

Structure-property Relation of a Soft Liner Material Used in Denture Applications

Orhan Murat DOĞAN¹, Selda KESKİN², Arife DOĞAN³, Hande ATAMAN³ and Ali USANMAZ²

¹Department of Prosthodontics, Faculty of Dentistry, Cumhuriyet University, Sivas, Turkey

²Department of Chemistry, Middle East Technical University, Ankara, Turkey

³Department of Prosthodontics, Faculty of Dentistry, Gazi University, Ankara, Turkey

Corresponding author, Arife DOĞAN; E-mail: adogan@gazi.edu.tr, adogan1956@yahoo.com

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With a view to understanding the structure-property relation of a silicone-based soft lining denture material after polymerization, its chemical composition and viscoelastic properties were investigated. Chemical compositions of the cured and uncured polymers of a commercial silicone permanent soft liner were determined by infrared spectroscopic analysis, nuclear magnetic resonance (NMR), and X-ray photoelectron spectroscopy. Dynamic mechanical analysis (DMA) method was used to investigate the viscoelastic behavior of the cured polymer of liner.

Spectroscopic analysis showed that the main component of soft liner was vinyl-terminated poly(dimethylsiloxane), and the adhesive was 3-methacryloxypropyltrimethoxy silane. NMR results revealed that other components included benzoyl peroxide as initiator for polymerization and also silicic acid. Surface analysis by XPS provided interesting insights about the nature of adhesive bonding, as well as diffusion of silicic acid through the matrix of the processed material and leaching-out. DMA results showed a two-phase character, and that the cured polymer was highly elastic.

Keywords: Liner, Chemical composition, Viscoelasticity

INTRODUCTION

Soft liner materials are used for patients who are unable to tolerate a hard denture base because of advanced resorption of the residual alveolar ridge or due to the presence of a thin and relatively non-resilient mucosa¹⁻⁷. These materials are commonly proposed in instances whereby the clinician is dealing with fragile supporting tissue and where the patient's comfort is of primary importance⁸. Against this background, soft denture liners should be effective in evenly distributing functional stress on the residual ridge and absorbing energy during mastication to reduce transmission of that energy to the mucosa⁹. In this light, the efficacy of their use lies in their viscoelastic properties and durability for long-term use^{4,5}. Among the various methods used to determine the viscoelastic properties of soft denture liners⁴⁻¹³, dynamic mechanical analysis is claimed to be a powerful technique because it allows the determination of these properties as a function of temperature and loading frequency^{9,12}. The viscoelastic parameter of loss tangent ($\tan \delta$) is considered to reflect the cushioning effect required in clinical situations, and this parameter is also a sensitive indicator of crosslinking⁶.

Currently, most of the available commercial soft lining materials are made of silicone, methyl/ethyl methacrylate, polyphosphazine fluoroelastomer, or polyurethane^{4,8,14,15}. Silicones have properties such as excellent heat resistance, low toxicity, biocompatibility, high oxygen permeability, poor wettability, extremely low surface tension, low glass

transition temperature, resistance to radiation, special rheological properties, and outstanding electrical isolation¹⁶. All these properties are advantageous for their use as a soft lining material. However, a prominent problem with this type of material is its insufficient bonding to the PMMA denture base: as such, they are usually supplied with adhesives^{1,15}. In particular, if hydrophilic fillers and/or additives were used with this type of soft denture liners with a view to improving the viscoelastic properties for long-term clinical use, they may consequently lead to high water absorption and solubility of components. Therefore, to achieve safe use of silicone-based soft denture liners, there must be reliable adhesive bonding to the acrylic denture base.

In the present study, we sought to have a better understanding of silicone-based soft liner materials, and thereby the nature of adhesive bonding to acrylic denture base, by examining the composition of the raw material *versus* that of the processed product. Presently, even for a commercial product with the same brand name, its formulations differ among different manufacturers. One of the most commonly used silicone-based soft lining materials is Molloplast-B, which contains General Electric RTV 108 [96.2% (w/w)] as its main ingredient. It is a mixture of hydroxyl-terminated poly (dimethylsiloxane) (PDMS), fumed silica filler, methyltriacetoxysilane, and dibutyltin dilaurate. The other components are PMMA [2.56% (w/w)], silane 174 [1.22% (w/w)], and TiO₂ [0.01% (w/w)]^{1,15}. In this study, the chemical compositions of the uncured (raw

material) and cured (processed product) polymers were determined by FTIR, NMR, and XPS analyses. Dynamic mechanical properties were also measured.

MATERIALS AND METHODS

Specimen preparation

Materials used in this study were a heat-cured acrylic resin as the denture base material (Meliodent, Heraeus Kulzer Ltd., Newbury, Berkshire, UK) and a permanent soft liner which was a two-pot material with solid silicone-based polymer and an adhesive (Molloplast-B and Primo Detax, Ettlingen, Germany).

Chemical compositions of cured polymer, uncured polymer, and adhesive of the soft liner were evaluated by several spectroscopic techniques. For curing of specimens, the material was packed into a Teflon mold, pressed at 200 kg/cm² for 15 minutes, and then immersed in a boiling water bath (Kottermann Labortechnik GmbH, Hanigsen, Germany) for two hours.

FTIR analysis

A Bruker Vertex 70 Fourier Transform Infrared spectrometer (FTIR) (Bruker Optics Inc., Ettlingen, Germany) was used with a Pike MIRacle Attenuated Total Reflectance (ATR) accessory that contained a diamond crystal. FTIR spectrum of adhesive was taken by placing a few drops on potassium bromide (KBr) pellet. As for the ATR-FTIR spectra of both the cured and uncured polymers of soft lining material, they were obtained by placing the surfaces of peeled samples to be analyzed on the diamond crystal.

NMR analysis

Nuclear Magnetic Resonance (NMR) spectra were recorded with an instrument (Bruker DSX 400, Bruker BioSpin GmbH, Karlsruhe, Germany) operating at 400 MHz. A 20-mg sample was dissolved in 1 ml of deuterated dimethyl sulfoxide (DMSO-d₆) (Merck KGaA, Darmstadt, Germany), and tetramethylsilane was used as an internal standard for ¹H and ¹³C NMR study. ¹³C spectrum of the cured specimen, that was insoluble in deuterated dimethyl sulfoxide, was recorded with a Bruker 300 MHz wide bore NMR spectrometer (Bruker Avance™, Bruker Biospin GmbH, Karlsruhe, Germany) operating with a 4-mm Magic Angle Spinning (MAS) probe.

XPS analysis

To facilitate the peel test, soft liner-PMMA specimens were prepared according to ASTM D 903-98 (Standard test method for peel or stripping strength of adhesive bonds) in dimensions of 75 × 25 × 2 mm. Peel test was performed on a universal

testing machine (Lloyd LRX, Lloyd Instruments Ltd., Fareham, Hampshire, UK) at 180 ° peel. Following the peel test, XPS analysis of soft liner/adhesive interface/denture base resin material was performed.

By means of an X-ray Photoelectron Spectroscopy system (XPS) (Sage 150, Specs GmbH, Berlin, Germany) with a Mg/Al dual anode, the interface and surface properties of processed liner-resin composite were investigated. Unmono-chromatized Mg K radiation (1253.6 eV) was used, and the spectrometer was operated in constant analyzer energy (CAE) mode at a pressure of 10⁻⁸ to 10⁻⁹ mbar. Binding energies were referenced to carbon-carbon bond which was assigned a binding energy of 284.5 eV. Surface composition was determined using SpecsLab software.

DMA measurement

Rheological measurements of specimens were recorded with a Dynamic Mechanical Analyzer (DMA) (DMA 983, TA Instruments Ltd., West Sussex, UK) operated at a fixed frequency and a temperature scan from -200 to 400 °.

Test specimens for DMA were prepared according to ASTM D4065 (Standard Test Method for Plastics: Dynamic Mechanical Properties: Determination and Report of Procedures), which were rectangular bars of 50 × 10 × 4 mm dimensions.

RESULTS

Figure 1 shows the FTIR spectra of the cured and uncured polymers of soft liner. Peak assignments for the uncured polymer spectrum (Fig. 1b) were:

(C-H) in CH₃ at 2942 cm⁻¹, (C-H) in Si-CH₃ at 1260 cm⁻¹, _a(Si-O-Si) in Si-O-Si at 1091 cm⁻¹, _s(Si-O-Si) in Si-O-Si at 1023 cm⁻¹, and (C-H) in Si-CH₃ at 801 cm⁻¹. With the cured polymer (Fig. 1a), there was a shift in the peak positions and the peaks became broader. Spectrum of the cured polymer, recorded by ATR with very thin films of sample, was almost identical with that of uncured polymer.

Figure 2 shows the FTIR spectrum of adhesive. Peaks assigned were: C-H at 2942 cm⁻¹, =C-H at 2860 cm⁻¹, -C=O at 1745 cm⁻¹, CH₂=CH- at 1650 and 990 cm⁻¹, -CH₃ at 1350 and 862 cm⁻¹, Si-CH₃ at 1260 cm⁻¹, and C-O-C at 1100 cm⁻¹.

Figure 3 shows the ¹H NMR spectra of (a) adhesive, (b) uncured polymer, and (c) cured polymer of soft liner. Assigned peaks to the adhesive (Fig. 3a) were: -Si(CH₃) at 0.6, Si-CH₂- at 1.18, =C-CH₃ at 1.68-1.73, Si-CH₂-CH₂- at 1.88, -O-CH₂- at 3.5, Si-O-CH₃ at 3.7-4.0, =CH_a at 5.48, and =CH_b at 5.81-6.1 ppm. Assigned peaks to the uncured polymer (Fig. 3b) were: -Si(CH₃)₂ at 0, -O-CH=CH₂ at 1.3, DMSO at 2.42, O-CH=CH₂ at 3.4, and C₆H₅- at 7.4-7.8 ppm. Assigned peaks to the cured polymer

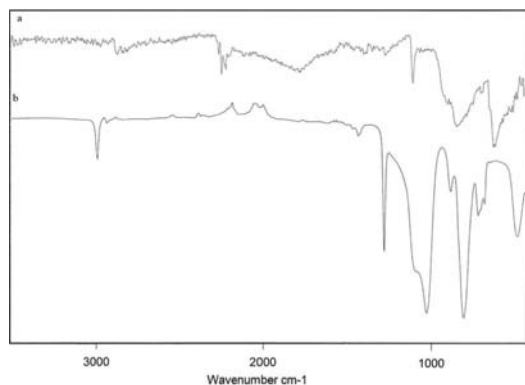


Fig. 1 FTIR spectra of: (a) cured polymer and (b) uncured polymer of soft lining material.

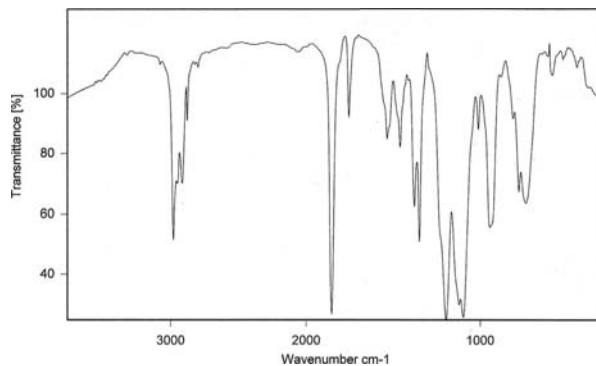


Fig. 2 FTIR spectrum of adhesive.

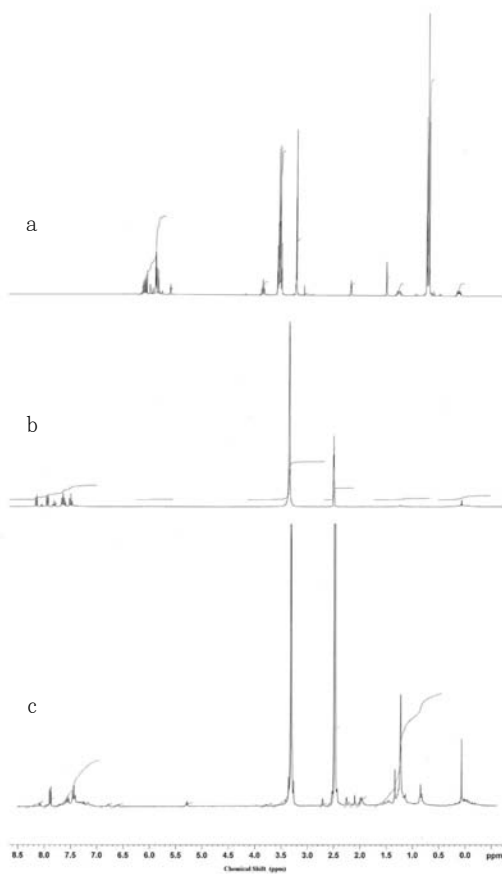


Fig. 3 ^1H NMR spectra of: (a) adhesive; (b) uncured polymer; and (c) cured polymer of soft liner.

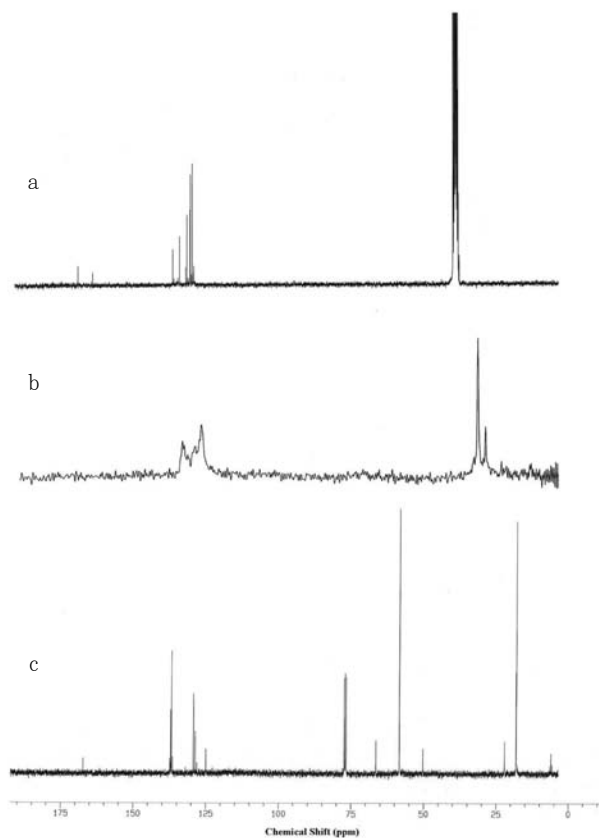


Fig. 4 ^{13}C NMR spectra of: (a) uncured polymer and (b) cured polymer of soft liner, and (c) adhesive.

(Fig. 3c) were: $\text{Si}(\text{CH}_3)_2$ at 0, $\text{Si}-\text{CH}_a-$ at 0.8, $\text{Si}-\text{C H}_b-$ at 1.2, DMSO at 2.42, $\text{C}_6\text{H}_5-\text{O}-\text{CH}_2-\text{CH}_2$ at 3.3, $\text{C}_6\text{H}_5-\text{O}-\text{CH}_2-\text{CH}_2$ at 5.4, and C_6H_5- at 7.4 - 7.8 ppm.

Figure 4 shows the ^{13}C NMR spectra of (a) uncured polymer, (b) cured polymer, and (c) adhesive of soft liner. Assigned peaks of uncured polymer (Fig. 4a) were: benzoyl peroxide at 40, 162, and 167,

and vinyl group at 128 - 135.6 ppm. Assigned peaks of cured polymer (Fig. 4b) were: $\text{Si}(\text{CH}_3)_2$ at 0, $\text{Si}-\text{CH}_2-$ at 29 - 31, and $\text{C}_6\text{H}_5-\text{O}-$ at 120 - 140 ppm. Assigned peaks of adhesive (Fig. 4c) were: $=\text{C}-\text{CH}_3$ at 6 and 18, $\text{Si}-\text{CH}_2-\text{CH}_2-$ at 22, $\text{Si}-\text{CH}_2-$ at 50, $\text{Si}-\text{CH}_2-\text{CH}_2-$ at 50, $-\text{CH}_2-\text{O}-$ at 66, $-\text{O}-\text{CH}_3$ at 77, $-\text{C}=\text{CH}_2-$ at 124, 129, and 137, and $-\text{C}=\text{O}$ at 167 ppm.

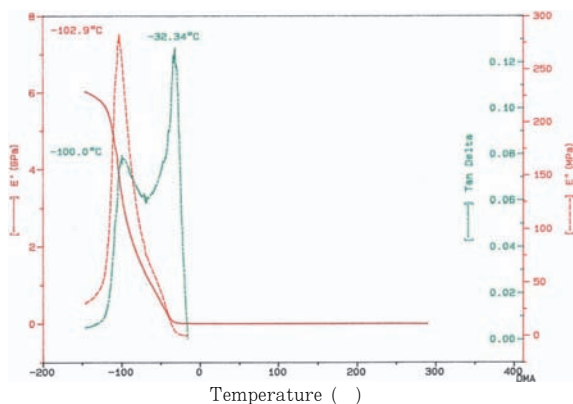


Fig. 5 DMA spectrum of soft liner polymer.

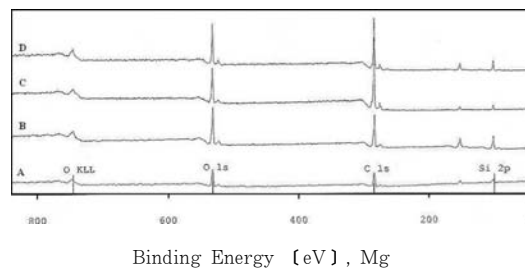


Fig. 6 XPS spectra for the surfaces of: (a) soft liner containing no adhesive; (b) soft liner peeled from PMMA resin; (c) PMMA resin containing no adhesive; and (d) PMMA resin peeled from soft liner.

Table 1 Quantitative values of C, O, and Si obtained from XPS analysis

Surface	%mol C	%mol O	%mol Si
Soft liner polymer containing no adhesive	60.2	25.4	14.4
Soft liner polymer after peeling	54.3	24.6	21.1
PMMA polymer containing no adhesive	76.6	17.5	5.9
PMMA polymer after peeling	67.0	20.6	12.4

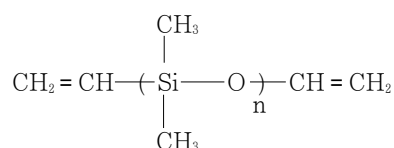
Figure 5 shows the DMA spectrum of soft liner polymer. relaxation (tan peak) corresponded to the T_g value of backbone chain, which was -32.3 . relaxation corresponded to the secondary glass temperature and was observed at -100.0 as a broader peak. Storage modulus (E') was 6.0 GPa. Loss modulus showed a sharp peak at -102.9 and a value of 270 MPa.

Figure 6 shows the XPS spectra of samples taken after the peel test: (a) soft liner containing no adhesive; (b) soft liner peeled from PMMA resin (containing adhesive); (c) PMMA resin containing no adhesive; and (d) PMMA resin peeled from soft liner (containing adhesive). Table 1 then shows the quantitative values of C, O, and Si on each of the abovementioned surfaces.

DISCUSSION

Chemical composition of a polymer-based soft liner was determined by several spectroscopic methods. FTIR analysis showed that the material was poly (dimethylsiloxane) (PDMS). It should be noted that although FTIR is a very effective method for identifying functional groups in a sample, it has limited resolution. As such, functional groups or impurities with concentration less than 5% cannot be observed accurately. Against this background, FTIR analysis has to be supplemented by other analysis methods and thus, NMR and XPS methods were also employed in this study.

^1H and ^{13}C NMR spectra are very effective means to analyze the end groups of a polymer chain and other compounds that cannot be observed by the FTIR method. In this study, NMR results showed that the main compound of polymer-based soft liner was PDMS prepolymer bearing vinyl end groups (as shown below) which was clearly observed from the ^1H and ^{13}C NMR spectra of uncured polymer and cured polymer, respectively:

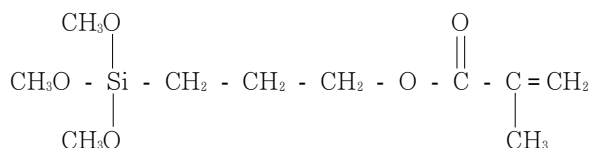


The other components were found to be benzoyl peroxide (initiator), silicic acid, and colorant. Decomposition of peroxides is temperature-dependent and may cause small molecules like CO_2 to be expelled¹⁷. When the material in the present study was cured at 100 for two hours, benzoyl peroxide decomposed into benzoyloxy radicals. These radicals then degraded, liberating carbon dioxide to give phenyl radicals which were conjugated to the vinyl groups at the end of PDMS chain to initiate further polymerization.

Some soft liners with the same commercial name are hydroxyl-terminated PDMS with alkyl tin as the initiator. On the other hand, in some commercial vinyl-terminated PDMS prepolymers, platinum

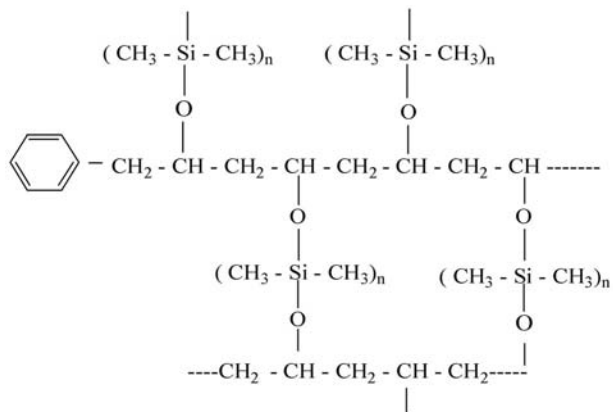
complexes are the initiators^{1,15}. Due to these differences in chemical composition, there may be considerable property differences in their clinical applications. During crosslinking or combination with the methacrylate, the vinyl groups of silicone will be added to the vinyl groups of methacrylate. However, if PDMS were terminated with a hydroxyl group, interesterification with methacrylates will occur. Differences in reaction type arising from differences in chemical composition will then influence thermal and mechanical properties.

As for the adhesive supplied with the soft liner material, FTIR analysis and ¹H and ¹³C NMR spectra showed that it was 3-methacryloxypropyltrimethoxy silane. It is also known as silane A-174 and used extensively in dentistry to increase the interfacial strength between fiber and resin¹⁸⁻²⁰. Its chemical formula is as follows:



The methacrylate end of the adhesive was bound chemically to PMMA resin (denture base material) while the silicone end with soft lining material. PMMA, which has a double bond terminated by disproportionation and other active centers, was compatible with the methacrylate end of the adhesive. As such, there would be both addition reaction through vinyl groups as well as physical forces between similar groups (methacrylates). On the other hand, Si groups from the silicone soft lining material reacted with the methoxy-Si groups from silane A-174¹. As a result, the adhesive was bonded strongly to the soft lining material.

Previously, the viscoelastic properties of silicone-based soft liner material (Molloplast B) were reported in the form of statistical evaluation of DMA results, but the spectra were not given^{4-6,9,10}. Therefore, direct comparison with the present data could not be made. In the DMA spectrum, and relaxations were observed on tan curve. The relaxation showed T_g of backbone chain, while relaxation showed the glass transition temperature of the second phase of PDMS. Therefore, vinyl group polymerization formed the backbone chain and PDMS prepolymer crosslinked this backbone. The sharp peak observed for loss modulus, E'' , then indicated the material's high elasticity. In summary, when the DMA results were combined with those of FTIR and NMR, the following network structure could be suggested for the soft lining material:



DMA results of this study were in good agreement with the results of previous studies, whereby silicone soft liners were found to be elastic^{4-6,9,10}. The viscoelastic properties of soft denture liners are important, since they characterize the ability of a material to exert a cushioning effect on the oral tissues and maintain shape during normal function¹¹. For Molloplast-B silicone soft liner, it was thus confirmed through the DMA results of the present study that it was suitable for long-term clinical use because of its elastic nature. This material could retain its shape and respond viscously to accommodate functional and nonfunctional forces. A small amount of elastic deformation thus served to allow adaptation to changes in the tissues underlying the dentures^{4,9}.

By means of XPS analysis, the surface composition results of C, O, and Si (in atomic mol percent) on different parts of processed materials yielded interesting insights. Typically, no Si should be observed on the side of PMMA resin with no adhesive. However, 5.9 mole% Si was observed. This could be due to the diffusion of silicic acid. Accordingly then, the mole ratios of Si on the surfaces of other parts of processed materials (Table 1) reflected the diffusion process. These results were subsequently confirmed by the manufacturer. Therefore, the XPS values of Si on peeled surfaces further indicated that the methacrylate end of adhesive was bonded to PMMA and the silicone end to soft liner film. In light of this finding, cohesive failure would be expected to be more prevalent than adhesive failure.

CONCLUSIONS

By means of FTIR and NMR analyses, it was revealed that the main component of a commercial product tested in this study was vinyl-terminated PDMS, and that benzoyl peroxide was the initiator. By means of dynamic mechanical analysis, it was

confirmed that the soft liner had elastic property. By means of XPS analysis after peeling test, it was suggested that cohesive failure might be the more prevalent mode of failure for the soft liner. Another interesting insight was the presence of silicic acid in the polymeric matrix of soft lining material, indicating that silicic acid had diffused through the PMMA denture base material and leached out.

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