpreted the increase in resilience is an indication of prolonged service life.

Because of the scant information published on the effectiveness of mono-poly, the absence of properly designed clinical studies, and the fact that it is not the result of polymerization but only a coat of adhering polymers molecules, the advantage of coating temporary soft denture liners with this material is very much still in question. It is also not certain if the properties of a surface sealer and glaze coating would be beneficial across a wide range of temporary soft liners or if it is limited to certain categories of liners with a particular chemistry system.

#### Proposed Study

We propose in this study to evaluate several physical attributes such as weight change, leachants in and pH of surrounding water, surface hardness, elasticity, and plastic deformation recovery across a range of temporary denture soft lining materials. It is hoped that consistency among some results may yield a more accurate picture of the effect of sealer/glaze coatings on tissue conditioners.

## CHAPTER 2 HYPOTHESES

Resiliency, as described by the American Society for Testing & Materials, is the energy returned by an elastomeric polymer when it is suddenly released from a state of strain deformation. Resilience, as defined in the Glossary for Prosthodontic Terms (1999) is the adjective for an object that is capable of withstanding shock without permanent deformation or rupture or tending to recover from or easily adjust to change. The synonym is elastic. Resilience, according to Anusavice,<sup>27</sup> is the amount of energy absorbed by a structure when it is stressed to its elastic limit, which is equivalent to the integrated area under the elastic region of the stress strain curve. It is a measure of the ability of the material to store elastic energy similar to a compressed spring. In the field of prosthodontics, resiliency, or the ability to recover its original shape when subjected to stress, is a property desired for functional impression materials and permanent soft liners. Although Gronet *et al.*<sup>28</sup> associated resilience with enhanced life of temporary soft liners, because softness or plastic deformation is desired for this material, another variable that also allocates for the time factor would be more appropriate. It is the rate of viscoelastic recovery.

This rate of viscoelastic recovery reflects the ability of the material to rebound with time. By inference, if a soft liner retains its plasticizer within its matrix, its rate of recovery should be maintained with time. Otherwise, if there is a variation in rate of recovery, there is a change in plasticizer content. In other terms, the loss of plasticizer

will lead to less viscoelastic properties (shorter recovery time) in favor of elastic properties (higher modulus of elasticity).

In addition to the modulus of elasticity and rate of recovery, other properties may also be associated with the degradation of the material. Such properties include weight change, Shore A hardness, acidity of the surrounding liquid and leachants concentration in the same liquid. Since previous studies have investigated only part of the list, there may not be enough information to conclude the effectiveness of the coating. It is necessary that all five parameters be measured in order to confirm the effectiveness of the treatment.

The purpose of this study is to test the hypothesis that coating with surface sealer and/or curing in pressurized environment can maintain the physical and mechanical properties of the temporary soft liners at the level recorded when they were processed.

This study has nine qualitative factors divided in two groups, materials and treatment. The five materials studied were Lynal, Coe-Comfort, Coe-Soft, Tempo, and Flexacryl-Soft. The four treatments applied were: prepared as per the manufacturer's instruction (control); same as before followed by heat and pressure processing; followed by coating with mono-poly, and followed by coating with Jet Seal, a commercial sealer.

The null hypothesis,  $H_0$ , is there is no significant difference between the treated groups and the control group with time using the following response variables:

- weight change by balance
- leachants in surrounding water by UV spectrophotometry
- pH of surrounding water
- surface hardness by Shore A

- elastic modulus
- viscoelastic recovery rate

The alternate hypothesis,  $H_a$ , is there is a significant difference between the treated groups and the control group in at least one material with time using the above response variable

## CHAPTER 3 MATERIAL AND METHODS

### Material Selection

#### Types of Coating

There are many coatings available commercially besides the laboratory prepared mono-poly. One category is air-dried e.g. Jet Seal, a commercial sealer from Lang Dental Manufacturer (Wheeling, IL) and the other category is light cured e.g. Palaseal by Kulzer. Even though Gronet *et al.*<sup>26</sup> in their study considered Palaseal as a suitable liner coating, we have observed in our preliminary tests that it was a stiff and brittle coating. The additional rigidity of the Palaseal coating would augment the surface hardness of the soft denture liner. Its brittle property would favor fracture development in the coating when the underlying liner deforms viscoelastically in order to comply with the healing mucosa. Therefore it was deemed unsuitable as a resilient liner coating. Verbal communication with Mr. Stephen Domschke, product manager for Heraeus Kulzer, confirmed these observations and the unsuitability of its use as a glaze coat for soft denture liners. Jet Seal was chosen because of its explicit suitability as a surface sealant to be used for soft relines in the manufacturer's instructions. The general properties of mono-poly and Jet Seal are described below.

### Properties of Mono-Poly

Mono-poly is the name coined by Gardner and Parr<sup>21</sup> for a coating prepared by dissolving one part of heat-activated clear polymethyl methacrylate (PMMA) powder to 10 parts of autopolymerizing orthodontic methyl methacrylate monomers (MMA). It is suggested in their paper that the longevity of a temporary soft liner could be extended by using this coating to render a smooth surface, and seal its porous surface. The authors stated that after applying it with a brush, the mono-poly sealer should be allowed to dry for 4 to 5 minutes while held approximately 2 inches away from a 50 or 60 watt lamp. This process should be repeated twice more. Unfortunately, no study was presented to support any of the conjectures or how the formula was arrived at.

Mono-poly for this study was prepared according to the instructions given by Gardner and Parr.<sup>21</sup> Hygienic Clear heat-polymerizing denture polymer powder (Hygenic Corp., Akron, OH) was added in a proportion of 1:10 by weight to a 25-mL conical flask containing Lang's Orthodontic auto-polymerizing monomer liquid (Lang Dental Manufacturer, Wheeling, IL) preheated in a water bath at 55°C using a stirring hot plate. The mix was homogenized using a magnetic stirrer for 10 minutes.

In an [earlier study](#), submitted for publication, it has been demonstrated that there is no polymerization in the coating resulting from a solution of 10 parts of either heat activated or autopolymerizing monomer to 1 part of polymer of either type. The dry film weight constitutes 1% of the initial liquid preparation weight. In other terms, in the dry coat, 99% of the initial monomer evaporated from the preparation. In the absence of polymerization, the coating's properties will depend on the polymer used in the preparation. The manuscript, as submitted for publication, is included in the [Appendix](#).

### Properties of Jet Seal

Jet Seal is a Lang Dental mfg. Co (Wheeling, IL) product advertised as a self-curing sealant composed of less than 100% inhibited methyl methacrylate monomer.

According to the manufacturer's instructions, Jet Seal is a surface sealant to be used for soft relines, hard relines, dentures, temporary crowns and bridges, restorations and denture repairs. It is also stated that Jet Seal fills in surface porosity and increases color stability. Chemically, Jet Seal is an autopolymerizing resin. It air-dries in approximately one minute and will provide a hard surface finish with excellent aesthetics without any polishing.

### Temporary Soft Denture Liners

Temporary soft denture liners are supplied in the form of a polymer powder and a liquid. After mixing the powder and the liquid to a paste consistency, it is applied to the tissue side of the prosthesis. Once gelation has reached a satisfactory level for the application involved, the prosthesis is inserted in the mouth. At this stage, the material is compliant and will flow from areas of pressure, yet have enough body to stay in place. Once the appropriate shaping and molding procedures are performed and the prescribed gelation time has evolved, the prosthesis is removed and the material is trimmed.

Five commercial products representing broad categories of indications and chemistry were selected for this study. They are Lynal Tissue Conditioner (L.D. Caulk), Coe-Comfort (GC America), Tempo (Lang), Coe-Soft (GC America), and Flexacryl-Soft (Lang). The composition and applications of these materials are described below.

### Lynal

According to the manufacturer's instructions Lynal is indicated for use as a tissue conditioner, a soft liner and a functional impression material.

Scant information is available in the published literature regarding this material. The manufacturer, Dentsply/Caulk (Milford, DE), when contacted could not provide further information about the chemistry of this material. The Material Safety Data Sheet included with the merchandise did not reveal its chemistry make-up. An updated MSDS located at <http://www.caulk.com/MSDSDFU/LynalMSDS.html> provided some information. Although the information is incomplete, it showed that the liquid contains ethyl alcohol and an organic phthalate plasticizer while the powder is made up of polyethyl methacrylate and benzoyl peroxide.

The mixed gel has a translucent color that becomes opaque with time in clinical usage.

### Coe-Comfort

This material is marketed by GC-America Inc. as a tissue conditioner. Its instruction pamphlet states that after two to four days, the material is no longer responsive to tissue movement and needs to be replaced. The reason for its early loss of resiliency may be due to its high concentration of the plasticizer benzyl benzoate (85-87% of the liquid component) that is also a fungicide. Due to this plasticizer's small molecular size, it has relatively higher water solubility.<sup>12</sup>

Braden<sup>8</sup> recovered by hydrolysis of butyl alcohol and phthalic acid in the Coe-Comfort liquid, confirming the presence of n-butyl phthalate, an aromatic ester<sup>8</sup> used as a plasticizer. The mixed gel has a white opaque color.

### Coe-Soft

According to the manufacturer, GC-America Inc, this product is indicated for temporary lining of acrylic resin dentures, as a soft liner. The main ingredient of its liquid component is the plasticizer BPBG (81%) which has a higher molecular weight than benzyl benzoate used in Coe-Comfort, hence lower water solubility. It also has a higher ethanol content than Coe-Comfort (15% vs. 8%).

The mixed gel has an opaque pink color.

### Tempo

According to the MSDS, this material contains 3% benzoyl peroxide, which is a polymerizing initiator. Interaction between this benzoyl peroxide and the mono-poly coating, which as mentioned previously has been found not to polymerize, may be possible.

The relatively high Ethanol content (25%) of this material, which according to several studies, accounts for the main weight loss, would indicate that it would be the one to have the most weight loss. The plasticizer used is dialkyl phthalate, an ester resulting from the combination of butyl alcohol and phthalic acid.

It is mentioned in the instruction pamphlet that the material should be durable for 3 months.

### Flexacryl-Soft

Flexacryl-Soft is indicated as a soft formulation self-curing reline acrylic. This material differs chemically from the other materials included in the study in that it does not contain any alcohol as a gel forming solvent in the liquid. In fact, the liquid is composed of n-butyl methacrylate monomer and the plasticizer DBP in equal proportions. The remainder is comprised of trimethylolpropane trimethacrylate, in the

range of 3% and a minute amount of dimethyl-p-toluidine, which is a quaternary ammonium used as an activator.<sup>10</sup> The powder is composed mostly of polyethyl methacrylate.

According to the MSDS, like Tempo, this material contains 2% benzoyl peroxide, which is a polymerizing initiator. Interaction between this benzoyl peroxide and the mono-poly coating may be possible.

Flexacryl-Soft has a hard formulation equivalent, Flexacryl-Hard, which does not contain any dibutyl phthalate, the ester plasticizer. According to the MSDS, the hard material also has a longer chain component. The manufacturer claims that Flexacryl-Soft is a self curing denture relining plastic that will set to a soft cushion-like consistency and will remain soft for at least 12 months. Of the five materials tested, Flexacryl-Soft is the only material that is exothermic after mixing of the powder and liquid components, indicating polymerization.

The mixed gel has an opaque orange color.

The components of the four temporary soft denture liners that we have data on are summarized in Table 1. Table 2 shows the batch number of the materials used in this study.

Table 1. Chemical composition of soft liners

<b>Lynal (DENTSPLY Caulk) from MSDS</b>	
<b>Liquid</b>	<b>Powder</b>
Organic phthalate plasticizer Ethyl alcohol	Polyethyl methacrylate Benzoyl peroxide
<b>Coe-Comfort (GC)</b>	
<b>Liquid</b>	<b>Powder</b>
Benzyl benzoate 85% <sup>8</sup> 87.3% <sup>12</sup> (antifungal) <sup>7</sup> Ethyl alcohol 6% <sup>8</sup> 8.2% <sup>12</sup> Dibutyl phthalate <sup>30</sup> 4.5% <sup>6</sup> Dicyclohexyl phthalate <sup>8</sup>	Polyethyl methacrylate <sup>8,29,30</sup>  Polybutyl methacrylate <sup>8</sup> Zinc undecylenate (antifungal) 1% <sup>12,31</sup>
<b>Coe-Soft (GC)</b>	
<b>Liquid</b>	<b>Powder</b>
Di-n-butyl phthalate <sup>30</sup> 4.3% <sup>12</sup> Benzyl salicylate <sup>30</sup> Butyl phthalyl butyl glycolate 80.9% <sup>12</sup> Ethyl alcohol <sup>30</sup> 14.8% <sup>12</sup>	Polyethyl methacrylate <sup>29,30</sup> Zinc undecylenate (antifungal) 1% <sup>12,31</sup>
<b>Tempo (Lang) from MSDS</b>	
<b>Liquid</b>	<b>Powder</b>
Dialkyl phthalate < 75% Ethyl alcohol 25% <sup>8</sup> < 25%	Polyethyl methacrylate < 99% Residual monomers < 1% Benzoyl peroxide < 3.0% Mineral pigments < 0.01%
<b>Flexacryl-Soft (Lang) from MSDS</b>	
<b>Liquid</b>	<b>Powder</b>
N-butyl methacrylate monomer <50% Dibutyl phthalate <50% Trimethylolpropane Trimethacrylate <3% Dimethyl-p-toluidine <1%	Polyethyl methacrylate < 99% Benzoyl peroxide < 2.0%

Table 2. Batch numbers

Material	Manufacturer	Batch number
Lynal	L.D. Caulk	980819
Coe-Comfort	GC America Inc. (Alsip, IL 60803)	L0361698A
Coe-Soft	GC America Inc. (Alsip, IL 60803)	L062298A
Tempo	Lang Dental mfg. Co (Wheeling, IL 60090)	090398
Flexacryl-Soft	Lang Dental mfg. Co (Wheeling, IL 60090)	090898
Jet Seal	Lang Dental mfg. Co (Wheeling, IL 60090)	121498 QC2

### Substrate for Soft Reline Resins

Because immediately after mixing, the temporary soft denture liners have the consistency of a viscous liquid, they needed to be confined between the denture hard resin base and the oral mucosa or in our case a mold during for the initial set. In addition, the variable waiting periods between different materials for transition from the plastic phase to the viscoelastic phase or gel like made standardization of the time needed for the material preparation difficult.

For in vitro sample preparations, a review of the literature mentioned jar caps<sup>32</sup> and cylindrical containers,<sup>10,23,26</sup> were used as molds for specimen preparation. Dominguez *et al.*,<sup>25</sup> and McCarthy and Moser<sup>33</sup> used a cylindrical sleeve sandwiched between 2 flat surfaces to form the specimens which were then extruded. Because in our study, the specimens were tested dynamically using an Instron Dynamic Testing System to compress them, any holder or substrate for the resilient materials having vertical walls cannot be used. This would impede the compression of the specimen. A heat cure methacrylate substrate flat sheet of 2 mm, which is the recommended thickness of denture resin bases, would approximate clinical settings best. Such a substrate would introduce another parameter to contend with, namely, contaminants such as MMA and hydroquinone from the substrate itself into the surrounding immersion liquid.<sup>34-36</sup> Lucite-ES, a commercial extruded acrylic resin sheet is a close substitute and would minimize this factor. It is assumed that the heat extrusion industrial process would not leave any trace chemical in the Lucite sheet to leach out. As detailed later in the number of sample section, control bare samples of the Lucite sheet immersed in water were prepared to verify this assertion using pH change of the surrounding water and UV

spectrophotometry detection. Two hundred squares of 25 x 25 mm (1 x 1 inch) of Lucite-ES were prepared for the study. They were marked with a serial number in series of 6 using an electric engraver and weighed individually.

## Methods

### Samples Preparation

To understand the effect of processing conditions on the properties of the soft liners, four processing techniques or parameters were applied: (1) prepared according to the manufacturer's recommendation; (2) prepared according to the manufacturer's recommended procedure followed immediately by placing in a pressure pot at 55°C at 30 psi for 15 minutes; (3) coat the specimen with mono-poly after normal processing; and (4) coat the specimen with Jet Seal after normal processing.

### Number of Samples

Soft liner specimens with a dimension of 30(length) x 30(width) x 6(thickness) mm were prepared according to the manufacturer's recommendation. Twenty-four (6 x 4) samples were made from each material and divided into four groups as described in experimental conditions. Each group except for the control group would receive an additional treatment immediately after the normal preparation. This design would give us 6 replications for each condition. Throughout the entire experiment, each specimen were stored in a Corning Snap-Seal No. 1730 container with 50 ml of distilled water and aged individually at room temperature (25°C).

Considering that the type of soft liner forms five (5) qualitative factors, the type of coating forms four (4) qualitative factors, that six specimen are needed per factor for replication, a total of 120 ( $6 \times 4 \times 5$ ) samples were prepared. The Shore A hardness involves dimpling the material surface with an indenter to a depth of about 2 mm, which may damage the surface of the sealer. In consideration of the possibility of damage to the coating, separate samples were prepared for this test. The penetration point was resealed with the appropriate coating after each test and subsequent testing was done at a different spot. Therefore, an additional sixty (60) sample with coatings was prepared, thirty (30) each for experimental condition 3 and 4. This brought the total number of samples to 180 ( $((6 \times 4 \times 5) + (6 \times 2 \times 5))$ ). An additional 6 Snap-Seal vials filled with 50 ml of distilled water and blank Lucite squares were also prepared for leachant verification by UV spectrophotometry and pH test.

#### Powder to Liquid Ratio

For clinical convenience, tissue conditioner manufacturers generally recommend volume measures for preparing the conditioner mix. Because volumetric measures are notoriously inaccurate when measuring powder, the manufacturer's weight ratio recommendations for preparing the liners were used in preference when available. For this study, should that recommendation be unavailable, a powder weight to liquid weight ratio was established by weighing the respective contents of the measuring cups that were provided with the kit. The powder container was fluffed before filling the measuring cup for this purpose. The mixing proportions used for preparing the five materials are shown in Table 3.

Table 3. Powder-to-liquid ratio

	Powder	Liquid	Powder	Liquid	Ratio
	Volumetric measures per portion		Weight measures per portion		Powder:liquid ratio
Lynal	10cc	4cc	6g	4g	3:2
Coe-Comfort	9cc	5cc	6g	5g	6:5
Coe-Soft	N/A	8cc	11g	8g	11:8
Tempo	10cc	6cc	6g	6g	1:1
Flexacryl-Soft	10cc	6cc	6g	6g	1:1

Based on Table 3, Tempo and Flexacryl-Soft have the smallest powder to liquid weight ratio, while Lynal has the largest. In between, Coe-Soft has a larger ratio than Coe-Comfort. Because the chemicals that could be leached out are in the liquid component of the material, this ratio may have an influence in our findings.

#### Preparation Time

Immediately after mixing, the mixture is generally too fluid for intra oral insertion, hence the manufacturer generally includes a certain waiting time from the start of mix before oral insertion. This varies from 30 seconds to 3 minutes. We have elected to apply the mix into the mold immediately after mixing (i.e., 30 seconds after from start of mix). This was done because total setting time is the predominant factor and it is easier to insert the mix into the mold while in a fluid consistency.

After insertion, the mix needed to remain in contact with the oral cavity or in our case, the mold, for a certain time for gelation to occur before it can be withdrawn for manipulation and still retain the shape of the mold surfaces. Times needed prior to manipulation of the material indicated by manufacturers are presented in Table 4.

Table 4. Times needed prior to manipulation

Material	Manufacturer's recommended time
Lynal	7-8 minutes from start of mix
Coe-Comfort	4-5 minutes intra-oral
Coe-Soft	3 minutes intra-oral, remove for trimming, reseal for another 5 minutes
Tempo	3 minutes intra-oral
Flexacryl-Soft	Muscle trim + 3 minutes static + 20 minutes bench cure

In their experiment, Dominguez *et al.*,<sup>25</sup> and Gronet *et al.*<sup>26</sup> allowed 20 minutes setting time for all specimens before specimen removal from the mold. McCarthy and Moser<sup>33</sup> allowed 15 minutes. Yoeli *et al.*<sup>32</sup> did not specify the setting time.

In order to have a standardized time, we allowed on average a total of 25 minutes of setting time from the start of mix in our study before testing. The molding time (time during which the material left to rest in the mold) was 10 minutes before removal. The specimens prepared as per the manufacturer's instruction had a 15-minute bench rest after retrieval from the mold. The heat and pressure specimens were placed in a heated pressure pot for 15 minutes. The coated ones were dip coated and allowed to bench rest until 25 minutes had elapsed from initial mixing of the powder/liquid.

During mixing, we made the same observation as Yoeli *et al.*,<sup>32</sup> who found that Flexacryl-Soft was more fluid and Lynal was more viscous immediately after mixing. Tempo and Flexacryl-Soft had the essentially the same initial fluidity, while Coe-Comfort and Coe-Soft were more viscous and Lynal had the highest viscosity.

### Specimen Forming

Two wooden specimen formers were constructed to be used as mold or former for specimen preparation as shown in Figure 1. These molds have an internal dimension of 150 x 25 x 8 mm. Before receiving the materials, their walls were lubricated with

petroleum jelly. The dimension of these jigs was calculated to accommodate 6 Lucite squares. When six specimens were made from one mix made at a time, intra material data variations associated with preparation would be minimized. Before mixing the resilient material, the mold's bottom was lined with masking tape, 1 inch wide, adhesive side up and six pre-weighed Lucite squares marked as a series were aligned on the tape. The resilient material was mixed, poured into the mold, and covered with wax paper. A glass sheet was placed atop and held down for 10 minutes to obtain a flat surface for testing. After this period, the resilient material was retrieved and cut into individual pieces using Bard Parker knives or piano wire strung over a coping saw. An additional 15 minutes bench rest was allowed before testing.



Figure 1. Molds used in specimen forming. In the foreground are the six Lucite squares backed by masking tape ready for insertion in the mold. In the background is a wooden mold with the Lucite squares in place, ready to receive the tissue conditioner

In clinical situations, the recommended clinical thickness of tissue conditioner as a liner under a complete denture prosthesis is 1.5 mm to 3 mm.<sup>3,37</sup> It is not possible to keep within this recommendation because this thickness would not have yielded valid hardness data since the Shore A specification requires a minimum material thickness of 6 mm. Therefore this is the thickness of the tissue conditioner specimens manufactured from the mold former after subtracting the 2 mm Lucite substrate thickness from the 8 mm depth.

#### Instruments for Data Collection

At each prescribed interval, the following measurements were made:

1. Shore A hardness.
2. Release of plasticizer in the immersion solution.
3. Weight changes of the specimen.
4. Dynamic mechanical test of the specimen.
5. pH of the solution.
6. Surface appearance by visual examination and photographic record when change was detected.

It is expected that there would be a trend between weight loss and the other variables, facilitating the understanding of the transformations that the material goes through and allowing cross validation of the measurements obtained.

#### Weight Loss by Balance

Weight change was monitored by weighing the specimen at each prescribed interval with a Denver Instrument XL-410 electronic balance with a precision of 0.001g

(Denver, CO, Max 410g, S/N 0075163). The weight changes in conjunction with plasticizer leaching would allow estimation the true quantity of water absorption. That data would also be used to establish if there is a correlation between the water absorption and the changes in mechanical properties.

Each Lucite-ES substrate was weighed before receiving the designated soft-liner; the final specimen was also weighed to determine the actual weight of the soft-liner. At each prescribed time of replacing storage medium, the specimens were dab dried with Kimwipe<sup>®</sup> before weighing.

### Shore A Hardness

The hardness of the material was measured using a Shore Durometer type "A-2" shown in Figure 2. This Durometer was attached to an operating stand with a standard 1 kg mass securely affixed to it and centered on the axis of the indenter. The operating stand was then placed on an adjustable platform such that the dial gauge was at eye level to minimize parallax errors and minimize eye strain. The adjustable on which the specimen was placed was then moved within 2 cm of the foot of the Durometer and locked in place. The specimen to be tested was then placed on the adjustable with the indenter facing a spot that has not been previously tested and the Durometer foot was lowered steadily onto the material's surface. At this moment of contact, a chronometer was started and the reading made from the analog dial gauge at the appropriate time. Because the readings tended to level after 2 minutes of penetration by the Shore A indenter, it was decided to record the 30 seconds and 2 minutes readings. If the specimen tested was coated, the penetration point was marked with a permanent marker and covered with a new dab of the coating material.



Figure 2. Shore A Durometer

### Dynamic Mechanical Test

An Instron Model 8511 Frame F Plus Dynamic Testing System, mounted with a Sensotec Model 45/8130-05 1KN(200lbs) S/N 654651 load cell (Canton, MA) was used to test the samples while measuring their compressive strength under load.

Instead of subjecting specimens to a pre-determined amount of stress and observing the stress relaxation behavior of the lining materials, we elected to load the specimen using a cyclic mode up to 15 cycles and recorded the peak load at each cycle. The protocol was comprised of three steps: (1) compress the specimen by 0.15 mm to assure contact between the actuator head and the specimen; (2) continue the compressing movement of the actuator head to 0.65 mm at a rate of 0.05 mm per sec; (3) when the

actuator head reaches 0.65 mm, the actuator head switches to cyclic motion, which uses 0.65 mm as the midpoint and cycles with an amplitude of  $\pm 0.5$  mm at the rate of  $\frac{1}{2}$  cycle per second for 15 cycles. At the end of 15th cycle, the actuator head moved back to its original non-stress position. The entire process took 39 seconds to complete. This mode of dynamic test yields two sets of data. The first set records the load exerted on the specimens as the actuator head compresses the specimen to the predetermined position, approximately 0.65 mm. This set of data was used to estimate the modulus of elasticity of the specimen. The second set records peak loads as the actuator head compresses and cycles between 0.15 mm and 1.15 mm depth of the specimens. The data was used to estimate the recovery of the specimen between cycles.

A viscoelastic material will respond to loading with an instant elastic deformation and a time-dependent viscous deformation. As the load is being removed, the elastic strain will recover instantly but the time-dependent deformation will require certain time to recover. In the present testing protocol, the rate of cycling does not allow the time-dependent deformation to recover completely when the actuator head reverses from unloading back to loading. The immediate result is that the peak load of subsequent loading will always be less than the previous loading cycle. The decay of the peak load can be expressed as follows:

$$L_n = L_o \exp\left(-\frac{n}{\eta}\right) \quad (1)$$

Where,  $L_n$  is the peak load at respective cycle  $n$ ,  $L_o$  is the estimated maximum peak load at  $n = 0$ , and  $\eta$  is a constant unique to a specific testing condition and material. The variable  $\eta$ , which we call rate of recovery, reflects the ability of the material to

rebound elastically; a higher value means more elastic, while a lower value means more viscous flow.

### UV Spectrophotometer

A Shimadzu UV 160U UV/Visible Recording Spectrophotometer, S/N 28D6370 (Columbia, MD) was used to quantify plasticizer leakage. In our preliminary study, leachants from set soft liner specimens into the surrounding water solution were found to share similar UV absorbency profiles as those of the corresponding liquid component of the soft liner. This absorbency spectrum appears between 200-400 nm. Figure 3 shows the typical absorbance profile of leachants, in this case, from Coe-Soft along with the peaks used for measuring leachant quantity. When we attempted to prepare standard solutions from the liquid component as reference for estimating the quantity of release, we found that the liquids were not miscible with water and the quantity that dissolved in water was negligible. We did find that these liquid components were soluble in 25% ethanol/water solution, as implied by Jones *et al.*<sup>12</sup> We then prepared a series of reference solutions with known concentration of the liquid in ppm. The UV spectrophotometer does not detect the presence of ethanol because ethyl alcohol is transparent to UV from the visible into the ultraviolet range near 205 nm.

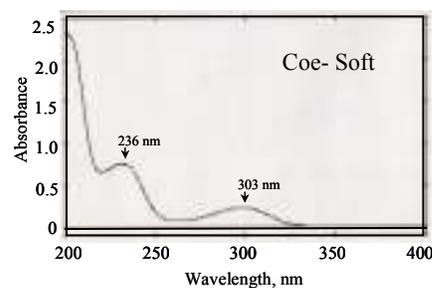


Figure 3. Typical UV absorption curve

When the absorbance of the released content exceeded the detection limit of the instrument, series of dilution were carried out to bring the concentration to within the limit.

#### pH of the Solution

Distilled water can register pH in the neighborhood of 5.5, which can change in the presence of the soft liner and with time. It was not known a priori if that would have a significance influence on the other values collected. The pH values were recorded weekly for each specimen with an Orion Research Expandable Ion Analyzer model EA920 S/N 1192. The pH probe was rinsed with distilled water between each measurement. Six vials of distilled water without any specimens as controls were also prepared. The pH values were used to complement the other data collected.

#### Macro Photography and Micro Photography

Systematic microscopic observation of the tissue conditioner's surface did not yield any information and was therefore abandoned. Instead, macroscopic observation via macro photography was substituted.

When macroscopic surface changes were apparent, selected specimen with representative and noticeable features were selected for macro photography using a Minolta 350si RZ camera equipped with a Minolta AF100 mm f 1:2.8 (32) macro lens. Lighting was supplemented by a Minolta 3500 XI slave flash on remote mode placed at a narrow angle to the specimen. Because of the translucency of the coatings, not all the visible changes were observable on macro photographs, hence the selection of the most evident ones. The use of polarizing filters did not help in enhancing the details.

Microscopic examination of the samples showing surface changes did not yield any evident difference between different areas nor remarkable features.

At the end of the data collection period, a thin section from a specimen of each coated series was prepared for microscopic examination and photographed using a Bausch & Lomb Stereo-Zoom 7 microscope attached to a Nikon AFX-II camera system. The placement of a stage microscale  $100 \times 0.01 = 1$  mm by Graticules, Tonbridge, Kent, England, under each section allowed measurement of the thickness of the coating. Special attention was given to areas where gradient changes in color from the surface inwards, detachment of the coating and voids were observed.

#### Data Collection and Statistical Analysis

Data were collected at the time of preparation (0 week), 48 hours, 1st, 2nd, 4th, 6th, 8th and 12th week. Each sample was examined for surface change, blotted dry, weighted, if they are non coated, tested for hardness with the Shore A Durometer and for viscoelasticity using with the Dynamic Instron machine. The 50ml of distilled water in the SnapSeal container were replaced every time data collection was made. Twenty (20) ml of the immersion liquid was saved in a Dilu-Vial (Fisher Scientific) container for later pH and UV spectrophotometry measurements. Ideally, it should have been replaced as frequently as possible, but for practical purposes, it was not possible to do it more frequently than at data collection time. According to the literature, the rate at which plasticizers would leach out of the material would be most intense during the first two weeks. Therefore after the first two weeks, longer data collection periods before leachants saturation in the surrounding liquid was attained would be satisfactory.

Monitoring of the initial data did not reveal any need to intensify the data collection periods.

The effect of treatment and storage time on the individual variable was first analyzed by two-way analysis of variance to show their influence on the values of the measurements. When statistically significant influence was observed, the Tukey's studentized range tests were performed to group surface treatments or storage times with mean values that are not significant different on the values at  $\alpha=0.05$ . In order to identify if there are correlations between the values of variables, we conducted a series of linear regression between any two of the following variables: weight loss in water, leachant by UV at high and low wavelength, modulus of elasticity, and rate of recovery.

## CHAPTER 4 RESULTS

### Surface Resilience by Shore A Hardness

Although literature reviewed had reported Shore A hardness values of some of the material we used, it was found in this study that none of the materials used gave a stable value. In fact, the dial hand would jump to an initial value and started to decrease immediately, defeating any attempt at an early accurate reading. The hand then either dropped to zero (a total penetration of the indenter) or stabilized at a number after a few minutes. This phenomenon is mostly caused by viscoelastic behavior. There was an instant elastic resistance to the loading that yielded a maximum deflection of the dial hand. This was followed by a creep phase represented by the continuing reduction in hardness value with time. Since we were unable to read the value accurately before it began to decrease, it was decided to take readings at 30 s and 2 min after the indenter was lowered on the specimen.

Tables 5 and 6 show the Shore A hardness results recorded at 30 s and 2 min after placing the load, respectively. Several materials show zero values. We also attempted to record the duration it would take to reach zero value. Although there is a general trend for longer time to zero with specimen storage time, the results are not conclusive and are not shown. It is interesting to note that the Shore A hardness values increased immediately after the mono-poly coating has dried, which is about 15 minutes after

application. Specimens from as prepared, the heat and pressure, and with the Jet Seal coating exhibited similar behaviors. Two-way Analysis of Variance of treatment and storage time shows that both variables have statistically significant influence on the

Table 5. Shore A hardness values 30 sec after indentation

Material	Time, day	Control	Pressure/Heat	Mono-poly	Jet Seal
Coe-Comfort	0	0 (-)	0 (-)	0 (-)	0 (-)
Coe-Comfort	2	0 (-)	0 (-)	0 (-)	0 (-)
Coe-Comfort	7	0 (-)	0 (-)	0 (-)	0 (-)
Coe-Comfort	14	0 (-)	0 (-)	0 (-)	0 (-)
Coe-Comfort	28	0 (-)	0 (-)	2 (3)	0 (-)
Coe-Comfort	42	0 (-)	0 (-)	1 (1)	0 (-)
Coe-Comfort	63	1 (-)	0 (-)	7 (4)	0 (-)
Coe-Comfort	84	1 (-)	1 (-)	5 (4)	0 (-)
Coe-Soft	0	0 (-)	0 (-)	4 (1)	0 (-)
Coe-Soft	2	0 (-)	0 (-)	1 (1)	0 (-)
Coe-Soft	7	0 (-)	3 (1)	1 (2)	0 (-)
Coe-Soft	14	3 (1)	4 (-)	4 (1)	1 (1)
Coe-Soft	28	3 (-)	4 (1)	7 (1)	4 (1)
Coe-Soft	42	2 (2)	5 (1)	8 (1)	4 (1)
Coe-Soft	63	7 (2)	5 (1)	11 (3)	6 (1)
Coe-Soft	84	5 (2)	7 (1)	10 (2)	7 (2)
Flexacryl-Soft	0	29 (1)	31 (-)	56 (8)	22 (2)
Flexacryl-Soft	2	29 (1)	32 (-)	55 (9)	24 (3)
Flexacryl-Soft	7	30 (1)	32 (1)	51 (9)	25 (2)
Flexacryl-Soft	14	31 (1)	32 (-)	53 (11)	26 (1)
Flexacryl-Soft	28	31 (1)	30 (1)	49 (13)	27 (1)
Flexacryl-Soft	42	30 (1)	30 (1)	52 (12)	27 (1)
Flexacryl-Soft	63	30 (1)	31 (1)	55 (11)	29 (2)
Flexacryl-Soft	84	31 (1)	31 (1)	47 (8)	30 (1)
Lynal	0	0 (-)	14 (1)	20 (4)	2 (3)
Lynal	2	13 (1)	15 (1)	17 (3)	8 (3)
Lynal	7	14 (1)	18 (1)	16 (4)	10 (1)
Lynal	14	15 (2)	17 (1)	18 (1)	11 (2)
Lynal	28	14 (-)	17 (1)	19 (1)	9 (1)
Lynal	42	14 (1)	17 (1)	20 (2)	14 (2)
Lynal	63	14 (1)	14 (2)	20 (4)	15 (2)
Lynal	84	15 (1)	15 (1)	20 (2)	16 (2)
Tempo	0	0 (-)	0 (-)	6 (5)	0 (-)
Tempo	2	0 (-)	0 (-)	0 (-)	4 (2)
Tempo	7	0 (-)	0 (-)	3 (2)	0 (-)
Tempo	14	0 (-)	0 (-)	5 (1)	0 (-)
Tempo	28	0 (-)	0 (-)	10 (5)	0 (-)
Tempo	42	0 (-)	0 (-)	5 (5)	0 (-)
Tempo	63	1 (1)	0 (-)	11 (2)	1 (-)
Tempo	84	0 (-)	1 (-)	9 (6)	1 (1)

Note: The values in parenthesis are standard deviation.

hardness values at  $P$  values less than 0.01. Further analysis by Tukey's grouping test confirmed that mono-poly had a significant influence on the Shore A hardness values while the other three treatments in general behave similarly. Table 7 shows the summary

Table 6. Shore A values measured 2 min after indentation

Material	Time, day	Control	Pressure/Heat	Mono-poly	Jet Seal
Coe-Comfort	0	0 (-)	0 (-)	0 (-)	0 (-)
Coe-Comfort	2	0 (-)	0 (-)	0 (-)	0 (-)
Coe-Comfort	7	0 (-)	0 (-)	0 (-)	0 (-)
Coe-Comfort	14	0 (-)	0 (-)	0 (-)	0 (-)
Coe-Comfort	28	0 (-)	0 (-)	0 (-)	0 (-)
Coe-Comfort	42	0 (-)	0 (-)	0 (-)	0 (-)
Coe-Comfort	63	1 (-)	0 (-)	1 (3)	0 (-)
Coe-Comfort	84	1 (-)	1 (-)	0 (-)	0 (-)
Coe-Soft	0	0 (-)	0 (-)	0 (-)	0 (-)
Coe-Soft	2	0 (-)	0 (-)	0 (-)	0 (-)
Coe-Soft	7	0 (-)	0 (-)	0 (-)	0 (-)
Coe-Soft	14	0 (-)	0 (-)	0 (-)	0 (-)
Coe-Soft	28	0 (-)	0 (-)	2 (1)	0 (-)
Coe-Soft	42	0 (-)	1 (1)	2 (2)	1 (1)
Coe-Soft	63	2 (1)	1 (-)	5 (2)	1 (1)
Coe-Soft	84	1 (1)	2 (1)	4 (2)	2 (2)
Flexacryl-Soft	0	24 (-)	23 (2)	52 (8)	17 (2)
Flexacryl-Soft	2	25 (1)	27 (1)	53 (14)	18 (2)
Flexacryl-Soft	7	25 (1)	28 (1)	48 (12)	20 (2)
Flexacryl-Soft	14	27 (1)	28 (1)	47 (11)	21 (1)
Flexacryl-Soft	28	27 (1)	26 (1)	43 (10)	24 (1)
Flexacryl-Soft	42	25 (1)	28 (1)	47 (12)	24 (1)
Flexacryl-Soft	63	27 (1)	27 (1)	47 (9)	24 (3)
Flexacryl-Soft	84	27 (1)	27 (1)	41 (6)	25 (2)
Lynal	0	0 (-)	10 (1)	25 (17)	0 (-)
Lynal	2	9 (1)	11 (1)	11 (2)	4 (2)
Lynal	7	10 (1)	12 (1)	11 (3)	6 (1)
Lynal	14	10 (1)	12 (1)	12 (1)	7 (2)
Lynal	28	10 (-)	13 (2)	14 (1)	6 (1)
Lynal	42	11 (1)	13 (2)	15 (2)	9 (1)
Lynal	63	10 (-)	10 (2)	14 (4)	11 (1)
Lynal	84	10 (-)	11 (1)	14 (3)	12 (1)
Tempo	0	0 (-)	0 (-)	0 (-)	0 (-)
Tempo	2	0 (-)	0 (-)	0 (-)	1 (1)
Tempo	7	0 (-)	0 (-)	0 (-)	0 (-)
Tempo	14	0 (-)	0 (-)	0 (-)	0 (-)
Tempo	28	0 (-)	0 (-)	4 (4)	0 (-)
Tempo	42	0 (-)	0 (-)	1 (1)	0 (-)
Tempo	63	0 (-)	0 (-)	4 (1)	0 (-)
Tempo	84	0 (-)	1 (-)	3 (3)	0 (-)

Note: The values in parenthesis are standard deviation.

Table 7. Tukey's grouping of the surface treatment on Shore A hardness

Material	30 second	2 minutes
Coe-Comfort	M <u>C</u> <u>J</u> <u>P</u>	<u>M</u> <u>C</u> <u>P</u> <u>J</u>
Coe-Soft	M P <u>J</u> <u>C</u>	M <u>J</u> <u>P</u> <u>C</u>
Flexacryl-Soft	M P <u>C</u> <u>J</u>	M <u>P</u> <u>C</u> <u>J</u>
Lynal	M P C J	M P C J
Tempo	M <u>J</u> <u>C</u> <u>P</u>	M <u>J</u> <u>C</u> <u>P</u>

Note: C=Control; J=Jet Seal; M=Mono-poly; P=Pressure/heat. The groups are arranged in descending order from left to right.

The underlined group treatments that are not statistically different at  $\alpha=0.05$ .

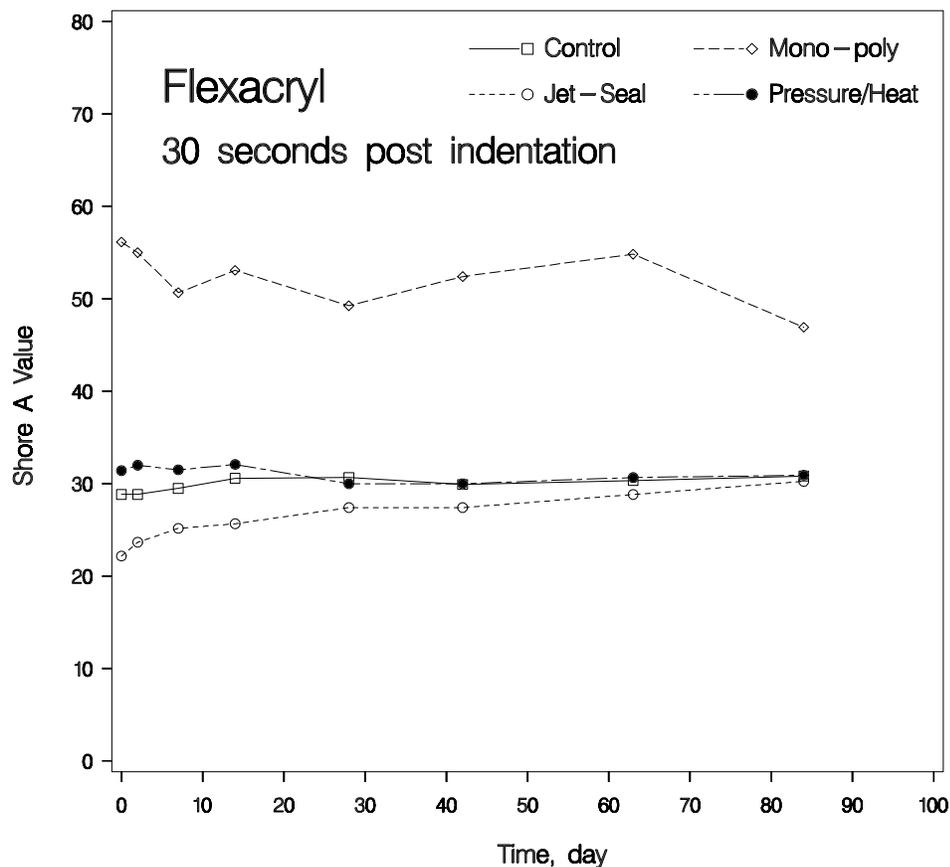


Figure 4. Hardness values 30 seconds post indentation of Flexacryl-Soft

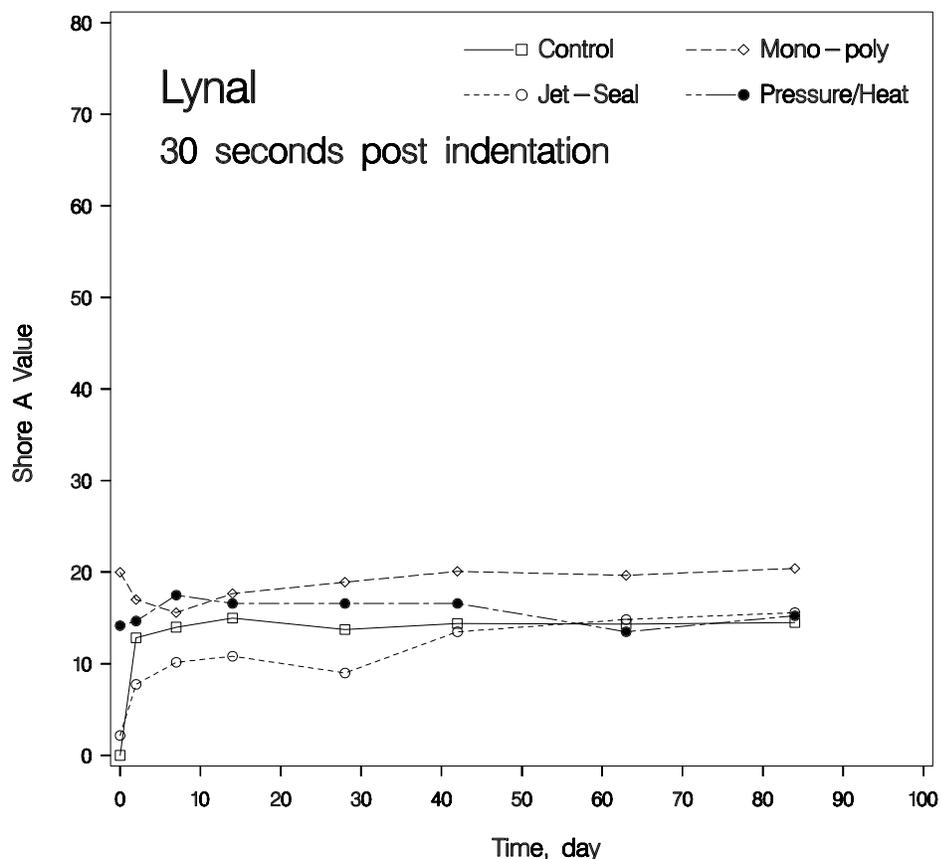


Figure 5. Hardness values 30 seconds post indentation of Lynal

of Tukey's grouping for the effect of treatments. This can be illustrated by Figures 8 and 9, which show the hardness values 30 seconds post indentation of Flexacryl-Soft and Lynal as influenced by treatment and time, respectively.

#### Dynamic Mechanical Test of the Specimen

Table 8 shows the calculated values of elastic modulus of the specimens as influenced by the treatment and time of immersion; each value has the unit of MPa. Higher values mean the material is more rigid. Table 9 shows the rate of recovery of the specimen as influence by the treatment and the duration of water immersion; the value has a unit of  $\text{cycle}^{-1}$ . Higher values mean that the peak load decay is less, which indicates the material is more elastic. In other words it recovers more rapidly. On the

other hand, a lower value means the material is softer and will not recover as much when the load is removed.

Table 8. Elastic modulus of soft liners as result of surface treatment and time

Materials	Time, day	Control	Pressure/Heat	Mono-poly	Jet Seal
Coe-Comfort	0	0.44 (0.04)	0.50 (0.09)	0.36 (0.08)	0.45 (0.07)
Coe-Comfort	2	0.65 (0.07)	0.55 (0.09)	0.69 (0.25)	0.62 (0.05)
Coe-Comfort	7	0.74 (0.08)	0.94 (0.18)	0.80 (0.21)	0.54 (0.31)
Coe-Comfort	14	0.87 (0.11)	0.91 (0.18)	0.80 (0.16)	0.75 (0.15)
Coe-Comfort	28	0.96 (0.10)	0.73 (0.12)	0.85 (0.21)	0.75 (0.18)
Coe-Comfort	42	0.98 (0.10)	0.89 (0.09)	0.89 (0.22)	0.89 (0.13)
Coe-Comfort	63	0.93 (0.11)	0.87 (0.09)	0.96 (0.25)	0.86 (0.13)
Coe-Comfort	84	1.03 (0.11)	0.85 (0.12)	0.77 (0.33)	0.83 (0.13)
Coe-Soft	0	0.42 (0.12)	0.34 (0.11)	0.53 (0.12)	0.53 (0.02)
Coe-Soft	2	0.44 (0.14)	0.66 (0.22)	0.97 (0.24)	0.69 (0.04)
Coe-Soft	7	0.61 (0.12)	1.00 (0.14)	1.09 (0.12)	0.83 (0.08)
Coe-Soft	14	0.80 (0.13)	0.91 (0.09)	1.06 (0.26)	0.80 (0.17)
Coe-Soft	28	0.96 (0.10)	1.30 (0.24)	1.12 (0.18)	1.04 (0.18)
Coe-Soft	42	0.97 (0.11)	1.30 (0.24)	1.30 (0.17)	0.95 (0.26)
Coe-Soft	63	1.06 (0.19)	1.36 (0.27)	1.15 (0.28)	1.00 (0.22)
Coe-Soft	84	1.20 (0.12)	1.51 (0.39)	1.04 (0.32)	1.15 (0.26)
Flexacryl-Soft	0	3.26 (0.40)	4.27 (0.30)	6.36 (0.35)	3.53 (0.52)
Flexacryl-Soft	2	3.37 (0.72)	3.84 (0.32)	7.97 (0.93)	4.53 (0.62)
Flexacryl-Soft	7	3.86 (0.71)	4.84 (0.54)	6.98 (1.17)	4.02 (0.69)
Flexacryl-Soft	14	4.06 (0.46)	4.92 (0.42)	6.71 (0.86)	4.98 (0.71)
Flexacryl-Soft	28	3.95 (0.38)	4.83 (0.64)	7.37 (1.08)	4.96 (0.68)
Flexacryl-Soft	42	4.23 (0.53)	4.89 (0.20)	7.13 (0.78)	5.24 (0.81)
Flexacryl-Soft	63	3.78 (0.38)	5.00 (0.31)	8.49 (0.99)	5.21 (1.06)
Flexacryl-Soft	84	4.62 (0.70)	5.20 (0.47)	7.12 (0.80)	5.22 (1.13)
Lynal	0	0.16 (0.05)	0.28 (0.13)	1.18 (0.23)	1.08 (0.17)
Lynal	2	0.60 (0.40)	0.29 (0.11)	1.67 (0.25)	1.08 (0.32)
Lynal	7	0.90 (0.45)	1.38 (0.49)	1.53 (0.21)	1.12 (0.39)
Lynal	14	1.34 (0.38)	1.29 (0.35)	1.66 (0.17)	1.07 (0.31)
Lynal	28	1.19 (0.28)	0.75 (0.34)	1.50 (0.11)	1.36 (0.49)
Lynal	42	1.29 (0.33)	0.47 (0.12)	1.49 (0.19)	1.46 (0.32)
Lynal	63	1.38 (0.44)	0.53 (0.16)	1.34 (0.19)	1.34 (0.29)
Lynal	84	1.33 (0.37)	0.45 (0.08)	1.30 (0.10)	1.22 (0.35)
Tempo	0	0.31 (0.06)	0.36 (0.05)	0.50 (0.08)	0.31 (0.02)
Tempo	2	0.54 (0.14)	0.46 (0.12)	0.65 (0.07)	0.59 (0.05)
Tempo	7	0.78 (0.19)	1.17 (0.14)	1.02 (0.19)	0.62 (0.23)
Tempo	14	0.87 (0.20)	1.12 (0.13)	0.68 (0.37)	0.93 (0.13)
Tempo	28	1.07 (0.20)	0.81 (0.25)	0.60 (0.28)	0.97 (0.21)
Tempo	42	1.05 (0.24)	1.11 (0.17)	0.92 (0.36)	1.08 (0.24)
Tempo	63	1.14 (0.21)	1.10 (0.20)	0.75 (0.47)	1.07 (0.23)
Tempo	84	1.04 (0.25)	1.04 (0.16)	0.68 (0.33)	1.03 (0.25)

Note: The values are in MPa; the values in parenthesis are standard deviation.

The results of Two-way Analysis of Variance indicate that the effects of treatment and storage time on the elastic modulus values and rate of recovery are statistically significant. Further analysis with Tukey's grouping test shows that

Table 9. Rate of recovery

Material	Time, day	Control	Pressure/Heat	Mono-poly	Jet Seal
Coe-Comfort	0	55.1 (2.1)	64.0 (2.8)	44.4 (4.9)	43.1 (5.7)
Coe-Comfort	2	80.0 (6.5)	72.0 (3.2)	56.6 (8.5)	61.4 (6.8)
Coe-Comfort	7	84.3 (12.7)	84.3 (12.7)	69.7 (6.8)	70.6 (7.2)
Coe-Comfort	14	75.8 (10.0)	86.0 (8.7)	68.6 (6.6)	72.7 (6.9)
Coe-Comfort	28	86.5 (21.5)	95.4 (12.5)	75.9 (5.7)	95.1 (16.5)
Coe-Comfort	42	86.4 (4.2)	88.0 (3.6)	74.0 (5.4)	87.3 (10.0)
Coe-Comfort	63	96.5 (21.1)	80.9 (3.1)	88.5 (6.3)	98.7 (15.0)
Coe-Comfort	84	97.0 (16.7)	86.1 (1.3)	85.1 (4.8)	97.2 (13.4)
Coe-Soft	0	65.6 (4.2)	54.6 (5.2)	67.1 (4.2)	51.1 (2.1)
Coe-Soft	2	80.2 (2.7)	77.3 (5.8)	68.9 (5.0)	64.0 (2.0)
Coe-Soft	7	87.7 (7.4)	80.1 (5.6)	63.7 (1.8)	77.7 (3.9)
Coe-Soft	14	96.2 (4.8)	97.0 (9.0)	63.7 (1.8)	89.2 (4.3)
Coe-Soft	28	124.4 (19.0)	103.4 (7.9)	82.6 (5.4)	94.7 (8.4)
Coe-Soft	42	104.4 (18.2)	98.1 (2.7)	83.4 (3.5)	92.5 (1.9)
Coe-Soft	63	145.3 (31.1)	110.0 (19.7)	98.5 (10.4)	105.6 (5.0)
Coe-Soft	84	102.7 (6.4)	97.5 (5.1)	95.9 (7.3)	89.9 (3.9)
Flexacryl-Soft	0	112.0 (19.7)	110.9 (6.4)	55.0 (3.5)	112.0 (19.6)
Flexacryl-Soft	2	115.6 (7.7)	105.6 (12.3)	72.5 (8.6)	107.8 (6.0)
Flexacryl-Soft	7	109.3 (17.7)	72.3 (5.7)	81.4 (6.9)	118.7 (7.6)
Flexacryl-Soft	14	128.4 (11.3)	115.2 (6.0)	95.5 (9.0)	127.8 (10.5)
Flexacryl-Soft	28	125.0 (14.0)	82.9 (4.9)	83.7 (7.9)	160.7 (16.9)
Flexacryl-Soft	42	136.4 (8.0)	128.5 (9.4)	89.5 (12.8)	126.8 (14.0)
Flexacryl-Soft	63	115.3 (3.6)	110.1 (7.2)	68.5 (6.4)	121.3 (9.5)
Flexacryl-Soft	84	113.6 (10.9)	98.7 (8.7)	72.9 (6.5)	165.2 (28.5)
Lynal	0	33.7 (3.8)	164.0 (19.2)	137.9 (16.3)	96.9 (1.4)
Lynal	2	136.7 (47.5)	177.9 (17.0)	128.7 (16.8)	110.2 (6.2)
Lynal	7	165.2 (20.4)	137.1 (3.8)	143.6 (11.8)	120.5 (6.2)
Lynal	14	131.9 (7.2)	165.8 (4.5)	120.6 (7.6)	128.9 (10.9)
Lynal	28	161.6 (32.7)	156.2 (11.7)	124.7 (6.2)	142.6 (31.0)
Lynal	42	160.5 (13.4)	159.0 (19.8)	125.1 (8.1)	132.6 (5.4)
Lynal	63	176.1 (15.9)	163.7 (14.9)	121.9 (5.9)	137.9 (7.3)
Lynal	84	162.1 (8.6)	152.3 (12.6)	124.1 (9.9)	146.7 (9.7)
Tempo	0	42.5 (4.5)	55.4 (3.3)	44.1 (1.3)	37.2 (2.0)
Tempo	2	79.2 (6.3)	67.1 (2.7)	52.2 (1.6)	53.2 (1.4)
Tempo	7	86.7 (17.7)	72.8 (10.2)	54.0 (3.3)	71.2 (3.6)
Tempo	14	94.0 (4.0)	87.2 (4.2)	61.9 (7.0)	75.9 (1.8)
Tempo	28	127.3 (18.0)	99.4 (8.3)	78.6 (9.9)	80.9 (1.9)
Tempo	42	101.7 (2.1)	99.3 (3.3)	67.7 (5.7)	77.5 (2.3)
Tempo	63	90.5 (5.8)	91.6 (1.8)	85.1 (11.9)	81.1 (4.2)
Tempo	84	104.8 (1.2)	100.3 (3.8)	78.2 (5.1)	83.1 (2.7)

Note: The values are in cycle<sup>-1</sup>; the values in parenthesis are standard deviation.

significant changes often occur during the first two weeks. After that initial period, the values began to fluctuate. Table 10 shows the summary of Tukey's grouping for the effect of treatment on the elastic modulus and rate of recovery.

Table 10. Tukey's grouping of the surface treatment on dynamic tests

Material	Modulus of Elasticity	Rate of recovery
Coe-Comfort	<u>C P M J</u>	P <u>C J M</u>
Coe-Soft	<u>M P J C</u>	C P <u>J M</u>
Flexacryl-Soft	M <u>J P</u> C	J C P M
Lynal	M J P C	P <u>M J</u> C
Tempo	<u>P C J M</u>	C P <u>J M</u>

Note: C=Control; J=Jet Seal; M=Mono-poly; P=Pressure/heat.

The groups are arranged in descending order from left to right.

The underlines group treatments that are not statistically different at  $\alpha=0.05$ .

#### Release of Plasticizer in the Immersion Solution by UV/VIS Spectrophotometer

Tables 11 and 12 show the mean plasticizer release based on the high and low wavelength, respectively. Ideally, the calculated amount of release from the liners should be the same using either wavelength. That, however, is not the case when we compare the two tables. The possible explanation is that each wavelength represents materials (i.e., plasticizer) of different chemical nature. In addition, these materials do not exhibit the same molar extinction coefficient. Therefore, the use of UV absorption as a mean of estimating the absolute quantity of plasticizer leaching should be limited to illustrate the effect of various processing methods on the release of plasticizer. For example, the quantity of release at lower wavelength are higher with Mono-poly and Jet Seal; this is not surprising since that range of wavelength, 221 to 232 nm, is associated with MMA and both coatings consist of significant amount of MMA. The information collected here will not be used to quantify the actual amount of leachants but used to

compare with those collected from the actual weight loss of the specimen. The results of Two-way Analysis of Variance show that both treatment and storage time have statistically

Table 11. Estimated leachant loss by UV absorbance at higher wavelength

Material	Time, day	Control		Pressure/Heat		Mono-poly		Jet Seal	
Coe-Comfort	0	0.0	0.0	0.1	(0.0)	0.0	0.0	0.0	0.0
Coe-Comfort	2	5.0	(0.4)	6.3	(0.2)	5.3	(0.7)	4.0	(0.4)
Coe-Comfort	7	10.3	(0.5)	11.9	(0.3)	9.3	(1.2)	4.2	(0.4)
Coe-Comfort	14	15.5	(0.9)	15.3	(0.7)	13.8	(1.6)	10.4	(0.6)
Coe-Comfort	28	22.8	(1.9)	20.9	(0.9)	21.0	(2.6)	15.4	(0.7)
Coe-Comfort	42	29.7	(3.1)	29.9	(1.1)	27.6	(3.6)	24.1	(1.3)
Coe-Comfort	63	38.8	(4.8)	40.6	(2.1)	36.7	(4.7)	33.3	(1.5)
Coe-Comfort	84	50.2	(5.4)	54.2	(3.0)	44.5	(5.9)	41.0	(1.6)
Coe-Soft	0	0.0	0.0	0.2	(0.0)	0.0	0.0	0.0	0.0
Coe-Soft	2	0.3	(0.0)	0.5	(0.0)	0.2	(0.0)	0.2	(0.0)
Coe-Soft	7	0.5	(0.0)	0.7	(0.0)	0.4	(0.0)	0.4	(0.0)
Coe-Soft	14	0.8	(0.0)	0.9	(0.0)	0.6	(0.0)	0.7	(0.0)
Coe-Soft	28	1.1	(0.1)	1.2	(0.0)	1.0	(0.1)	1.0	(0.0)
Coe-Soft	42	1.4	(0.1)	1.6	(0.1)	1.3	(0.2)	1.5	(0.1)
Coe-Soft	63	2.1	(0.5)	2.0	(0.1)	1.9	(0.2)	2.0	(0.1)
Coe-Soft	84	3.1	(0.8)	2.5	(0.2)	2.4	(0.2)	2.5	(0.1)
Flexacryl-Soft	0	0.0	0.0	1.5	(0.1)	0.0	0.0	0.0	0.0
Flexacryl-Soft	2	4.7	(0.3)	4.3	(0.2)	0.8	(0.2)	1.4	(0.1)
Flexacryl-Soft	7	5.8	(0.4)	6.9	(0.4)	1.2	(0.3)	2.8	(0.2)
Flexacryl-Soft	14	8.0	(0.5)	8.0	(0.5)	1.7	(0.6)	4.4	(0.2)
Flexacryl-Soft	28	10.4	(0.7)	9.9	(0.7)	2.2	(0.6)	6.4	(0.3)
Flexacryl-Soft	42	12.0	(0.8)	11.6	(0.7)	2.8	(0.7)	8.2	(0.4)
Flexacryl-Soft	63	13.9	(0.9)	13.1	(0.8)	3.6	(0.8)	10.4	(0.5)
Flexacryl-Soft	84	15.2	(1.0)	14.4	(0.9)	4.3	(0.9)	12.4	(0.6)
Lynal	0	0.0	0.0	0.1	(0.0)	0.0	0.0	0.0	0.0
Lynal	2	0.2	(0.0)	0.2	(0.0)	0.2	(0.0)	0.1	(0.1)
Lynal	7	0.3	(0.0)	0.3	(0.0)	0.3	(0.0)	0.3	(0.1)
Lynal	14	0.4	(0.0)	0.4	(0.0)	0.4	(0.0)	0.4	(0.1)
Lynal	28	0.5	(0.0)	0.6	(0.0)	0.6	(0.0)	0.5	(0.1)
Lynal	42	0.7	(0.0)	0.8	(0.1)	0.7	(0.0)	0.7	(0.1)
Lynal	63	1.0	(0.0)	1.0	(0.1)	0.9	(0.0)	0.8	(0.1)
Lynal	84	1.3	(0.1)	1.4	(0.2)	1.1	(0.0)	1.0	(0.1)
Tempo	0	0.0	0.0	0.1	(0.0)	0.0	0.0	0.0	0.0
Tempo	2	0.2	(0.0)	0.4	(0.0)	2.2	(0.1)	8.3	(1.4)
Tempo	7	0.4	(0.0)	0.6	(0.0)	3.5	(0.1)	13.2	(1.8)
Tempo	14	0.6	(0.0)	0.7	(0.0)	4.8	(0.3)	15.9	(3.1)
Tempo	28	0.8	(0.1)	0.9	(0.0)	6.9	(0.5)	17.8	(3.5)
Tempo	42	1.1	(0.1)	1.2	(0.1)	8.5	(0.6)	19.4	(3.7)
Tempo	63	1.5	(0.1)	1.6	(0.1)	10.4	(0.6)	20.6	(3.7)
Tempo	84	1.8	(0.1)	1.8	(0.1)	12.2	(0.7)	21.5	(3.8)

Note: The values are in mg/g; the values in parenthesis are standard deviation.

Table 12. Estimated leachant loss by UV absorbance at lower wavelength

Material	Time, day	Control	Pressure/Heat	Mono-poly	Jet Seal
Coe-Comfort	0	0.0 (0.0)	0.1 (0.0)	0.0 (0.0)	0.0 (0.0)
Coe-Comfort	2	0.2 (0.0)	0.3 (0.0)	0.9 (0.1)	0.8 (0.1)
Coe-Comfort	7	0.3 (0.0)	0.5 (0.0)	1.3 (0.2)	1.1 (0.1)
Coe-Comfort	14	0.5 (0.0)	0.6 (0.0)	1.8 (0.3)	1.7 (0.1)
Coe-Comfort	28	0.7 (0.0)	0.7 (0.0)	2.5 (0.4)	2.1 (0.2)
Coe-Comfort	42	0.9 (0.1)	0.9 (0.0)	3.1 (0.4)	2.7 (0.2)
Coe-Comfort	63	1.3 (0.2)	1.3 (0.0)	3.9 (0.4)	3.2 (0.3)
Coe-Comfort	84	1.6 (0.3)	1.8 (0.1)	3.9 (0.4)	3.8 (0.3)
Coe-Soft	0	0.0 (0.0)	0.1 (0.0)	0.0 (0.0)	0.0 (0.0)
Coe-Soft	2	0.2 (0.0)	0.4 (0.0)	0.6 (0.1)	0.7 (0.0)
Coe-Soft	7	0.4 (0.0)	0.5 (0.0)	0.8 (0.1)	1.3 (0.1)
Coe-Soft	14	0.6 (0.0)	0.7 (0.0)	1.1 (0.1)	1.7 (0.1)
Coe-Soft	28	0.8 (0.0)	0.9 (0.0)	1.7 (0.1)	2.2 (0.1)
Coe-Soft	42	1.0 (0.0)	1.1 (0.0)	2.1 (0.2)	2.7 (0.1)
Coe-Soft	63	1.4 (0.3)	1.4 (0.1)	2.7 (0.2)	3.2 (0.0)
Coe-Soft	84	2.0 (0.4)	1.8 (0.1)	3.3 (0.2)	3.6 (0.1)
Flexacryl-Soft	0	0.0 (0.0)	1.1 (0.0)	0.0 (0.0)	0.0 (0.0)
Flexacryl-Soft	2	3.1 (0.2)	3.0 (0.1)	1.9 (0.3)	10.8 (1.7)
Flexacryl-Soft	7	3.9 (0.3)	4.8 (0.3)	2.6 (0.3)	16.6 (2.0)
Flexacryl-Soft	14	5.5 (0.3)	5.6 (0.4)	3.2 (0.4)	21.6 (2.2)
Flexacryl-Soft	28	7.2 (0.5)	6.7 (0.5)	3.9 (0.5)	25.5 (2.1)
Flexacryl-Soft	42	8.2 (0.6)	7.8 (0.6)	4.6 (0.6)	28.9 (2.4)
Flexacryl-Soft	63	9.4 (0.6)	8.7 (0.7)	5.4 (0.6)	32.3 (2.7)
Flexacryl-Soft	84	10.2 (0.7)	9.4 (0.7)	5.5 (0.6)	35.2 (2.9)
Lynal	0	0.0 (0.0)	0.1 (0.0)	0.0 (0.0)	0.0 (0.0)
Lynal	2	0.1 (0.0)	0.1 (0.0)	2.7 (0.5)	2.4 (0.3)
Lynal	7	0.2 (0.0)	0.2 (0.0)	3.8 (0.6)	6.2 (1.1)
Lynal	14	0.2 (0.0)	0.2 (0.0)	4.6 (0.7)	7.8 (1.1)
Lynal	28	0.3 (0.0)	0.3 (0.0)	5.6 (0.9)	9.2 (1.2)
Lynal	42	0.5 (0.0)	0.5 (0.1)	6.4 (0.9)	10.5 (1.2)
Lynal	63	0.7 (0.0)	1.3 (0.3)	7.2 (0.9)	11.6 (1.3)
Lynal	84	1.0 (0.1)	1.6 (0.4)	7.2 (0.9)	12.5 (1.4)
Tempo	0	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)
Tempo	2	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	5.8 (0.6)
Tempo	7	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	9.7 (1.0)
Tempo	14	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	11.8 (2.2)
Tempo	28	0.0 (0.0)	0.0 (0.0)	0.0 (0.0)	13.3 (2.4)
Tempo	42	0.0 (0.0)	0.0 (0.0)	0.7 (0.1)	14.7 (2.6)
Tempo	63	0.3 (0.0)	0.3 (0.1)	1.4 (0.1)	15.7 (2.7)
Tempo	84	0.5 (0.0)	0.5 (0.1)	2.1 (0.1)	16.3 (2.7)

Note: The values are in mg/g; the values in parenthesis are standard deviation.

significant influence on the quantity of leaching. Table 13 shows the summary of Tukey's grouping of the effect of treatment on the leaching; it confirms the observation that specimens with coatings leach more.

Table 13. Tukey's grouping of the effect of treatment on the leaching by UV

Material	Higher wavelength	Lower wavelength
Coe-Comfort	<u>P C</u> M J	M J P C
Coe-Soft	<u>P C J M</u>	J M P C
Flexacryl-Soft	<u>C P</u> J M	J <u>C P</u> M
Lynal	P <u>C M</u> J	J M <u>P C</u>
Tempo	J M <u>P C</u>	J <u>M C P</u>

Note: C=Control; J=Jet Seal; M=Mono-poly; P=Pressure/heat. The groups are arranged in descending order from left to right. The underlines group treatments that are not statistically different at  $\alpha=0.05$ .

There was no detectable leachants by UV spectrophotometry in the containers with the bare Lucite substrates.

#### Weight Changes of the Specimen

Table 14 shows the mean weight loss in distilled water along with respective standard deviation for each treatment at each weighing. Figures 6 and 7 show the weight loss with time for Lynal and Tempo, respectively. They represent two extremes of weight loss. Each data point represents the mean of six replications. The effect of the coating on the loss does appear consistent through out all five materials. It is also noted that there is more loss when Jet Seal is used, and less weight loss with mono-poly.

Table 14. Weight change of soft-liners in water with time as influenced by treatment

Materials	Time, day	Control	Pressure/Heat	Mono-poly	Jet Seal
Coe-Comfort	2	-11.88 (0.60)	-12.58 (0.65)	-9.86 (2.16)	-9.56 (2.13)
Coe-Comfort	7	-16.33 (0.62)	-16.93 (1.09)	-15.71 (2.64)	-21.09 (3.09)
Coe-Comfort	14	-19.54 (0.69)	-19.65 (1.05)	-18.27 (3.79)	-28.33 (3.38)
Coe-Comfort	28	-23.35 (0.72)	-23.69 (0.59)	-23.43 (4.94)	-31.53 (3.55)
Coe-Comfort	42	-23.92 (0.69)	-23.24 (1.21)	-24.25 (5.63)	-38.12 (3.13)
Coe-Comfort	63	-23.50 (0.67)	-24.63 (0.65)	-29.27 (5.72)	-38.19 (3.19)
Coe-Comfort	84	-22.82 (0.79)	-21.05 (1.66)	-29.99 (5.64)	-38.03 (4.00)
Coe-Soft	2	-18.73 (0.98)	-18.30 (0.51)	-3.71 (0.51)	-5.94 (2.26)
Coe-Soft	7	-26.49 (1.00)	-27.61 (0.56)	-10.49 (2.77)	-28.50 (3.09)
Coe-Soft	14	-33.96 (0.90)	-30.68 (0.82)	-7.94 (4.27)	-40.07 (2.15)
Coe-Soft	28	-41.11 (1.13)	-38.65 (0.68)	-16.97 (1.34)	-38.85 (3.04)
Coe-Soft	42	-43.35 (1.15)	-40.26 (1.26)	-17.69 (0.94)	-50.44 (1.62)
Coe-Soft	63	-44.13 (1.05)	-43.17 (1.38)	-19.03 (0.94)	-50.91 (1.67)
Coe-Soft	84	-43.92 (1.65)	-41.81 (1.19)	-19.31 (0.92)	-50.26 (1.82)
Flexacryl-Soft	2	-1.50 (0.89)	-3.12 (0.79)	2.18 (0.87)	-6.70 (1.36)
Flexacryl-Soft	7	-2.03 (0.61)	-2.37 (0.66)	2.82 (1.12)	-10.65 (1.36)
Flexacryl-Soft	14	-1.50 (0.79)	-2.29 (0.83)	5.19 (1.51)	-12.76 (1.31)
Flexacryl-Soft	28	-2.17 (0.93)	-2.02 (1.27)	4.55 (1.47)	-12.53 (0.81)
Flexacryl-Soft	42	-2.32 (0.95)	-2.53 (0.56)	7.58 (1.51)	-17.94 (1.37)
Flexacryl-Soft	63	-2.79 (0.96)	-3.91 (0.89)	6.06 (1.56)	-19.04 (1.45)
Flexacryl-Soft	84	-3.27 (1.38)	-4.35 (1.66)	7.00 (1.70)	-19.87 (1.72)
Lynal	2	-0.33 (1.75)	-1.58 (0.71)	-2.01 (1.21)	-0.69 (0.73)
Lynal	7	-5.17 (0.76)	-3.46 (0.40)	-4.12 (1.40)	-5.67 (0.49)
Lynal	14	-5.39 (2.67)	-4.88 (0.49)	-1.68 (1.61)	-9.07 (0.55)
Lynal	28	-8.72 (1.01)	-7.72 (0.55)	-3.08 (2.07)	-8.53 (0.84)
Lynal	42	-9.87 (0.93)	-8.26 (0.80)	-1.24 (2.41)	-14.69 (0.62)
Lynal	63	-9.62 (1.20)	-10.53 (0.67)	-3.30 (2.34)	-14.68 (0.81)
Lynal	84	-9.80 (1.18)	-9.03 (1.12)	-2.63 (2.66)	-15.04 (0.98)
Tempo	2	-42.86 (0.77)	-42.40 (0.76)	-10.93 (1.67)	-35.37 (0.82)
Tempo	7	-56.22 (1.23)	-64.08 (1.41)	-25.35 (3.94)	-66.77 (1.10)
Tempo	14	-66.74 (1.32)	-69.02 (1.22)	-29.68 (5.34)	-80.98 (1.50)
Tempo	28	-72.46 (1.84)	-77.12 (0.89)	-40.97 (5.12)	-82.87 (1.45)
Tempo	42	-72.72 (1.97)	-77.75 (1.23)	-41.84 (5.56)	-89.21 (1.64)
Tempo	63	-71.98 (1.54)	-78.65 (1.21)	-47.86 (5.64)	-88.60 (1.36)
Tempo	84	-73.73 (1.85)	-78.02 (1.66)	-48.51 (5.16)	-88.46 (1.69)

Note: The values are in mg/g; the values in parentheses are standard deviation.

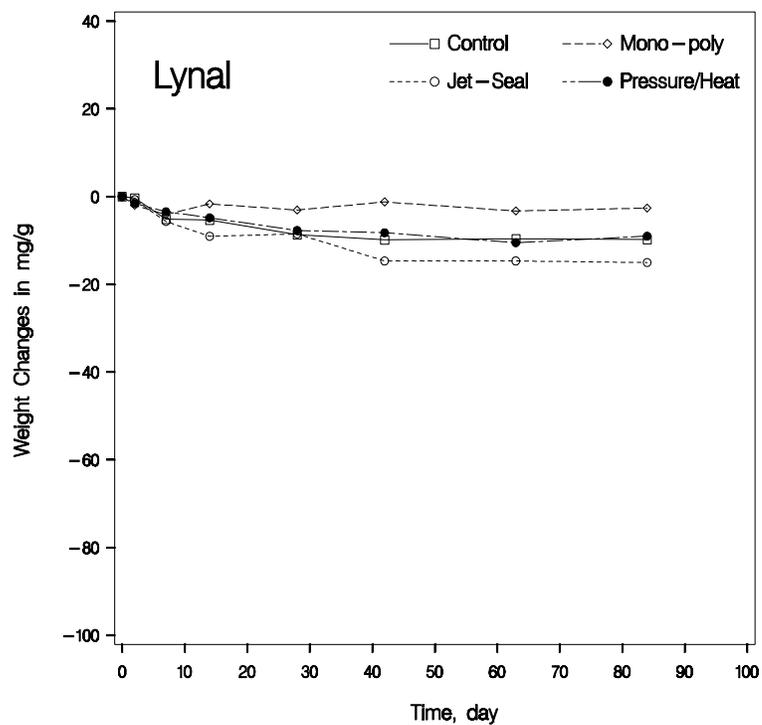


Figure 6. Weight loss with time for Lynal

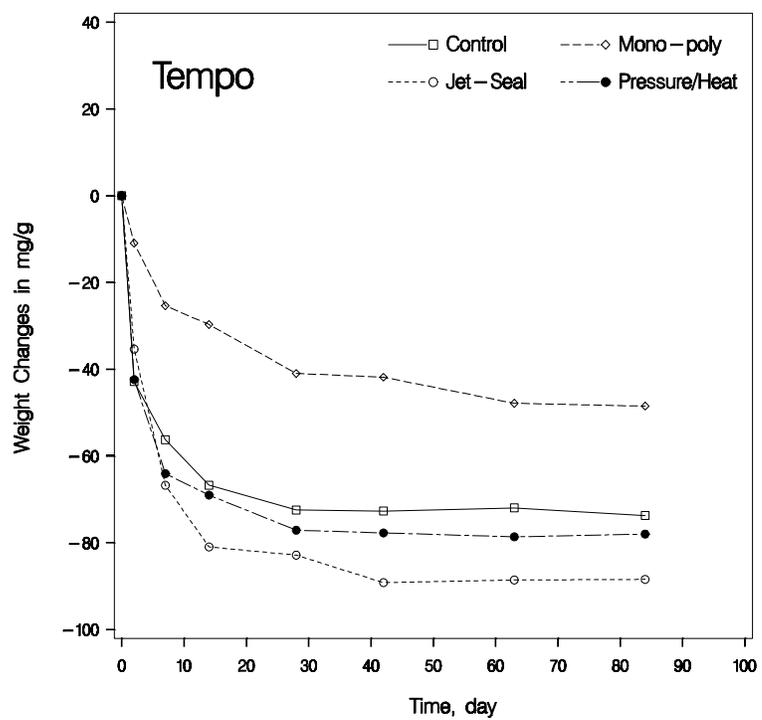


Figure 7. Weight loss with time for Tempo

Although weight loss in air has no clinical significance to the performance of the material, the results represent the loss of alcohol from the mixture and can be used for comparison purposes. Table 15 shows the mean weight loss of control and mono-poly coated specimens up to 30 days in air. Figures 8 and 9 illustrate the weight loss with time for the control and mono-poly coated specimens, respectively. It is clear that the weight loss in air has reached a plateau while the mono-poly coated ones continued to lose weight but at a very slow pace.

Table 15. Weight loss in air

Material	Time, day	Control		Mono-poly	
Coe-Comfort	0	0.00	(0.00)	0.00	(0.0)
Coe-Comfort	1	-11.07	(1.36)	-17.47	(2.36)
Coe-Comfort	7	-28.27	(1.93)	-39.97	(3.35)
Coe-Comfort	12	-30.93	(2.28)	-45.40	(3.95)
Coe-Comfort	16	-32.03	(2.28)	-49.20	(3.95)
Coe-Comfort	30	-31.63	(2.73)	-56.47	(4.72)
Coe-Soft	0	0.00	(0.0)	0.00	(0.0)
Coe-Soft	1	-17.93	(2.02)	-13.60	(3.50)
Coe-Soft	7	-47.83	(1.83)	-32.50	(3.18)
Coe-Soft	12	-52.23	(1.30)	-36.97	(2.25)
Coe-Soft	16	-54.40	(1.34)	-41.03	(2.32)
Coe-Soft	30	-55.90	(1.39)	-49.70	(2.40)
Flexacryl-Soft	0	0.00	(0.0)	0.00	(0.0)
Flexacryl-Soft	1	-8.07	(0.43)	-2.93	(0.74)
Flexacryl-Soft	7	-11.60	(0.57)	-4.73	(0.99)
Flexacryl-Soft	12	-11.97	(0.46)	-5.40	(0.79)
Flexacryl-Soft	16	-12.57	(0.50)	-5.80	(0.87)
Flexacryl-Soft	30	-8.77	(0.62)	-5.43	(1.07)
Lynal	0	0.00	(0.0)	0.00	(0.0)
Lynal	1	-6.00	(1.46)	-18.63	(2.53)
Lynal	7	-15.40	(2.14)	-30.60	(3.70)
Lynal	12	-17.63	(2.34)	-33.67	(4.06)
Lynal	16	-19.10	(2.43)	-35.73	(4.21)
Lynal	30	-21.50	(2.58)	-39.97	(4.47)
Tempo	0	0.00	(0.0)	0.00	(0.0)
Tempo	1	-33.87	(0.47)	-14.23	(0.81)
Tempo	7	-82.10	(1.92)	-62.67	(3.32)
Tempo	12	-89.67	(1.81)	-71.60	(3.13)
Tempo	16	-91.83	(1.66)	-77.03	(2.87)
Tempo	30	-92.37	(1.15)	-83.50	(2.00)

Note: The values are in mg/g; the values in parenthesis are standard deviation.

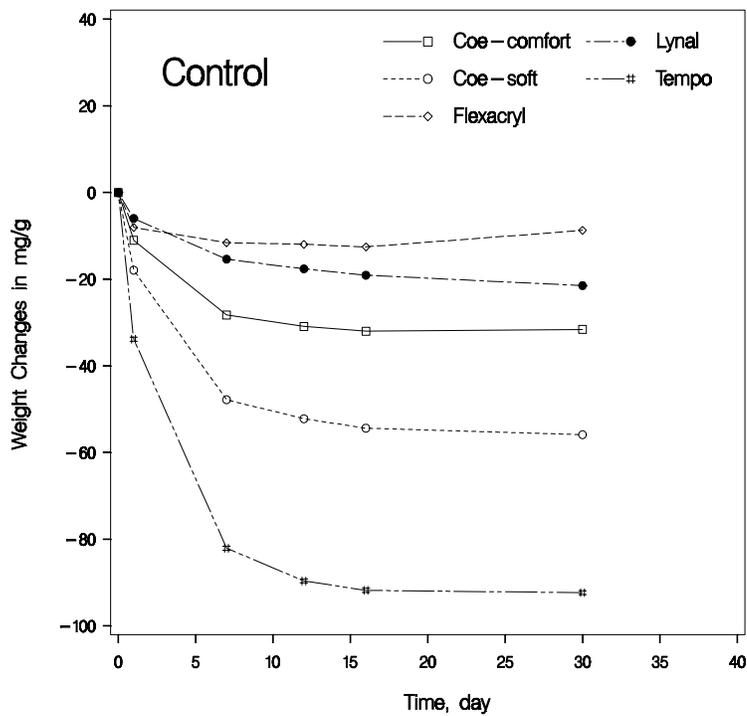


Figure 8. Weight loss with time for the control specimens

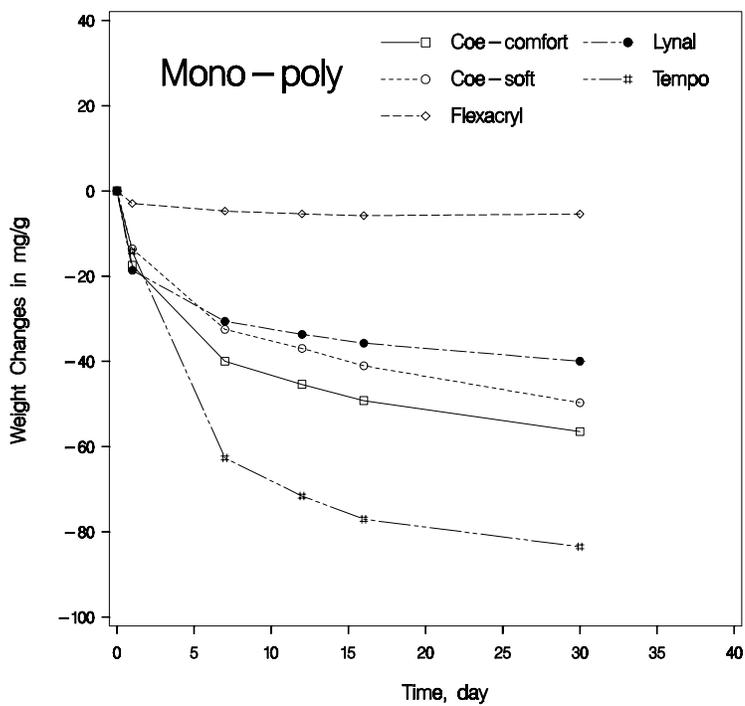


Figure 9. Weight loss with time for the mono-poly coated specimens

The results of Two-way Analysis of Variance show that both treatment and storage time have a statistically significant influence on the weight loss in water and in air. Table 16 shows the summary of Tukey's grouping of the treatment.

Table 16. Tukey's grouping of the effect of surface treatment on the weight change

Material	In water	In air
Coe-Comfort	J <u>M P C</u>	M C
Coe-Soft	J C P M	C M
Flexacryl-Soft	J P C M	<u>C M</u>
Lynal	J <u>C P</u> M	M C
Tempo	J P C M	C M

Note: C=Control; J=Jet Seal; M=Mono-poly; P=Pressure/heat. The groups are arranged from highest loss to highest gain  
The underline groups treatments that are not statistically different at  $\alpha=0.05$ .

### pH of the Solution

Each time the storage solution was replaced, part of the solution was tested for the pH. The pH values of the distilled control water, which did not contain any specimen, were consistently at  $5.5 \pm 0.1$  through out the entire experiment. Table 17 shows the mean pH values along with respective standard deviation at each water change for each treatment. The pH values for pressure and heat treated specimens were taken from the solution used for processing. The results of Two-way Analysis of Variance show that both storage time and treatment have exerted statistical significant influence on the pH values. The pH values decreased with time from as high as 6.5 and reached a plateau in the neighborhood of 4.0.

Table 17. pH values of storage solutions at the time of replacement

Materials	Time, day	Control		Pressure/heat		Mono-poly		Jet Seal	
Coe-Comfort	0	-	-	5.85	(0.08)	-	-	-	-
Coe-Comfort	2	5.58	(0.22)	5.24	(0.19)	5.56	(0.38)	5.27	(0.05)
Coe-Comfort	7	5.18	(0.06)	5.48	(0.19)	5.09	(0.07)	4.14	(0.02)
Coe-Comfort	14	5.70	(0.48)	5.74	(0.14)	4.80	(0.07)	4.30	(0.04)
Coe-Comfort	28	4.98	(0.24)	5.47	(0.12)	4.19	(0.06)	4.12	(0.04)
Coe-Comfort	42	4.72	(0.31)	4.68	(0.10)	4.16	(0.05)	4.12	(0.05)
Coe-Comfort	63	4.21	(0.13)	4.21	(0.05)	3.92	(0.03)	4.10	(0.04)
Coe-Comfort	84	4.03	(0.06)	4.13	(0.09)	4.07	(0.09)	4.05	(0.16)
Coe-Soft	0	-	-	6.18	(0.08)	-	-	-	-
Coe-Soft	2	6.16	(0.07)	5.89	(0.04)	5.32	(0.09)	5.37	(0.09)
Coe-Soft	7	5.93	(0.12)	5.80	(0.06)	5.54	(0.24)	4.93	(0.05)
Coe-Soft	14	5.87	(0.11)	5.71	(0.06)	5.22	(0.10)	4.41	(0.02)
Coe-Soft	28	5.24	(0.15)	5.29	(0.14)	4.21	(0.14)	4.14	(0.02)
Coe-Soft	42	4.96	(0.19)	4.82	(0.03)	4.19	(0.06)	4.01	(0.03)
Coe-Soft	63	4.24	(0.29)	4.32	(0.07)	3.93	(0.02)	3.96	(0.03)
Coe-Soft	84	4.00	(0.18)	4.27	(0.11)	4.01	(0.04)	4.11	(0.02)
Flexacryl-Soft	0	-	-	4.11	(0.02)	-	-	-	-
Flexacryl-Soft	2	3.80	(0.02)	3.88	(0.01)	5.27	(0.79)	4.05	(0.02)
Flexacryl-Soft	7	3.95	(0.01)	3.95	(0.05)	5.06	(0.14)	4.04	(0.02)
Flexacryl-Soft	14	3.98	(0.03)	4.41	(0.59)	4.70	(0.31)	4.00	(0.03)
Flexacryl-Soft	28	3.94	(0.04)	4.07	(0.11)	4.58	(0.08)	3.90	(0.03)
Flexacryl-Soft	42	4.13	(0.06)	4.09	(0.05)	4.41	(0.06)	3.92	(0.02)
Flexacryl-Soft	63	4.03	(0.04)	4.17	(0.08)	4.25	(0.04)	3.90	(0.02)
Flexacryl-Soft	84	4.16	(0.07)	4.19	(0.10)	4.24	(0.05)	3.94	(0.02)
Lynal	0	-	-	6.45	(0.11)	-	-	-	-
Lynal	2	6.34	(0.08)	6.00	(0.20)	5.28	(0.18)	4.40	(0.02)
Lynal	7	5.60	(0.11)	5.31	(0.09)	4.84	(0.14)	4.66	(0.19)
Lynal	14	5.36	(0.15)	5.66	(0.29)	4.47	(0.06)	4.11	(0.03)
Lynal	28	4.86	(0.05)	4.90	(0.05)	4.19	(0.04)	4.05	(0.01)
Lynal	42	4.75	(0.08)	4.84	(0.22)	4.20	(0.04)	4.03	(0.04)
Lynal	63	4.55	(0.09)	4.43	(0.09)	4.05	(0.04)	3.98	(0.03)
Lynal	84	4.40	(0.11)	4.45	(0.08)	4.10	(0.03)	3.96	(0.04)
Tempo	0	-	-	5.30	(0.10)	-	-	-	-
Tempo	2	5.26	(0.25)	4.94	(0.11)	4.24	(0.12)	4.69	(0.11)
Tempo	7	5.20	(0.15)	5.26	(0.45)	4.20	(0.05)	4.61	(0.04)
Tempo	14	5.04	(0.13)	5.67	(0.25)	4.20	(0.29)	4.32	(0.02)
Tempo	28	4.75	(0.14)	5.07	(0.21)	3.93	(0.04)	4.22	(0.07)
Tempo	42	4.50	(0.08)	4.63	(0.12)	3.96	(0.06)	4.13	(0.05)
Tempo	63	4.40	(0.04)	4.45	(0.11)	3.84	(0.03)	4.18	(0.06)
Tempo	84	4.55	(0.07)	4.67	(0.15)	3.91	(0.03)	4.18	(0.06)

Note: The values are means of six specimens; numbers in the parenthesis are the standard deviation. pH values of pressure/heat specimens at time=0 day were taken from the water in processing chamber.

Table 18. Tukey's grouping of the effect of surface treatment on the pH of storage solutions.

Material	Tukey's Grouping
Coe-Comfort	P C M J
Coe-Soft	P C M J
Flexacryl-Soft	M P C J
Lynal	P C M J
Tempo	<u>P</u> <u>A</u> <u>J</u> <u>M</u>

Note: C=Control; J=Jet Seal; M=Mono-poly; P=Pressure/heat. The groups are arranged in descending order from left to right. The underlines group treatments that are not statistically different at  $\alpha=0.05$ .

Two-way Analysis of Variance analysis of the pH of the water in the six Snap-Seal containers with the Lucite-ES squares and the control water indicated that there is no difference between them at  $\alpha=0.05$ .

#### Statistical Correlation between Parameters

To identify if there is any significant correlations between any two parameters measured in this study, we ran a series of linear regression between several pairs of parameter. Only the coefficients of determinations,  $r^2$ , will be shown. Table 19 shows the  $r^2$  values between the leachants measured by UV at low and high wavelength. It shows relative high correlations. Table 20 shows the results between weight loss by balance and leachant by UV at high wavelength.

Table 19. Coefficient of determination ( $r^2$ ) of linear regression between leaching by UV at high and low wavelength

Material	Control	Jet Seal	Mono-poly	Pressure/heat
Coe-Comfort	0.9796	0.9095	0.9281	0.9928
Coe-Soft	0.9960	0.9417	0.9780	0.9983
Flexacryl-Soft	0.9987	0.8912	0.8926	0.9970
Lynal	0.9814	0.9231	0.7826	0.8754
Tempo	0.6683	0.9945	0.7303	0.6429

Table 20. Coefficient of determination ( $r^2$ ) of linear regression between leaching at high wavelength and weight loss by balance

	Control	Jet Seal	Mono-poly	Pressure/heat
Coe-Comfort	0.5759	0.6690	0.8054	0.4825
Coe-Soft	0.5351	0.7186	0.7198	0.7026
Flexacryl-Soft	0.5749	0.8479	0.4846	0.4225
Lynal	0.6634	0.8303	0.0364	0.7592
Tempo	0.5541	0.8439	0.8589	0.5929

Tables 21 and 22 show the linear regression of weight loss by balance against modulus of elasticity and rate of recovery, respectively.

Table 21. Coefficient of determination of Linear regression between weight change in water vs. Modulus of Elasticity

	Control	Jet Seal	Mono-poly	Pressure/heat
Coe-Comfort	0.8091	0.4814	0.1519	0.3661
Coe-Soft	0.6911	0.4617	0.2755	0.72930
Flexacryl-Soft	0.2341	0.3751	0.0171	0.0220
Lynal	0.4622	0.0787	0.0143	0.0000
Tempo	0.6377	0.6700	0.0119	0.5755

Table 22. Coefficient of determination of linear regression between weight loss in water and rate of recovery

	Control	Jet Seal	Mono-poly	Pressure/heat
Coe-Comfort	0.3544	0.6178	0.5378	0.4833
Coe-Soft	0.4916	0.8489	0.5045	0.7240
Flexacryl-Soft	0.0108	0.1738	0.1505	0.0000
Lynal	0.4540	0.4606	0.0347	0.0000
Tempo	0.7444	0.9625	0.6663	0.9295

Tables 23 and 24 show the linear regression results of the leachant by UV at high wavelength against modulus of elasticity and rate of recovery, respectively.

Table 23. Coefficient of determination of linear regression between modulus of elasticity and leachant by UV absorbance at high wavelength

	Control	Jet Seal	Mono-poly	Pressure/heat
Coe-Comfort	0.5645	0.3566	0.1007	0.1771
Coe-Soft	0.7330	0.4253	0.0859	0.5931
Flexacryl-Soft	0.2698	0.3025	0.0177	0.3169
Lynal	0.3746	0.0526	0.0000	0.0000
Tempo	0.4836	0.6612	0.0000	0.3060

Table 24. Coefficient of determination of linear regression between rate of recovery and leachant by UV absorbance at high wavelength

	Control	Jet Seal	Mono-poly	Pressure/heat
Coe-Comfort	0.3466	0.5993	0.5957	0.1699
Coe-Soft	0.2956	0.6415	0.7870	0.4665
Flexacryl-Soft	0.0047	0.2904	0.0000	0.0000
Lynal	0.3309	0.4656	0.1189	0.0000
Tempo	0.3739	0.8535	0.6965	0.6779

Table 25 shows the linear regression results between modulus of elasticity and rate of recovery.

Table 25. Coefficient of determination of linear regression between modulus of elasticity and rate of recovery

	Control	Jet Seal	Mono-poly	Pressure/heat
Coe-Comfort	0.2499	0.2669	0.4984	0.1421
Coe-Soft	0.3549	0.4183	0.0000	0.5171
Flexacryl-Soft	0.0502	0.1067	0.0224	0.0000
Lynal	0.4066	0.2639	0.0000	0.0778
Tempo	0.4395	0.6289	0.0000	0.2851

### Macro Photography and Micro Photography

Both visual and optical microscope observations show that there are no detectable surface changes during storage for the control and pressure and heat treated specimens. In contrast, there were detectable surface changes for the mono-poly and Jet Seal coated specimens. At the end of the 2<sup>nd</sup> week, bubbling on the surface was observed on some of the mono-poly coated specimens, the most notable ones were with Lynal and followed by Coe-Soft and Tempo (Figure 10a and 10b). They were not obvious with Flexacryl-Soft and Coe-Comfort. Some specimens with Jet Seal coatings wrinkled as soon as 24 hours after water immersion; eventually all Jet Seal coated specimens exhibit various degree of wrinkling on the surface. Multiple superficial crack lines were evident on all Jet Seal coated specimens when observed under a light microscope. The frequency of

cracks varies from material to material. Figures 11 shows crack appearance of Lynal, Coe-Comfort, Coe-Soft, Tempo, and Flexacryl, respectively.

Figure 12 shows cross sections of selected coated specimens. The examination of the coating/soft liner interfaces in monopoly coated specimen showed that the blisters occurred at the interface between the coating and the bulk of the soft liner material. It is likely the result of water osmosis through the coating.

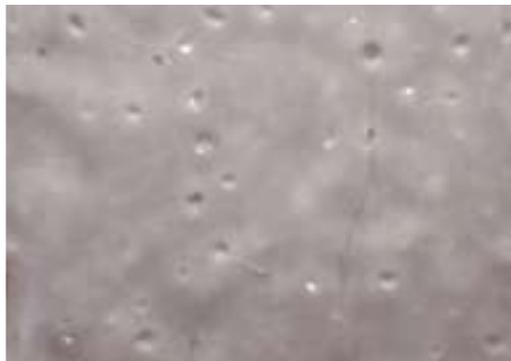
The thickness of either coating was measured using a stage microscope to be around 100 microns. Figure 12c shows the microscopic section of Coe-Soft with a crack visible in the Jet Seal coating but not extending into the tissue conditioner material. Contrary to our visual impression that the thickness of Jet Seal would be consistently thinner, it is within the same range as mono-poly. The observed homogenous thickness of the coating would support the use of dip coating when an even thickness is desired. Because of their similar thickness and even coating, these two factors could be eliminated as a cause for the different surface characteristics between the two coating materials. There is no apparent difference in the specimen appearance, such as population of voids.



a) Lynal specimen coated with mono-poly

b) Tempo specimen coated with mono-poly

Figure 10. Specimen coated with mono-poly



a) Lynal coated with Jet Seal at 6.6X



b) Coe-Comfort coated with Jet Seal at 3.3X



c) Coe-S coated with Jet Seal at 3.3X



d) Tempo coated with Jet Seal at 3.3X



e) Flexacryl-Soft coated with Jet Seal at 3.3X

Figure 11. Microscopic view of specimens coated with Jet Seal



a) Jet Seal coating on Tempo



b) Mono-poly coating on Tempo



c) Jet Seal coating on Coe-Soft



d) Mono-poly coating on Coe-Soft

Figure 12. Microscopic view of sections of Tempo and Coe-Soft samples

## CHAPTER 5 DISCUSSION

The hypothesis of this study is that coating with a surface sealer or curing in a heat and pressurized environment can maintain the physical and mechanical properties of the temporary soft liners at the same level when they are processed. Several papers<sup>20-24,28</sup> expect these additional steps to extend service life of these temporary soft relined materials in the clinical setting. The rationale is that surface treatment can prevent or retard leaching of plasticizer, which is incorporated in the material to render softness, and thus maintain resilience of the respective soft liners over a longer period of time. To test the hypothesis, we investigated three major categories of physical parameters: surface appearance, leaching by UV and weight loss, and dynamic mechanical properties.

### Effect of Surface Treatment on the Appearance of the Specimen

During the course of the study, we have not observed any detectable changes for the control and pressure/heat specimens, in spite of significant changes in the measurements of other parameters. It is believed that water will not normally alter surface texture of these temporary soft liners in static conditions. Specimens with coatings have exhibited several unique features; namely, ripple and crack on Jet Seal coated specimens and blistering on mono-poly coated specimens.

### Jet Seal Coating

As noted in the results, ripples on the surface of Jet Seal coated samples were observed as early as 24 hours after immersion, while surface cracks were not noticed until the examination was done with an optical microscope. Presence of rippling indicated some sort of swelling has occurred on the surface, possibly due to water absorption. The opaque whitish color exhibited by the coating instead of the initial transparency observed after drying also mitigated towards moisture absorption. We have observed in a separate study where Jet Seal was painted on glass slide covers that cracks developed as the coating dried in a few hours. The coating was fragile during our attempt to remove the film; a sign of brittle coating. Therefore, it is conceivable that the cracks could have occurred during the drying period of the Jet Seal coating. Mono-poly, on the other hand, did not crack and even exhibited slight ductility. Dynamic testing of the specimen could also have contributed to the crack formation. This is evidenced by the fact that specimens subjected to dynamic testing exhibited more cracks than specimens reserved exclusively for Shore A hardness tests. This kind of surface defect associated with Jet Seal could not be found in the specimens with the three other treatments. Further study needs to be conducted to shed light on the exact mechanism for water absorption and crack development in the Jet Seal coating.

### Mono-poly Coating

Mono-poly coated specimens were observed to blister after 2 weeks of water immersion. In contrast, none of the specimen coated with Jet Seal developed blisters. This is because the superficial cracks would allow free fluid exchange between the

internal and external compartments. In other words, the blisters, although unexpected, are an indication of the integrity of the coating. It was also observed through microscopic observation of a section through one of the blisters indicating that the blister formed at the interface between the coating and the material and not within the depth of the temporary soft denture liner. Systematic examination of each blister was not done because it is not within the aim of this study.

At the conclusion of the experiment, we were able to extract some liquid from inside of the blister with an 18-gauge syringe. The liquid is hydrophilic with consistency like water and has strong smell of methyl methacrylate. Dominguez *et al.*<sup>25</sup> concluded from their study that mono-poly coating allowed evaporation of alcohol but acted as a barrier to water and plasticizer. Should that be the case, because there is no water in temporary soft liners composition and the surrounding water could not penetrate through the coating, the liquid extracted from the blister should be hydrophobic since it could only contain plasticizer. Apparently, mono-poly in this study did not prevent water diffusion but allowed water osmosis through the coating; the blister is the result of water build-up. Presence of methyl methacrylate is from the mono-poly coating itself. Although of interest, it is beyond the scope and means of this project to determine the exact nature of the liquid accumulating in the blister. Further analysis of this liquid by High Performance Gas Chromatography should confirm these findings.

#### Accelerated Drying Using Heat

To minimize patient exposure to free monomer and chair time, accelerated drying of the mono-poly coating using a 50-60W incandescent light two inches from the coating for 4 to 5 minutes was recommended by Gardner and Parr<sup>21</sup>. Gronet *et al.*<sup>26</sup> reported no

nefarious side effect when this technique is used. We have observed that exposing the coated specimen as described has disfigured the specimens, especially to Coe-Comfort, Coe-Soft and Tempo. The specimens appeared to have swelled and the sharp edges rounded. Later, the specimen collapsed in the middle. It is hypothesized that the heat not only accelerates the evaporation of the monomer in the coating but also acts on the alcohol content of the specimen. Although the thickness of the coating may have retarded the initial escape of the alcohol but vaporization of the alcohol within the material may result in swelling, followed by collapse of the coating after the alcohol has time to escape. In addition, the high temperature may bring the tissue conditioner close to or beyond its glass phase transition temperature. That can result in softening of the tissue conditioner, as evidenced by the rounding of the edges. Both phenomena defeat the purpose of using tissue conditioner treatment to adapt a poorly fitting prosthesis to the mucosa surface. This drying method was not used in this study and should be avoided when the alcohol content of the temporary reline material is high and the glass transition temperature is low.

### Heat and Pressure Processing

Corwin and Saunders<sup>20</sup> recommended this technique for extending the useful life of temporary soft liners based on their observation of diminished surface porosity and internal voiding when processed with heat and pressure. The results of this study indicated that there is no improvement in surface quality after putting in the extra time for this procedure. Other parameters measured also indicate that there are limited changes between control and pressure/heat specimens. For example, the weight loss during immersion was almost identical for both control and pressure/heat specimens.

Processing temporary soft denture liners with pressure/heat needs further studies for validation.

#### Plasticizer Leaching, Weight Loss, and pH of Storage Medium

Temporary soft liners possess softness by the presence of alcohol and plasticizer. Both are reported to leach or evaporate with time. We selected two relative simple techniques to quantify the loss of these components to the surrounding environment. We used UV spectrophotometer to determine the leaching of plasticizer and weight loss of individual specimens in water and in air.

#### UV Spectrophotometry

The first samples tested in this experiment were pressure-treated, and aliquots of the liquid in which they were pressure treated were taken for UV spectrophotometry analysis at time zero. Peaks to be used for relative comparison of concentration were chosen from survey scans of samples from all the systems (Flexacryl-Soft, Coe-Soft, Coe-Comfort, Lynal, and Tempo). The peaks chosen for measurement were 272 nm and 221 nm for Flexacryl-Soft, 303 nm and 236 nm for Coe-Soft, 305 nm and 232 nm for Coe-Comfort, 280 nm and 225 nm for Lynal, and 223 nm for Tempo. The same wavelengths were used for all samples respectively, although another peak at 206 nm was detected and measured on some samples at a later date.

In an effort to construct calibration curves, the liquid components of the soft liner materials were diluted to 100 ppm in water. None of the liquid components of the soft liner materials were completely soluble in pure water; most simply formed beads of liquid within the water. Therefore, it was not possible to use pure water as a medium to

obtain reference curves to quantify the release of material from the cured specimens. It was proposed that the powder may act as a surfactant in combination with the liquid component, therefore liquid and powder components were mixed together in water to try to obtain absorbance calibration curves. The liquid did not dissolve completely even in the presence of powder, so calibration could not be performed in this manner either.

Some plasticizers used in Coe-Soft and Coe-Comfort such as benzyl benzoate, benzyl salicylate, and dibutyl phthalate were found by Jones *et al.*<sup>12</sup> to be soluble in ethyl alcohol. Ethyl alcohol has a useful transparent range from the visible into the ultraviolet range near 205 nm. The first liquid component tested, Coe-Soft, showed proportionality between the absorbance at 306 nm and the concentration of the liquid component in ethyl alcohol for concentrations from 100-300 ppm. The absorbance curves for the other liquid components also showed proportionality between the absorbance and the concentration of the liquid at the wavelengths chosen for measurements. A comparison of curves taken from liquid components dissolved in pure ethanol to curves taken from liquid components dissolved in mixtures of water and ethanol indicated that there is very little loss in absorbance peak value with the addition of water up to 50% v/v. The addition of water does reduce the absorbance of the ethyl alcohol itself, however, and serves to lessen the tendency of the ethyl alcohol to mask the lower wavelength absorbance of the liquid components.

Calibration curves were constructed from various concentrations of liquid components in 50% v/v water/ethanol. The mass of 50  $\mu$ l of liquid was measured by using a micropipette and a digital scale, and averages of at least five readings were taken using the same tip. Then, with the same tip used for measuring the mass, dilution was

made in a 100 ml volumetric flask by first adding 50 ml (by macropipette, 25 ml twice) of ethyl alcohol, then adding 50  $\mu$ l of the liquid component, and finally completing to the 100 ml mark with distilled water. This created a sample on the order of 1000 ppm depending upon the measured mass of the liquid. This 1000 ppm sample was then diluted to obtain other points on a calibration curve. All calibration points for each specimen are derived from the same parent dilution, so the relative accuracy is high but absolute accuracy is dependent upon the accuracy of the micropipette.

There was an odor evident in the water from those samples coated with Jet Seal, and survey spectrum scans of these samples showed an additional peak at 206 nm. Since Jet Seal contains a solution of polymethyl methacrylate (PMMA) in methyl methacrylate monomer (MMA), a survey spectrum scan of MMA in water was made which showed a comparable peak at 206 nm. Since the polymerization of MMA in Jet Seal is kept in check with an inhibitor, we also examined the spectrum of a common inhibitor, hydroquinone (HQ), in water. However, the spectrum of the Jet Seal coated samples matched that of MMA monomer and not that of HQ. It was concluded that the large peak at 206 nm that was superimposed upon the other soft liner spectra was from MMA and a calibration curve for MMA was constructed in water. Because this conclusion was reached a several weeks into the experiment, not all of the earlier Jet Seal coated samples were measured at 206 nm. To further test the hypothesis of MMA leaching from Jet Seal film coatings, release curves of plain Jet Seal and mono-poly films in water were obtained. These were tested for 74 days and showed continuing release of MMA.

Having determined the relationship between the absorbance value and the concentration of liquid components (ppm), the mass of released liquid components from

all samples was calculated. The assumption that only liquid components are able to leave the soft liner material is used here. The sample volume was consistently 50 ml, so this was also used in the calculation to determine the mass of material released with time.

#### Effect of Coating on the Plasticizer Leaching

According to Table 19, there is a high correlation between the plasticizer leaching measured at low and high wavelength. It confirms the belief that the two peaks should change proportionally. There is a difference in the effect of coating on the leaching at high and low wavelength. Using data from high wavelength, we found that both coatings reduced the leaching, except for Tempo. On the other hand, data from lower wavelength show that both coating has enhanced leaching significantly, except for Flexacryl-Soft with mono-poly. We know that MMA monomer has an UV peak around 206 nm, high extinct coefficient and the bandwidth can extend to 250 nm and higher with 20 ppm of MMA in solution. Therefore, the absorbance reading at wavelengths less than 250 nm can be confounded by MMA. This explains why there is leaching enhancement at lower wavelength. The abnormal behavior of Tempo at high wavelength, which was 223 nm, happened for the same reason. Consequently the leaching data gathered at high wavelength are more reliable. UV is not a suitable technique for Tempo. It is important to point out that Flexacryl-Soft by design does not contain plasticizers comparable to those in other materials tested; its results will be excluded from the discussion.

#### Effect of Coating on the Weight Loss by Balance

Table 16 shows that in contrast with the tendency of less weight loss in water for mono-poly coated specimens, Jet-Seal coated specimens suffered greater weight loss

than the uncoated specimens. Although this finding was totally unexpected, the observed wrinkles and cracks developed by the coating in Jet Seal coated specimens may have been the cause of the greater weight loss in time compared to uncoated specimens. These wrinkles and cracks could have resulted from the dimensional change of two sheets of material bonded together, e.g. imbibition of water by the Jet Seal coating and solvent evaporation from the tissue conditioner. This unbalanced area would induce tension in the superficial layer of the underlying substrate. It is known that substances under tension tend to release more leachants similar to hand wringing clothes after washing to remove as much water as possible. A less likely explanation would be that the cracks would have propagated into the substrate, therefore increasing the area available for molecular exchange. Cross sectional microscopic observation (Figure 12c) has eliminated this hypothesis. As greater weight loss of coated specimens vs. uncoated specimens has never been mentioned in the published literature, the reason for increased weight loss and therefore, accelerated leachants release by tissue conditioners when covered by a specific coating could only be the subject of speculation.

Table 16 also shows that mono-poly consistently reduce the weight loss in water. We concluded earlier that mono-poly coating slowed down the plasticizer leaching. It is likely that it also slowed down the weight loss in water. By the same token, we should expect the same situation for the weight loss in air. This, however, is not true with Coe-Comfort and Lynal. When we compare Figures 8 and 9, we also find that coated specimens continue to show weight loss after 30 days, while the control specimens have reached plateau after 16 days. A possible explanation is that some monomer from the coatings dissolved in the underlying temporary soft liner material instead of evaporating

into ambient air during the drying of the coating. It is also assumed that the temporary soft liner material has a higher monomer solubility than water. The continued weight loss would then be explained by the disappearance of monomer in the water, either by evaporation or after each water renewal, allowing monomer dissolved in the temporary soft liner to transfer to the surrounding water. In addition, the loss of monomer from coatings constituted part of initial weight loss, while the dry coating delayed the loss of alcohol from the bulk of the material. Both Coe-Comfort and Lynal contain lower alcohol content than Tempo and Coe-soft (Table 1); both materials also have lower weight loss in air (Table 15). Therefore, the increase in weight loss in Coe-Comfort and Lynal is due to the drying of the coating. It is likely that when eventually the alcohol in Tempo and Coe-Soft diffuses through the coating and evaporates, the coated specimen will show a greater weight loss.

Table 20 shows the correlation between weight loss in water and plasticizer leaching. The coefficient values are not as high as in Table 19 but show good correlation except a few incidents. Ideally, the weight loss measured by balance should equal the sum of weight loss in air and plasticizer leaching. That is not the case by Tables 11, 14 and 15. In fact, the weight loss in air alone is already greater than its respective weight loss in water. That is an indication that all specimens have absorbed significant amount of water in the process. Coe-Comfort has shown excessive plasticizer release compared to other materials tested; the amount even exceeds those of weight loss in water and approaching those in air. By the profile of leaching with time, one can conclude that the peak selected is relatively weak in the reference curve and may represent only noise background.

### pH of the Storage Solution

Although the pH of distilled water stored in normal environment can reach as low as 5.5, the consistent decrease of pH is surprising. For each material investigated, except Flexacryl-Soft, there are two distinct behaviors of pH changes with time. One group includes the control and pressure/heat; the other one includes both coated. Coated specimens generally exhibit lower pH values initially and continue to be lower with time. Flexacryl-Soft is the only exception that had a low pH without coating. It is necessary to point out that Flexacryl-Soft is the only material that contains methacrylate monomers, which is also the common component of the two coating materials. It seems that the presence of methacrylate monomer is the precursor to the low pH. It has been reported that acidic environment favor growth of *C. albicans*;<sup>38</sup> the effect of this reduction in pH induced by the presence of coating leachants requires further investigation

### Powder-to-liquid Ratio Influence on weight change

It is reasonable to assume that the more liquid contributing to the composition of a gel, the greater the potential quantity of available volatile components and leachants. The [powder to liquid ratio](#) (Table 3) of the materials used in this study is in descending order are Lynal (1.5), Coe-Soft (1.375), Coe-Comfort (1.2), Tempo and Flexacryl-Soft (1). The ranking of wet weight loss by balance in all treatment groups after 84 days (Table 14) are in ascending order of Flexacryl-Soft, Lynal, Coe-Comfort, Coe-Soft, and Tempo.

Flexacryl-Soft is the only material that undergoes polymerization when the liquid and powder components are mixed and would have less volatile ingredient to lose with

time. There is a correlation between the weight loss and powder:liquid ratio among the materials tested, except Flexacryl-Soft. For example, Lynal having the highest powder to liquid ratio also has the least of weight loss, while Tempo with the smallest powder to liquid ratio shows the largest weight loss. The pattern, however, does not exist between Coe-Comfort and Coe-Soft. Examination of Table 1 shows that there is more alcohol content in Coe-Soft , 14.8% vs. 6-8.2%. It should be noted that Tempo has the highest alcohol content, 25%, while Lynal is unknown. Since alcohol will eventually evaporate completely,<sup>12</sup> one can conclude that the weight loss should closely be related to the alcohol content of the mixture and powder liquid ratio.

No correlation could be found between leaching by UV spectrophotometry and powder to liquid ratio.

#### Leachants in Extruded Acrylic (Lucite-ES) Substrate

The data gathered by UV spectrophotometry indicated that there was no residual monomer leaching out from the Lucite-ES substrate. This is further supported by the absence of variation in pH values between the water used to store the substrate squares and the control water.

It is well known that the industrial extrusion process involves heating granules of the polymer from which the final material is made until it is homogeneously melted prior to the extrusion itself. Since this process does not use any chemical additive and the heat would vaporize any volatile component. If there had been any leachant, it would be safe to assume that it came from a process applied after the extrusion, leaving residues on the surface of the material itself. This was not the case.

Therefore, the use of Lucite as a substitute for heat cured methyl methacrylate in studies requiring the use of a chemically pure methacrylate denture base material to simulate clinical conditions is desirable. Plexiglas is another commercial name for this acrylic sheet.

### Mechanical Properties as Influenced by the Coating

Tissue conditioners, unlike permanent soft liners, should undergo viscous flow under load, in order to adapt to the changing contour of the supporting tissue and maintain a good adaptation of the denture base to the tissue. In describing how to extend service life of tissue conditioners, the published literature have used increased resilience value and Shore A hardness as the evidence. Either variable does not truly reflect the very quality needed for tissue conditioners; it is the ability to change contour under load. In this study, we examined not only Shore A hardness and modulus of elasticity which is related to resilience but also the viscoelastic behavior described by the rate of recovery.

### Hardness Evaluation by Shore A Durometer

The Shore A durometer is the oldest and best known instrument for testing the indentation hardness of rubber and elastomeric materials. Its equipment consists of two elements, a simple spring-loaded indenter or needle that is pressed into the elastomer and a dial indicator to measure the depth of penetration. This depth is calibrated to an arbitrary "A" or "D" number depending on the configuration of the indenter. The "A" tester uses a truncated needle point with a 822-gram mainspring; the "D" tester uses a needle with a relatively sharp point and a 10-lb mainspring (Figure 13).

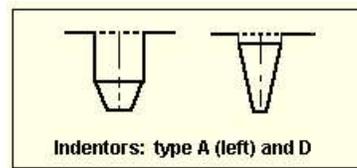


Figure 13. Shore Hardness indentors

All durometer indentors protrude with an extension of  $2.50 \pm 0.04$  mm ( $0.098 \pm 0.002$  in). Durometer hardness numbers, although arbitrary from 0 to 100 from soft to hard, have an inverse relationship to indentation by the indenter in thousandths of an inch. For example, a reading of 36 on Durometer A scale indicates an indenter indentation of 0.064 in. Similarly, a reading of 90 on a Neoprene faucet washer indicates an indenter indentation of 0.010 in. Figure 14 shows the relation of hardness number to the depth of indentation.

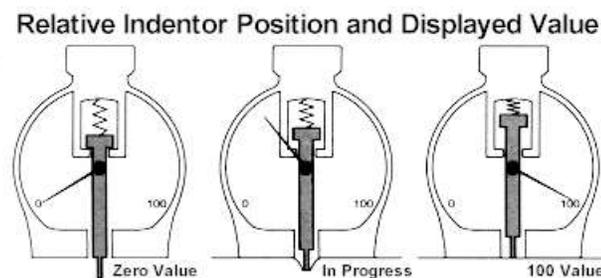


Figure 14. Shore A Durometer readings

The ASTM D2240, “Indentation Hardness of Rubber & Plastic by means of a Durometer” embodies an authoritative summary of recommended test procedures. The document specifies that the test specimens should have a minimum thickness of at least 6 mm (0.25 in.) unless it is known that identical results are obtained on thinner specimens. This requirement was not often followed or attended to in publications where this instrument was used. If the recommended thickness of tissue conditioner for lining a

hard denture base, which ranges from 1.5 to 3 mm,<sup>3,37</sup> is used, it is important that the thickness of the specimen should be reported along with the hardness values. In addition, because this thickness range does not fulfill the requirement of a minimum of 6 mm for hardness testing using the Shore A durometer according to ASTM standards, the values recorded are useable only when several layers of the same thickness of material stacked on to attain the 6 mm required would yield a similar value. Irregular or coarsely grained surface can interfere with the indenter penetration and give erroneous results. The temperature at which the test is made may have a significant effect on the readings; it is critical that readings should be recorded along with the test temperature if it is different from room temperature.

The Durometer reading should be taken within one second after firm contact between its flat bottom and the test specimen has been established. If the dial hand continues to recede on specimens exhibiting cold flow or creep characteristics, additional reading may be recorded after a specified time interval, say, 10 or 15 seconds. In our data collection procedures, we have noted that maximum Durometer readings varied according to the travel speed of the presser foot of the instrument as it was dropped on the material. The ASTM recommendation had anticipated this dependency and recommended a firm smooth downward action that will avoid shock. It further suggests using an operating stand that can control the rate of descent of the durometer to the test specimen. Such an instrument along with maximum reading capability will be ideal for testing temporary soft liner materials where there is a viscoelastic creep behavior. It is noted in section 5.1.1.8 of the ASTM that analog maximum indicating pointers have a nominal affect on the values attained. This effect is greater on Durometers of lesser total

mainspring loads, e.g., the effect of a maximum indicating pointer on Type D Durometer determinations would be less than those determinations achieved using a Type A Durometer. Therefore, a Digital Maximum Reading Durometer would be the instrument of choice for measuring tissue conditioner hardness.

The same document also cautions that readings less than 20 and above 90 are unreliable and should not be recorded. The majority of our readings are below 20, except those of Flexacryl-Soft and Lynal at 30 second. A review of the literature (Kawano *et al.*<sup>17</sup>, Yoeli *et al.*<sup>32</sup>, Andreopoulos *et al.*<sup>39</sup>, and Starcke *et al.*<sup>40</sup>) show that many studies having used this instrument for tissue conditioner hardness did not raise this issue.

Regardless of the statistical significant increase in Shore A hardness values with storage and surface treatment in [Table 7](#), the low values recorded, well below the ASTM recommended range of 20-90 for reliable readings, have rendered those values meaningless. Nonetheless, it is important to point out that specimens with mono-poly coating consistently exhibit the highest mean hardness values among all treatment, and those with pressure/heat treatment often rank second.

Surface examination of Shore A hardness specimen show that control and pressure/heat specimens usually exhibit distinct dents, which eventually recover with time while the dimples in the coated specimens will only recover partially. It is apparent that the Shore A indenter has penetrated through the surface coating. We can conclude that mono-poly alone contributes to the resistance near the superficial region but not in the bulk of the material. Jet Seal coating, although is relatively more brittle than mono-poly, does not provide the same degree of resistance and thus provides a lesser degree of hardness increase.

As observed in [Table 7](#), the mean hardness values of pressure/heat treated specimens often rank behind that of mono-poly. If the limitations of Shore A hardness test were disregarded, it can be asserted that additional surface treatment can effectively increase the resilience of the materials as measured by the Shore A hardness.

### Modulus of Elasticity

During the dynamic mechanical tests, the resistance of the material to the crosshead traveling toward the material to the mid-point of the dynamic test was recorded as load changes with distance of material displacement. The linear portion of the curve was taken to determine the modulus of the materials. In general, the elastic modulus was lower initially and increased with time up to two weeks. After this time, the values started to fluctuate around a median value, indicating that the changes have leveled off. The degree of change seemed to coincide with the weight loss measured by balance, which reached a plateau around two to four weeks after immersion. The one exception was the pressure/heat treated Lynal, which decreased to the initial level. The reason for this phenomenon is not known.

The effect of treatment on the elastic modulus is different from one material to another. The Jet Seal coated specimen often exhibited the highest weight loss elasticity mainly due to the loss of monomers from the coating. If we exclude the Jet Seal coated specimen, we would find that the ranking of the treatment for the weight loss and the elastic modulus are identical for Coe-Comfort, Coe-Soft and Lynal, and partial for Flexacryl-Soft. Tempo was the only one that shows opposite trend. One should expect to observe higher elastic modulus when more weight loss has occurred, presumably due to the loss of plasticizer. This information can only be obtained from [Tables 21](#) and [23](#).

Table 21 shows that the correlation between weight changes in water and modulus of elasticity are comparable to that between plasticizer leaching and modulus of elasticity (Table 23). Mono-poly group and Lynam group show the worst correlation, indicating any improvement of modulus of elasticity is not due to any leaching or weight loss. Even though our leaching data by UV absorbance indicated that the leaching of plasticizer from these temporary soft reline material were relatively low, which was only a few percent of the weight loss in water and in air, its role in the modulus of elasticity is the same as that of water loss. It is impossible to separate the two at this point. Dominguez *et al.*<sup>25</sup> have arrived at the same conclusion that there is no appreciable release of plasticizer in water. The significant changes with Flexacryl-Soft and those with coatings are mainly caused by the leaching of methacrylate monomers, which has the same boiling point as water. The weight loss of specimens stored in ambient air appeared to be greater than those stored in water. It signified that the majority of weight change is due to alcohol loss. The smaller weight change for specimens stored in water implied absorption of water by the specimens. In other words, total weight change resulted from the loss of alcohol and gain of water by absorption. Lesser weight loss of mono-poly coated specimens do not necessary mean more water absorption. It could be possible that those specimens contained less alcohol since each coated specimen have to be set aside for a while to allow drying of the coating in addition to the gelling period before coating, allowing more alcohol evaporation. This would have resulted in less alcohol at the initial base line. However, the standard total preparation time of 25 minutes before testing would have minimized this possibility. There is no doubt that the mono-poly coating retarded the ingress of water and thus provides higher elastic modulus

for the samples. Jet Seal coated specimen did not exhibit a similar behavior since there are cracks on those coatings.

### Rate of Recovery

The rate of recovery shows the degree of material recovery during cycling. If the material behaves elastically, the values as defined should be extremely high. On the other hand, if the material responds sluggishly to the cyclic loading, the value will be low. As in the result of elastic modulus, the rate of recovery generally is lower initially and increases with time up to two weeks. As the time progresses, the change becomes less significant or the values start to fluctuate. The degree of changes also coincides with the weight loss by balance, which reaches the plateau around two to four weeks after immersion. The most dramatic change belongs to the control of Lynam within the two days of immersion in water. The dependence on time corresponds to the exchanges of alcohol and water.

The mono-poly coated specimens registered the lowest rate of recovery for all materials except Lynam. However, if we eliminate the results of the first seven days, we would find the mono-poly coated groups with the lowest rate of recovery. The effect of Jet Seal on the rate of recovery is not as consistent. We concluded earlier that mono-poly yields higher elastic modulus because of less water absorption. The values of rate of recovery indicates that mono-poly coated specimen retained more viscous component, the sluggish behavior, than the other groups. Although we concluded that the leaching of plasticizer is insignificant in quantity, we also found that plasticizer leaching, determined by the high wavelength and in absolute quantity, from mono-poly coated specimens was

statistically significantly less than the other treatments. That small difference could contribute to the lower rate of recovery.

Tables 22 and 24 show that there is no correlation between modulus of elasticity and weight loss or plasticizer leaching for Flexacryl-Soft; this is consistent with the material properties. Lynam also exhibited the similar situation after pressure/heat treatment; it is not clear why. Both tables show that weight loss may have exhibited better correlation to rate of recovery than the plasticizer leaching, it is, however, not possible at this point to clarify that issue. It is likely that water absorption by the material has confounded our attempt to distinguish the effect of weight loss and plasticizer leaching. We may have to subject the specimens to dehydration process to reduce water content and measure the dynamic properties of the specimen in relation to the water remained in the specimen. Table 25 shows the correlation between and rate of recovery and modulus of elasticity. We learned from Table 10 that treatments have opposite effect to the rate of recovery and modulus of elasticity. It means that an increase in modulus of elasticity may be accompanied by a lower rate of recovery, such as in the case of Coe-Soft, Flexacryl-Soft and Lynam. However, when we compare the correlation between the modulus of elasticity and the rate of recovery, we find they all have positive slopes (not shown in the table) except those with zero coefficients of determinant. It suggests that one particular treatment may have opposite effects on the change of modulus of elasticity and rate of recovery, nonetheless, the relationship between the two physical parameters still maintains a positive relationship.

## CHAPTER 6 SUMMARY AND CONCLUSIONS

The objective of either coating or pressure/heat treatment is to render a surface different from the one generally formed on the temporary soft reline material if the manufacturer's instructions alone were followed. This improved surface is expected to help in maintaining or improving the properties of the bulk reline material; it is inferred that the service life of the underlying liner can be extended. We examined the effect of four treatment regimens on the surface appearance and six well-defined physical parameters of temporary soft reline materials. The results show that majority of changes occurred during the first two weeks, and different surface treatments can have different degree of effect on the physical and mechanical properties of each material. Flexacryl-Soft, which is normally used as a tissue conditioner, is in a class by itself; the effect of treatment on this material is often different relative to the other four materials. .

We found that, in terms of surface appearance, there was no clear overall advantage of additional surface treatment with time. Coating did provide glossy appearance but it can deteriorate due to swelling of mono-poly or cracking of Jet Seal. There is no apparent advantage to heat and pressure processing compared to preparation according to the manufacturer's instructions alone.

Although Shore A hardness value has been used to infer resilience of soft reline materials, their use to describe resilience of temporary soft reline material needs further qualification. Definite reading from the dial at prescribed time is difficult due to the

viscoelastic behavior of these materials. Readings less than 20 are not considered reliable by the industry standard, therefore only Flexacryl-Soft and some Lynal groups readings would be considered reliable. Our selection of 30 seconds for the first reading is unduly long but that was the only way to record values with reasonable reliability using the instrumentation available to us. In order to make this parameter meaningful, Shore A hardness values reported in dental literature should include the configuration of the specimen, such as thickness and substrate, and exact time duration of recording. If possible, a Digital Maximum Reading Durometer should be used.

Weight changes using a precise balance is simple and direct but cannot differentiate sources of changes, which can be from alcohol evaporation, plasticizer leaching and water absorption. UV spectrophotometer can determine quantity organic compounds leaching if precise reference curves are available, but it would not identify the exact compound by chemical makeup. The deficiency of this instrument is that a compound, which is not in the original references and part of its bandwidth covers the peak used for detection, the leaching can be overestimated. To identify potential contaminants, one will have to use high performance liquid chromatography. Despite that deficiency, we managed to obtain reasonable plasticizer leaching data. To examine the effect of water absorption on the mechanical properties will require a separate study.

Our study has confirmed that mono-poly could serve as a barrier to plasticizer leaching and weight loss, as shown by [Tables 12 and 14](#), respectively. However, it did not totally inhibit the process, it just slowed down the process. [Figures 8 and 9](#) clearly depict that phenomenon in air. Its influence on the mechanical properties, however, is not as clear-cut. One should keep in mind that retention of plasticizer or absorption of

water should render the bulk material more viscoelastic, which means lower modulus of elasticity and lower rate of recovery. This is not true for all occasions. The logical explanation is that the rigidity the mono-poly coating itself might have contributed to the increase of modulus of elasticity. As mentioned earlier, each discipline defined resilience differently. According to material science textbooks, it is one half the product of the modulus of elasticity and proportional limit, which was used in the literature that showed improvement of resilience due to coating. Very often the increase in value is due to increase in modulus of elasticity, which means the material has become more rigid. From prosthodontist's point of view, resilience implies softness and easy to adjust. By that definition, increase in modulus of elasticity will reduce resilience of the materials. Our experiment indicated that the rate of recovery for coated specimen is actually lower than control over time, which means more viscoelastic behavior has been retained by the coating.

Jet Seal has a significant effect in increasing the weight loss of all the above materials compared to the control. Jet Seal did not retard weight loss as in mono-poly due to cracks in the coating. The increase in weight loss can be attributed to the loss of monomer and the stress induced by the coating. More research is needed as to the effectiveness of Jet Seal in slowing down aging of tissue conditioners.

Coatings based on methyl methacrylate monomer lowered the pH of the storage medium with time. Flexacryl, which uses the same monomers, also induced lower pH to its storage medium. We concluded that methyl methacrylate monomer is the cause of lower pH, which still needs to be validated by a separate research.

Based on the result of this research, we can draw the following conclusions:

1. Pressure/heat process does not impart favorable appearance on the surface or retain the viscoelastic properties longer than the control groups.
2. Mono-poly coating renders a glossy appearance to the surface but also forms blister in time; the degree of severity of which differs among materials. It slows down the weight loss and plasticizer leaching which help the bulk of temporary soft reline loose its viscoelastic properties at a slower pace.
3. Jet Seal also yields an initial glossy appearance; the coating, however, cracks and is not capable of protecting as well as mono-poly can.

## APPENDIX

### POLYMERIZATION IN A METHACRYLATE PREPARATION WITH EXCESS MONOMER - MONO-POLY

#### **Abstract**

Purpose. Coating by a solution made of one part methyl methacrylate polymer in 10 parts of monomer was reported to have prolonged the service-life of soft liners. The purpose of this study is to examine if the coating has resulted from polymerization of accompanying monomers since these reports did not address that issue.

Materials and Methods. From one heat-activated and one autopolymerizing resin kits, we prepared four solutions by matching each powder with either of the monomers. Two mL of solution was spread per glass slide and allowed to sit in ambient air. Six slides were prepared per experiment. One extra set of heat-activated polymer in autopolymerizing monomer was exposed to 75W incandescent light for the first 20 minutes. The weight change was measured every minute for the first 20 minutes, and at the 24<sup>th</sup> and 48<sup>th</sup> hour.

Results. The results showed that greater than 99% of the original monomer had evaporated and the remainder constituted approximately 7.9 to 10.0 wt% of the final coating. Additional sets of slides of the same preparation were immersed in heated water (70 and 100°C) and pressurized to 30 psi for 15 minutes. The resultant coatings were placed in 25mL of acetone individually; complete dissolution of the coatings indicated no cross-linked resin, therefore no polymerization occurred. Only those immersed in 100°C water showed signs of polymerization. The remaining samples did not polymerize, indicating that they were residues of PMMA polymer after monomer evaporation.

Conclusion. Clinically, in the absence of polymerization, the effectiveness of the mono-poly coating will depend on the polymer used to make the solution. The substantial amount of monomer released could pose a health hazard for some patients.

**Index words.** methacrylate chemistry, sealer

## Introduction

Gardner and Parr<sup>21</sup> first suggested that the longevity of temporary soft liner could be extended by using a coating to render a smooth surface, and seal its porous surface. The coating material, mono-poly, was prepared by dissolving one part of heat-activated clear polymethyl methacrylate (PMMA) powder to 10 parts of autopolymerizing orthodontic methyl methacrylate monomers (MMA). The authors stated that after applying it with a brush, the mono-poly sealer should be allowed to dry for 4 to 5 minutes while held approximately 2 inches away from a 50- or 60-watt lamp. This process should be repeated two more times.

Casey and Scheer<sup>24</sup> showed by SEM micrographs that a temporary soft liner glazed with a mono-poly coat retained the original glass-like appearance, even after it had been worn by a patient for 30 days. The uncoated specimen given the same conditions had severely degraded, evidenced by the exposure of subsurface air bubbles incorporated during mixing. Casey & Sheer validated the smooth surface that Gardner and Parr<sup>21</sup> had predicted but did not indicate if the coating improved the longevity of the soft liners. Dominguez *et al.*<sup>25</sup> reported that mono-poly coating reduced water absorption and plasticizer loss from temporary soft liners immersed in water over a one-month period. They deduced that mono-poly coating acted as a barrier in preventing water absorption and loss of plasticizer. Gronet *et al.*<sup>24,26</sup> concluded that sealing the surface of temporary soft liners might have enhanced the life of these liners and extended their period of resilience. Aslan and Avci<sup>23</sup> found that autopolymerizing acrylic resin samples coated with mono-poly harbored fewer *E. coli* than uncoated samples after vigorous washing. Although it is known that a smooth surface can reduce fungal and bacterial growth that is often responsible for discoloration and eventual breakdown of the surface, they also speculated that the presence of MMA monomers might have inhibited the growth of *E. coli*.

The liquid component of an autopolymerizing acrylic resin consists of MMA monomer, a cross linking agent (such as ethylene glycol dimethacrylate), an inhibitor (such as hydroquinone), and activator (such as dimethyl-*p*-toluidine). The powder component has PMMA beads and benzoyl peroxide (initiator).<sup>41,43</sup> When an appropriate ratio of powder and liquid is mixed, polymerization occurs. The polymerization of monomers containing copolymers such as ethylene glycol dimethacrylate should yield an insoluble network, an evidence of crosslinking.<sup>44,45</sup> Although several authors<sup>21,25,26</sup> described mono-poly as semi-set mixture, they did not clarify if the ratio of ten parts liquid to one part powder used in mono-poly would result in polymerization. Very often prostheses made of autopolymerizing resins are immediately placed in a heated and pressurized vessel to increase the degree of polymerization and reduce porosity.<sup>46</sup> This is intended to improve the mechanical properties of the autopolymerizing resin although it is unsubstantiated in the literature.<sup>47</sup> Therefore, it is unknown whether heat and pressure would have any effect on mono-poly.

Dental acrylic resins are packaged as heat-activated and autopolymerizing depending on the designated activators. There are four possible ways to combine the powder and liquid found in one heat-activated and one autopolymerizing package. The reason for the selection of heat-activated polymer beads mixed with autopolymerizing monomer has not been fully explained. The purpose of this study is to test the hypothesis that polymerization will occur in any of the four combinations of mono-poly in ambient air or under an incandescent light. Also tested is the hypothesis that heating in a pressurized chamber will enhance the degree of polymerization.

## Material and methods

### *Preparation of mono-poly*

Lang Orthodontic autopolymerizing resin (Lang Dental Manufacturer, Wheeling, IL) and Hygienic Clear heat-activated denture resin (Hygenic Corp., Akron, OH) were used to prepare the following four mono-poly combinations: (1) heat-activated PMMA powder and autopolymerizing MMA liquid; (2) both heat-activated PMMA powder and MMA liquid, (3) both autopolymerizing PMMA powder and MMA liquid, and (4) autopolymerizing PMMA powder and heat-activated MMA liquid. We weighed approximately 15 grams of liquid in an empty 25-mL conical flask and 1.5 grams of corresponding powder separately on a weighing paper. A magnetic stirrer was placed inside the flask, which was then capped with a rubber stopper to prevent evaporation. The monomer flask was placed in a preheated water bath at 55°C by a stirring hot plate with the stirrer turned on. After two minutes, the powder was added while the

monomer was stirred. It took 5 to 10 minutes for the initial cloudy mixture to become clear. The flask was left on the stirring hot plate for a total of 15 minutes to assure complete dissolution.

#### *Preparation of solidified coating*

Two mL of the prepared mono-poly from each batch was spread widely on a pre-weighed 75 x 50 x 1 mm glass slide. A computer controlled balance with precision of  $\pm 0.001$ g (Model XL-410, Denver Instruments Co., Arvada, CO) was used to record the weight changes in ambient air at room temperature ( $22 \pm 1^\circ\text{C}$ ) for 20 minutes in real-time. The same slide was again weighed after 24 and 48 hours. The process was repeated six times for all four solutions prepared. Weight decrease for six additional slides coated with heat-activated polymer/autopolymerizing monomer placed at approximately 2 inch under a 75W lamp were recorded in the same time frame. The initial weight of the fresh mono-poly,  $W_i$ , was divided by 11 to obtain the original polymer weight,  $W_p$ . The difference between  $W_f$  and  $W_p$  is the contribution of monomer to the final weight, regardless of whether the monomer has polymerized or not.

$$\text{wt\% of monomer contribution} = \frac{W_f - W_p}{W_f} \times 100\% \quad (1)$$

The solid film on the glass slide was removed with a razor scraper for the polymerization test.

To test the effect of temperature on the final coating obtained after 48 hours in ambient air, the entire test described in the last paragraph was repeated without recording the weight changes with time. The films obtained were placed in  $100^\circ\text{C}$  water and pressurized to 30 psi for 15 minutes. The films were recovered, dried and stored for the polymerization tests.

To test the effect of temperature and pressure on the coating, 2 mL of mono-poly was layered between a Mylar<sup>®</sup> sheet and a glass slide to keep the liquid content from prematurely dispersing in the subsequent process. Four such preparations were prepared from each mono-poly solution and immediately placed in a pressure pot preheated to  $70^\circ\text{C}$ . The lid was closed with the temperature control unchanged and pressure maintained at 30 psi for 15 minutes. The same experiment was repeated again at  $100^\circ\text{C}$ . The resulting film was removed, dried and stored for the polymerization test. Calculation of the wt% of monomer contribution to the final weight was not performed since complete recovery of resulting film was not possible.

#### *Polymerization test*

Since both monomer liquids used in this study contain a crosslinking agent, films that occurred as a result of polymerization that incorporated the cross linking agent are insoluble in acetone. Each film was placed in a 25-mL cylindrical flask filled with 25 mL of acetone. The film was completely immersed in the solvent and observed for sign of dissolution for one week. Shavings of set heat-activated and autopolymerizing acrylic resins, obtained from denture processing and provisional fabrication, were also included as controls.

## **Results**

The weight values recorded at the 24<sup>th</sup> hour and 48<sup>th</sup> hour were virtually the same; the readings from the 24<sup>th</sup> hour were used in the analysis. The degree of weight loss indicates that greater than 99wt% of monomer has evaporated in the process. Table A-1 shows the mean and standard deviation of weight percent of monomer retained in the final coating. One way analysis of variance of the data showed that mono-poly made of autopolymerizing polymer in autopolymerizing monomer showed the least amount of monomer retained, while the other three formulations retained higher percent of monomer and were not statistically different among themselves at  $\alpha=0.05$ . Figure A-1 shows the typical weight change profiles in ambient air and under 75W lamp. It is clear that mono-poly lost weight faster under a 75W lamp and reached a plateau in 15 minutes. In ambient air, the weight loss was slower but the final weight 24 and 48 hours later were approximately the same. Statistically there was no difference between the two processes in the wt% of monomer retained in the final coating (Table A-1). Table A-2 shows the results of solubility tests. Films that dissolved always exhibited dissolution within 15 minutes of immersion. Only films obtained from processing mono-poly liquids at  $100^\circ\text{C}$  and 30 psi pressure have shown signs of

crosslinking. Figure A-2A shows the films collected from the experiment conducted in ambient air; Figure A-2B shows the same films after immersion in acetone for 15 minutes. Figure A-3A shows the films collected from the experiment conducted in 100°C water bath and 30 psi; Figure A-3B shows the same films after immersion in acetone after 1 week. From the scaffold left behind after dissolution, heat-activated monomers produce a much higher degree of crosslinking than autopolymerizing monomers. Both controls, which are shavings left over from denture processing and provisional fabrication, exhibited solvent resistance in a similar fashion.

## Discussion

The results of the solubility test clearly indicate that there is no polymerization in any of the combinations at room temperature. Apparently, the coating obtained at room temperature was the result of monomer evaporation. Even mono-poly prepared from autopolymerizing polymer and autopolymerizing monomer would not polymerize. For polymerization to begin, free radicals must be present. Heat, light or chemicals are three means of converting initiators to free radicals.<sup>43,48</sup> However, to prevent free radicals in the air from causing accidental polymerization of the monomer during storage, a small amount of inhibitor is added to all commercial MMA liquids included in heat-activated or autopolymerizing acrylic resin kits. The presence of inhibitor requires the addition of enough initiator to consume all of the former with some excess for polymerization when the correct powder to liquid ratio is used. Generally, it is two parts powder to one part liquid by weight. This inhibitor to initiator ratio should also allow for a generous error margin. In mono-poly preparation this ratio is exceeded by 20 fold, which is beyond any reasonable margin. This quantity of inhibitor will undoubtedly consume all available initiator in the mixture as soon as it is activated. Even when subjected to a 100°C water bath, the air-dried coatings, which still consists of 8-10wt% of monomer did not show signs of polymerization. This is expected since after MMA evaporation, the inhibitor concentration becomes even greater, restricting the polymerization of any residual monomer that trapped between the PMMA molecules.

These results seems to indicate that polymerization does not occur in mono-poly in a clinically applicable time. However, our study also show that polymerization occurs when liquid mono-poly is subjected to 100°C water bath and 30 psi pressure. The natural assumption would be that heat, which is an activator and has been linked to accelerated polymerization, might have caused thermal initiation of the monomer. Although MMA exhibits thermal self-initiation at high temperature, its rate of initiation is about 0.14% per hour at 127°C.<sup>49</sup> At this initiation rate spontaneous polymerization of the MMA at 100°C is unlikely<sup>50</sup>. We had observed in our pilot tests that mono-poly contained in a sealed vial and heated to 100°C for 15 minutes remained liquid as long as the integrity of the vial was maintained. This observation reaffirms that spontaneous polymerization by heat without initiator is not attainable in a short period of time.

On the same set of tests, we also observed that mono-poly which had leaked from vials during heating and come into contact with water, polymerized. These results prompted us to conduct the tests in 70 and 100°C water bath and 30 psi. Apparently, the presence of 100°C water has provided needed radicals for polymerization. According to the Merck Index, hydroquinone is soluble in water at a ratio 1 to 14. It is possible that majority of inhibitor may have diffused to water as soon as mono-poly comes in contact with water, so that there is enough initiator to complete the polymerization. This is not the case since the same results were not observe in those tests carried out at 70°C water, considering that benzoyl peroxide decomposes around 60°C. Pressure (30psi) has no effect since the same solvent resistance was observed in films prepared without pressure. It was also observed that mono-poly mixed with ten times its volume of water did not show signs of polymerization at room temperature over a month. The results obtained at room temperature and 70°C water bath indicated that reduction of inhibitor in mono-poly alone would not be enough to facilitate polymerization. This suggests that there must be a substantial output of radicals in the presence of 100°C water, enough to neutralize inhibitors and allow polymerization to complete. To identify the exact source of these radicals is beyond the scope of this study and will not be discussed further.

The presence of the crosslinking agent in the monomer component renders the final polymerized product non-soluble in acetone. Although only a small amount is needed, a slightly higher quantity can yield a more crosslinked, less soluble network. Judging by Table A-1, which shows that when

polymerized, mono-poly made of heat-activated monomer yield a less soluble film that those made of autopolymerizing monomer. Our results imply that heat-activated monomer contains more crosslinking agent than autopolymerizing monomers, agreeing with findings by Arima *et al.*<sup>44</sup> and the product's material safety data sheet disclosure of copolymer content.

During the preparation of mono-poly solutions, we observed that heat-activated polymer beads takes more than ten minutes to dissolve in monomer, while autopolymerizing polymer beads will take less than ten minutes. The consistency also appears thicker with solution made of heat-activated polymer beads. This suggests that heat-activated polymer beads are made of higher molecular weight PMMA than the autopolymerizing one.<sup>44,45,51</sup>

In the absence of polymerization under clinical conditions, monomer serves only as a solvent and could be replaced by another convenient organic diluent that may be less hazardous to the patient.<sup>52-58</sup> The weight change recorded for air-dried samples agrees with the findings of Dominguez *et al.*<sup>25</sup> that there is a continuous weight loss of the coating up to 24 hours after application. Exposing the coating to an incandescent lamp can reduce the drying process to 15 minutes. If this lamp exposure has no adverse effect on the underlying material then it should be used routinely. Should a smooth, glossy surface be the only objective for mono-poly, then lack of polymerization is inconsequential. We have found in our preliminary tests that there was a wide distribution of data in the calculation of residual monomer when the solutions were prepared by volumetric measures. The age of solutions, from freshly made to a few weeks old, also affected the results. It is likely due to the high volatility of the monomer. For clinical purpose, maintaining the exact ratio may not be critical. There may be room for clinicians to adjust the proportion according to their needs. A study on the gloss of film coated tablets showed that increasing polymer concentration in the coating material resulted in significant decrease in gloss.<sup>48</sup> This implies that the ratio of polymer powder to monomer may be modified by the individual clinician to obtain the level of gloss they prefer. Since there is no polymerization of the coating material, abrasion resistance of the coating may possibly be dependent on the molecular weight of polymer beads used and the amount of residual monomer in the final coating. The ability of this coating to restrict plasticizer elements in tissue conditioner or soft liner from leaching requires further investigation.

## Conclusion

The results do not support that MMA in mono-poly will polymerize in a normal clinical situation. Even though water at 100°C induces polymerization in all four mono-poly solutions, the dispersion of liquid mono-poly coats at this temperature precludes its clinical use. Within the confines of the brands we have used, the final coating is a film of linear polymer with 8-10wt% of residual MMA monomer. There is no need to store the mono-poly solution in a refrigerator as long as the container is sealed tight to avoid evaporation of monomers. Should the mixture thicken up during storage, mixing additional liquid monomer will restore the original consistency. Placing a fresh coat of mono-poly under a light bulb would hasten MMA evaporation, therefore minimizing patient exposure. Mono-poly should be used in a well ventilated area. The absence of polymerization of mono-poly raises questions related to the mechanism of how the coating extends the longevity of tissue conditioners.

## References

References for this appendix are incorporated in the main list of references.

Table A-1 Weight percent of monomer contribution in the final coating after 24 hours.

Types of mono-poly formulation	Wt% (SD)	Tukey's grouping*
Heat-activated polymer and autopolymerizing monomer (ambient air)	10.0 (0.8)	A
Heat-activated polymer and heat-activated monomer (ambient air)	9.9 (1.1)	A
Autopolymerizing polymer and heat-activated monomer (ambient air)	9.4 (1.3)	A
Heat-activated polymer and autopolymerizing monomer (75W lamp)	9.4 (0.7)	A
Autopolymerizing polymer and autopolymerizing monomer (ambient air)	7.9 (0.4)	B

\* Grouping with the same letter means they are statistically the same at  $\alpha=0.05$ .

Table A-2 Solubility test of final coating obtained in various conditions

Types of mono-poly formulation	Ambient air with or without 75W lamp	Ambient air then heat & pressure	70°C and pressurized	100°C and pressurized
Heat-activated polymer/ autopolymerizing monomer	Dissolved	Dissolved	Dissolved	Partially soluble
Heat-activated polymer/ heat-activated monomer	Dissolved	Dissolved	Dissolved	Insoluble
Autopolymerizing polymer/ heat-activated monomer	Dissolved	Dissolved	Dissolved	Insoluble
Autopolymerizing polymer/ autopolymerizing monomer	Dissolved	Dissolved	Dissolved	Partially soluble

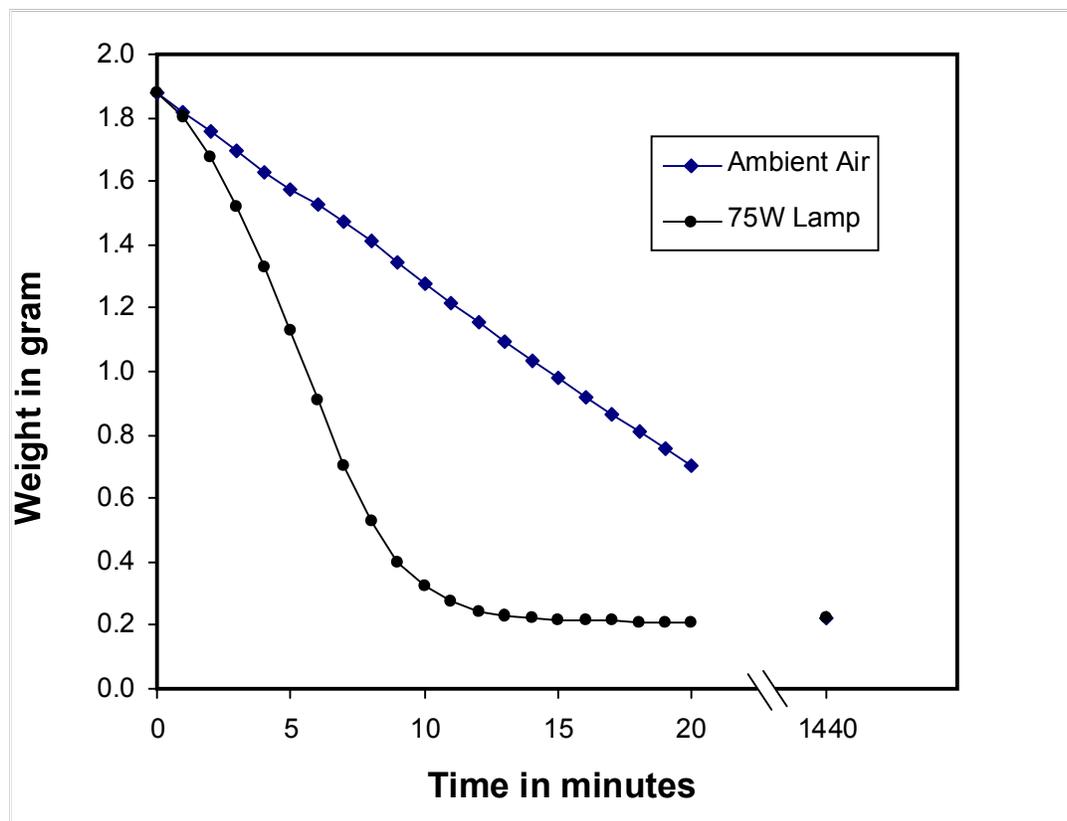


Figure A-1 Typical weight change profile for mono-poly solutions placed in ambient air and under a 75W lamp

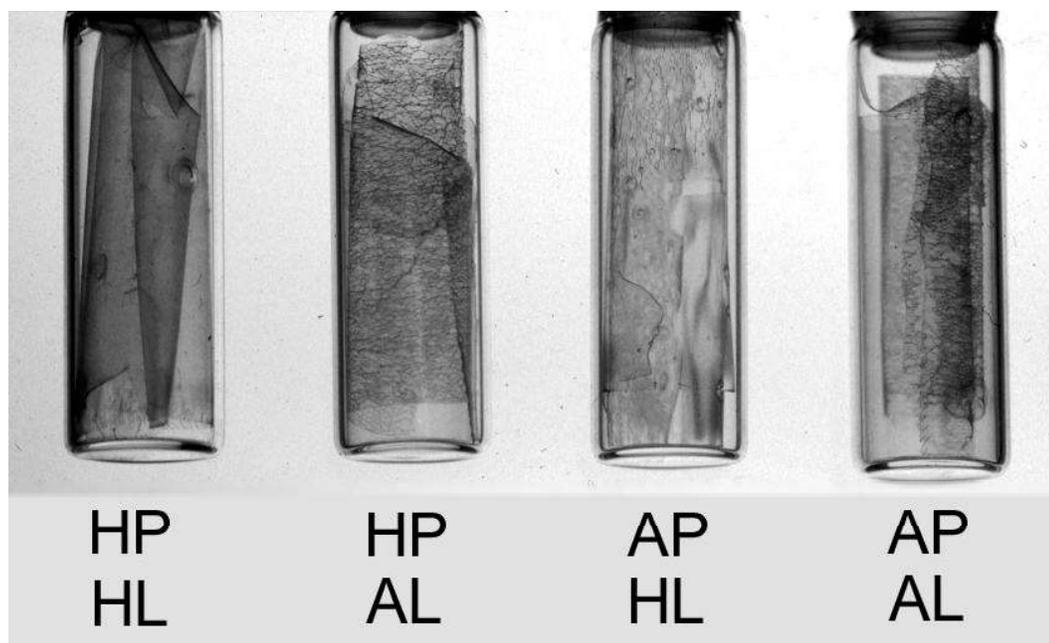


Figure A-2A Films harvested from mono-poly processed in ambient air.

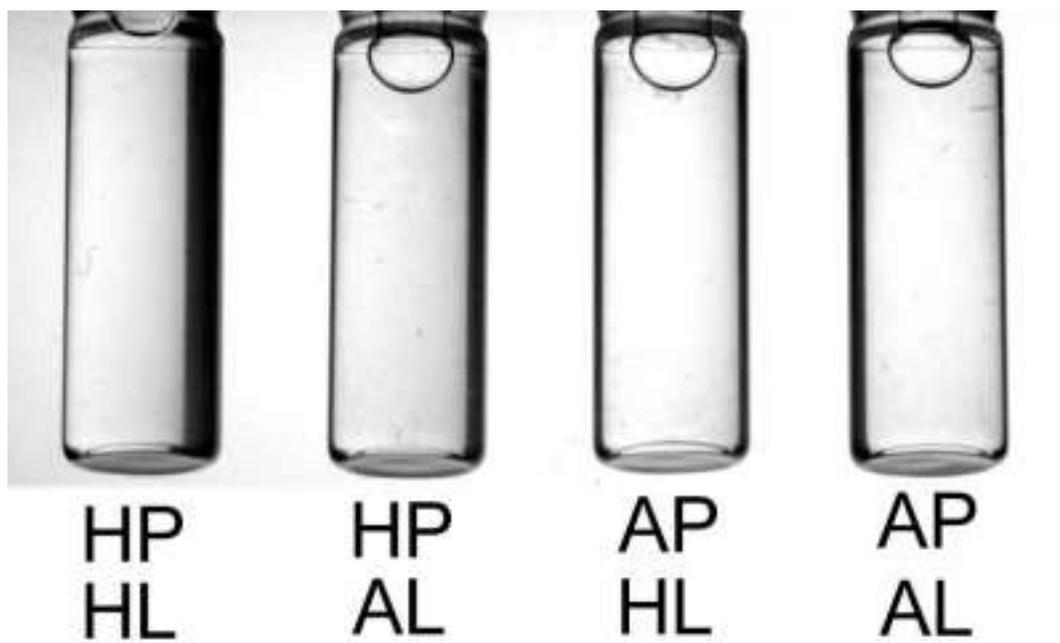


Figure A-2B The same film in A-2A after 15 minutes of immersion in acetone.

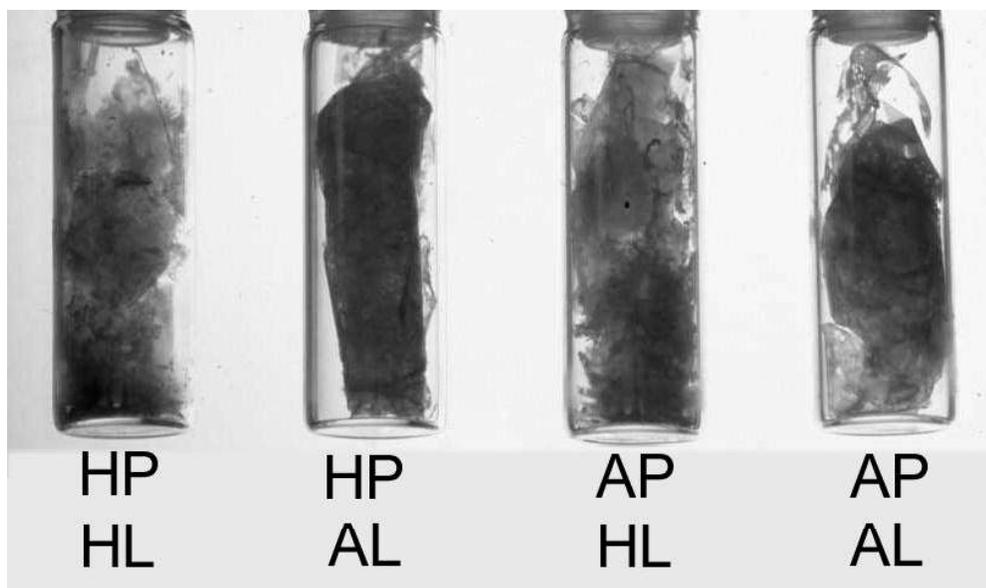


Figure A-3A Films harvested from mono-poly processing in 100°C water and 30 psi.

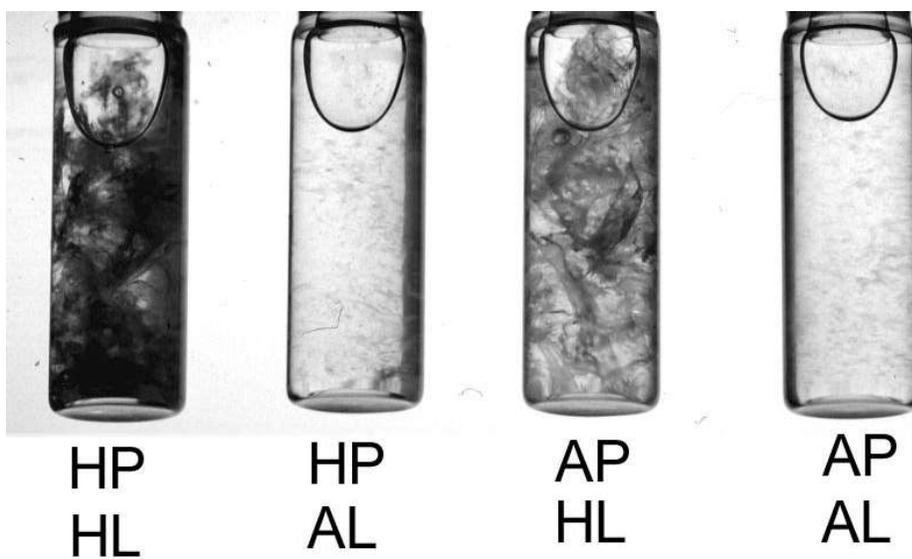


Figure A-3B Appearance of the same film in A-3A after one week of immersion in acetone.

## REFERENCES

1. Zarb GA. Improving the patient's denture-bearing areas and ridge relations, in: Zarb GA, Bolender CL, Gunnar CE (eds). *Boucher's Prosthodontic Treatment for Edentulous Patients*. Mosby Year-Book, Inc., St. Louis, MO,; 1997:88-108.
2. Bruce R. Conditioning of the mouth for dentures. *Dent Progress* 1963;3:262
3. Chase WW. Tissue conditioning using dynamic adaptive stress. *J Prosthet Dent* 1961;11:804
4. Cozza VJ. Resilient liners for dentures. *Tex Dent J* 1969;87:4-6.
5. Crum RJ, Loiselle RJ, Rooney-GE J. Clinical use of a resilient mandibular denture. *J Am Dent Assoc* 1971;83:1093-1096.
6. McCarthy JA, Moser JB. Tissue conditioners as functional impression materials. *J Oral Rehabil* 1978;5:357-364.
7. Marker VA, Shen C. Hydrocolloid impression materials, in: Anusavice KJ (ed). *Phillip's Science of Dental Materials*. W.B. Saunders Co., Philadelphia, PA; 1996, pp.111-137.
8. Braden M. Tissue conditioners I: Composition and structure. *J Dent Res* 1970;49:145-148.
9. Braden M. Tissue conditioners II: Rheologic properties. *J Dent Res* 1970;49:496-501.
10. Molnar EJ. Plastic impression compositions. US patent 3,558,540, Jan 26, 1971.
11. Wilson HJ, Tomlin HR, Osborne J. Tissue conditioners and functional impression materials. *Br Dent J* 1966;121:9-16.
12. Jones DW, Sutow EJ, Hall GC, Tobin WM, Graham BS. Dental soft polymers. plasticizer composition and leachability. *Dent Mater* 1988;4:1-7.
13. Braden M, Causton BE. Tissue conditioners III: Water immersion characteristics. *J Dent Res* 1971;50:1544-1547.
14. Ellis B, Lamb DJ, McDonald MP. A study of the composition and diffusion characteristics of a soft liner. *J Dent* 1979;7:133-140.

15. Graham BS, Jones DW, Sutow EJ. An in vivo and in vitro study of the loss of plasticizer from soft polymer-gel materials. *J Dent Res* 1991;70:870-873.
16. Jepson NJ, McCabe JF, Storer R. Age changes in the viscoelasticity of a temporary soft lining material. *J Dent* 1993;21:244-247.
17. Kawano F, Dootz ER, Koran A, Craig RG. Sorption and solubility of 12 soft denture liners. *J Prosthet Dent* 1994;72:393-398.
18. Braden M, Clarke RL. Viscoelastic properties of soft lining materials. *J Dent Res* 1972;51:1525-1528.
19. Wright PS. Composition and properties of soft lining materials for acrylic dentures. *J Dent* 1981;9:210-223.
20. Corwin JO, Saunders TR. Temporary soft liners - a modified curing technique to extend liner longevity. *J Prosthet Dent* 1992;68:714-715.
21. Gardner LK, Parr GR. Extending the longevity of temporary soft liners with a mono-poly coating. *J Prosthet Dent* 1988;59:71-72.
22. Nimmo A, Fong BJ, Hoover CI, Newbrun E. Vacuum treatment of tissue conditioners. *J Prosthet Dent* 1985;54:814-817.
23. Aslan Y, Avci M. Monopoly coating on acrylic resin surfaces: A bacteriologic study. *J Prosthet Dent* 1990;63:478-481.
24. Casey DM, Scheer EC. Surface treatment of a temporary soft liner for increased longevity. *J Prosthet Dent* 1993;69:318-324.
25. Dominguez NE, Thomas CJ, Gerzina TM. Tissue conditioners protected by a poly(methyl methacrylate) coating. *Int J Prosthodont* 1996;9:137-141.
26. Gronet PM, Driscoll CF, Hondrum SO. Resiliency of surface-sealed temporary soft denture liners. *J Prosthet Dent* 1997;77:370-374.
27. Anusavice, KJ. Mechanical properties of dental materials, in Anusavice KJ (ed). *Phillip's Science of Dental Materials*. W.B. Saunders Co., Philadelphia, PA; 1996, pp. 49-74.
28. Gronet PM, Driscoll CF, Hondrum SO. Resiliency of surface-sealed temporary soft denture liners. *J Prosthet Dent* 1997;77:370-374.
29. Jones DW, Hall GC, Sutow EJ, Langman MF, Robertson KN. Chemical and molecular weight analyses of prosthodontic soft polymers. *J Dent Res* 1991;70:874-879.

30. Qudah S, Harrison A, Huggett R. Soft lining materials in prosthetic dentistry: A review. *Int J Prosthodont* 1990;3:477-483.
31. Molnar E J. Antifungal resinous dental compositions and articles. US patent 3,476,854, Nov 4, 1969.
32. Yoeli Z, Miller V, Zeltser C. Consistency and softness of soft liners. *J Prosthet Dent* 1996;75:412-418.
33. McCarthy JA, Moser JB. Mechanical properties of tissue conditioners. Part I: Theoretical considerations, behavioral characteristics, and tensile properties. *J Prosthet Dent* 1978;40:89-97.
34. Lygre H, Solheim E, Gjerdet NR. Leaching from denture base materials *in vitro*. *Acta Odontol Scand* 1995;53:75-80.
35. Lygre H, Solheim E, Gjerdet NR, Berg E. Leaching of organic additives from dentures *in vivo*. *Acta Odontol Scand* 1993;51:45-51.
36. Ruyter IE, Oysaed H. Conversion in denture base polymers. *J Biomed Mater Res* 1982;16:741-754.
37. Schmidt-WF J, Smith DE. A six-year retrospective study of Molloplast-B-lined dentures. Part II: Liner serviceability. *J Prosthet Dent* 1983;50:459-465.
38. Nikawa H, Yamamoto T, Hayashi S, Nikawa Y, Hamada T. Growth and/or acid production of *Candida Albicans* on soft lining materials *in vitro*. *J Oral Rehabil* 1994;21:585-594.
39. Andreopoulos AG, Polyzois GL, Demetriou PP. Long-term behavior of soft liners in cleaning solutions. *QDT* 1993;27:132-135.
40. Starcke-EN, J, Marcroft KR, Fisher TE, Sweeney WT. Physical properties of tissue-conditioning materials as used in functional impressions. *J Prosthet Dent* 1972;27:111-119.
41. Phoenix RD. Denture base resins. Technical considerations and processing techniques, in: Anusavice KJ (ed). *Phillip's Science of Dental Materials*. W.B. Saunders Co., Philadelphia, PA, 1996, pp. 237-271.
42. Roulet JF. Polymer constructions used in Restorative dentistry, in: *Degradation of Dental Polymers.*, S. Karger AG, Basel, Switzerland, 1987, pp. 3-53.
43. Söderholm K-J. Chemistry of synthetic resins, in: Anusavice KJ (ed). *Phillip's Science of Dental Materials*. W.B. Saunders Co., Philadelphia, PA, 1996, pp.211-235.

44. Arima T, Murata H, Hamada T. Properties of highly cross-linked autopolymerizing reline acrylic resins. *J Prosthet Dent* 1995;73:55-59.
45. Shen C, Colaizzi FA, Birns B. Strength of denture repairs as influenced by surface treatment. *J Prosthet Dent* 1984;52:844-848.
46. Craig RG. *Restorative dental materials*, C.V. Mosby Co., St. Louis, MO; 1980.
47. Furnish GM, O'Toole TJ, von-Fraunhofer JA. The polymerization of acrylic resin orthodontic prostheses. *J Prosthet Dent* 1983;49:276-278.
48. Rowe RC. Gloss measurement on film coated tablets. *J Pharm Pharmacol* 1985;37:761-765.
49. Walling C. *Free Radicals in Solution*, Wiley, New York, NY, 1957.
50. Odian G. *Principles of Polymerization*, Wiley, New York, NY, 1981.
51. Dulik D, Bernier R, Brauer GM. Effect of diluent monomer on the physical properties of Bis-GMA-based composites. *J Dent Res* 1981;60:983-989.
52. Wesley RE, Brinsko JD. Toxicity of methyl methacrylate monomer in orbital and cranial surgery. *Ann Ophthalmol* 1992;24:307-309.
53. Bereznowski Z. Effect of methyl methacrylate on mitochondrial function and structure. *Int J Biochem* 1994;26:1119-1127.
54. Dahl OE, Garvik LJ, Lyberg T. Toxic effects of methyl methacrylate monomer on leukocytes and endothelial cells in vitro [published erratum appears in *Acta Orthop Scand* 1995 Aug;66(4):387]. *Acta Orthop Scand* 1994;65:147-153.
55. Clark BR, Brown JR, Matranga LF. Methylmethacrylate: Managing the toxicity. *J N J Dent Assoc.* 1993;64:25-29.
56. Shintani H, Tsuchiya T, Hata Y, Nakamura A. Solid phase extraction and HPLC analysis of toxic components eluted from methyl methacrylate dental materials. *J Anal Toxicol* 1993;17:73-78.
57. Giunta JL, Grauer I, Zablotzky N. Allergic contact stomatitis caused by acrylic resin. *J Prosthet Dent* 1979;42:188-190.
58. Weaver RE, Goebel WM. Reactions to acrylic resin dental prostheses. *J Prosthet Dent* 1980;43:138-142.

## BIOGRAPHICAL SKETCH

Anton The Hung Luu was born in Saigon, Vietnam, on January 19, 1957. He graduated from the Rosemont College in Montreal, Quebec, in 1977 and from the University of Montreal with a DMD in 1981. During his training in dentistry, he also received the Canadian Medical Research Council Scholarship commencing in 1978 and finishing in 1980. His dental education was followed up with a year of General Practice Residency concentrating on Oral Surgery at the Notre-Dame Hospital finishing in 1982. From 1982 to 1987, he was very active with two private practices as well as assuming one day of clinical assistant professor in the Oral Surgery Clinic of the University of Montreal. Burned out from the work overload, in 1987 he signed up for 3 months but stayed nine years, until 1996, serving the native population of the Hudson Bay peninsula which includes the Crees, Montagnais, Inuit, as well as the fishing communities along the Saint-Lawrence gulf under the auspices of the Quebec's Government Health Ministry. During this period, among other endeavors, he took and successfully passed the Florida Board of Dentistry exam to reassure himself of his proficiency in dentistry. In 1996, he pursued a specialization in Prosthodontics at the University of Florida, College of Dentistry, cumulating in the present study and document.

He hopes to pursue a more serene life and settle down after his training.