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HARDNESS, ELASTIC MODULUS, WATER SOLUBILITY AND FOURIER TRANSFORMATION INFRARED (FTIR) OF THE MODIFIED SOFT LINER WITH TWO TYPES OF PLASTICIZERS

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Abstract. Background: denture liners are frequently used for various applications in prosthetic dentistry. **Purpose:** Evaluate the effect of two types of plasticizers on the hardness, elastic modulus and water solubility and to study the changes induced after the incorporation of the additives used in this study. **Methods**: Soft liner specimens made of acrylic were created by mixing two distinct concentrations of (2% and 5%) % wt of plasticizers glycerol and Di-2-ethylhexyl phthalate (DEHP) plasticizers. The surface hardness of the modified soft liner, the disk-shaped specimens of 30 mm in diameter and 3 mm in thickness were constructed for the shore (A) hardness test, with Dumbbell-shaped specimens and a central cross- sectional area of (25 × 4 × 2 mm) for elastic modulus and specimens were prepared for water solubility, with the dimension of (10 diameter x 5mm thickness). Fourier transformation infrared (FTIR) study was performed to assess potential chemical reactions between plasticizers and acrylic-based soft liners. Data were analyzed with one-way ANOVA and Duncan's multiple range test. **Results:** The surface hardness (shore A) of both experimental groups was lower than that of the control group in the modified resin, with the 2% DEHP group exhibiting the lowest elastic modulus values and no statistically significant difference in the amount of water solubility of the control group when compared to that of experimental groups at $p \leq 0.05$. No chemical reaction between the soft liner and plasticizers at varied concentrations was observed. **Conclusion**: The hardness and elastic modulus were decreased with plasticizers, no chemical interaction between soft lining material and plasticizers.

Keywords: *Soft liner, Plasticizers, Hardness, elastic modulus, FTIR.*

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1. Introduction

In prosthetic dentistry, denture liners are frequently used to modify the tissue surfaces of dentures that come into contact with the oral cavity (Kreve *et al*., 2019). The tissue side of the denture is resurfaced using denture relining. Soft denture liners have been used to make wearing dentures easier, particularly for patients with strongly resorbed alveolar ridges and sharp knife-edge residual ridges who have a low tolerance to masticatory pressures and complained of pain and stiffness when wearing dentures (Raval *et al*., 2017). The Liner materials are categorized as either hard usually made of poly methyl methacrylate or resilient when plasticizers are added to the resin and the silicone elastomers (Kreve *et al*., 2019).

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The loss of resilience, hardness, water sorption, propensity for microbial adherence and development, color change and separation from the denture foundation are the most common issues seen in the clinical application of these materials (Dorocka-Bobkowska *et al*., 2017). Ethanol and plasticizer will leak out of tissue conditioner in the mouth when it comes into direct contact with oral fluid, while water or fluid will absorb (Ntounis *et al*., 2015).

However, when commercially available dental soft polymer materials are used in medical applications, they quickly lose their viscoelasticity over time as a result of water adsorption and plasticizers and other chemicals leaking into the mouth environment (Lima *et al*., 2016; Maciel *et al*., 2019). So, by adding certain additive compounds, like citrate ester-based plasticizers, the problem can be resolved. The plasticizer based on citrate ester gives important qualities that increase the longevity of dental soft polymer materials (Hong *et al*., 2020). The present study aimed to develop a safe, stable and long-lasting dental soft polymer material using glycerol and Di-2-ethylhexyl phthalate (DEHP) as plasticizers.

2. Materials and Methods

The weighted plasticizers were introduced into the acrylic-based soft liner (EZ-soft liner, Korea) by substituting an equivalent fraction volume percent of integrated plasticizers for the liquid's fraction volume percent (Table 1) (Naser *et al*., 2022).

Table 1. Plasticizers Concentrations used in this study

Additives	Concentration
Group A	0% (soft liner without additives)
Group B	2% wt glycerol
Group C	5% wt glycerol
Group E	2% wt DEHP
Group F	5% wt DEHP

The soft liner monomer with plasticizers additive was shaken by a dental vibrator for 5 minutes to obtain a homogenous blend of plasticizers with the monomer (Cevik & Yildirim-Bicer, 2018). In a stone mould that was produced with accurate measurements for every test, soft liner dough was packed and allowed to cure for 30 minutes at 70°C in a water bath (according to manufacturer instructions).

Surface hardness: Plastic moulds of disk-shape measuring 30mm in diameter and 3mm thickness have been used to create a mould spaces inside the dental stone control and experimental samples of soft liner prepared in the mould (Figure 1) (Abraham & Abdul-Fattah, 2017).

Before the shore a durometer (Time group TH200, China) testing procedure, the prepared specimens were stored in distilled water at 37ºC for a full day. The durometer indenter was 20 mm from the sample and the contact time was 5 seconds following penetration. Each sample performed an indentation, with an average being determined (Abdulrazzaq Naji & Al-Azzawi, 2022).

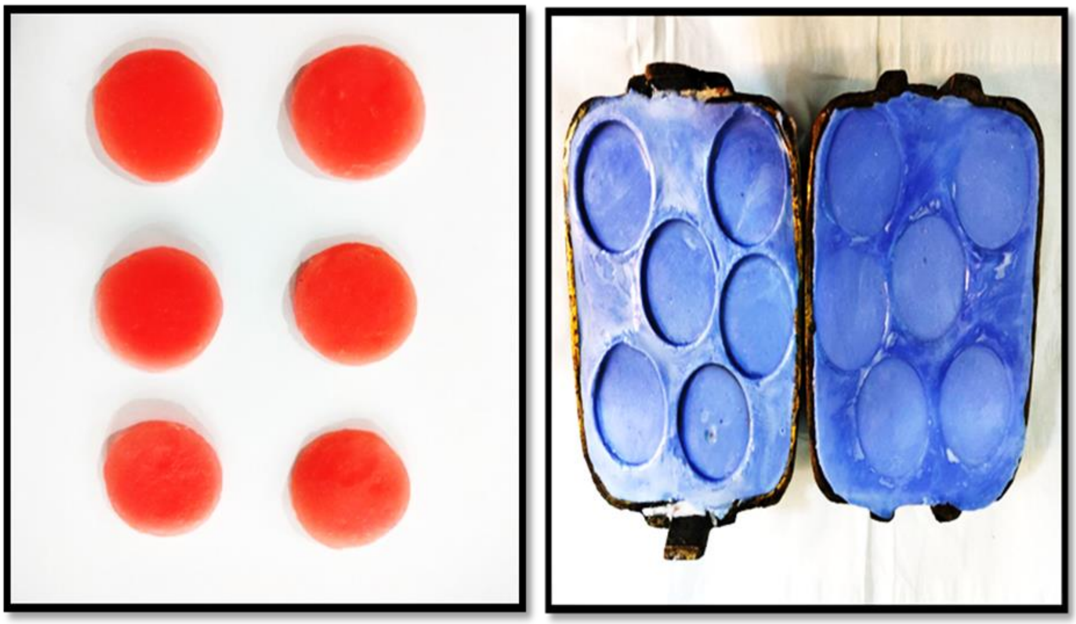

Figure 1. Samples of soft liner and stone moulds

The Elastic Modulus: According to ISO 37, (2017) specifications Type (2) dumb-bell shape specimens were fabricated as in (Figure 2).

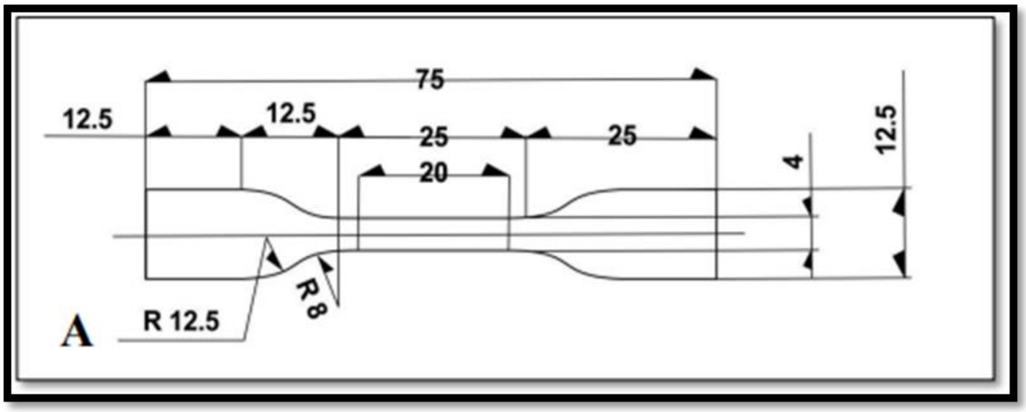

Figure 2. Dimensions of the tensile strength test specimen (Type 2) in mm^2

A universal testing machine (Gester, China) has been used for testing the samples at a constant rate of 500 mm/min speed (ISO 37, 2017). The elastic modulus (*E*) of a tensile test specimen can be calculated as follows:

$$\text{Stress} = P/A = \sigma,$$
$$\text{Strain} = \Delta L/L = \varepsilon,$$

where:
P = the applied force or load
A = the cross-sectional area of the material under stress
ΔL = the increase in length
L = the original length. Thus,

Δ E =Stress /Strain=$\frac{P/A}{\Delta L/Lo}$ … (Anusavice *et al*., 2012).

Water Solubility: In this study forty-five samples were prepared, 9 to each group, with the following dimension 5 mm thickness x 10 diameter (Figure 3) (Chauhan *et al*., 2021).

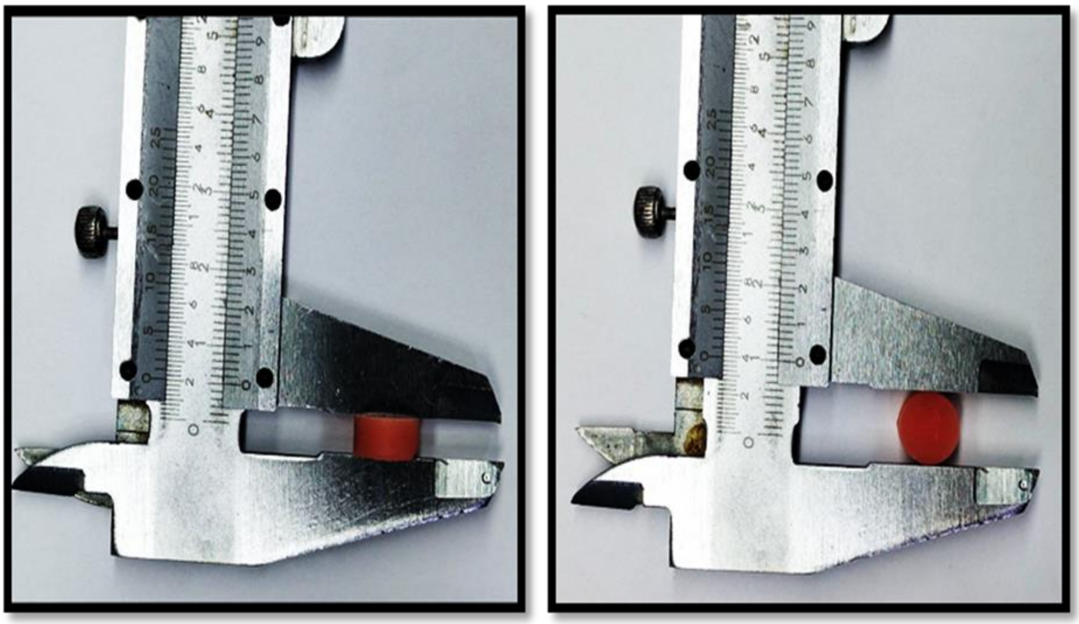

Figure 3. Water solubility specimen dimensions

After preparation of the specimens, they were dried over silica gel in a desiccator at 37 °C until constant weight were obtained this was the initial weight of specimens (W1). Then, the specimens were stored in distilled water at (37 ± 1) °C for 14 days in a thermostatically controlled incubator (Maciel *et al*., 2019). The specimens were dried in a desiccator containing silica gel at 37°C. The specimens reweighed digital electrical balance of 0.001 accurecy at regular intervals until a constant weight was reached. This is recorded as the final weight after dryness (W2) (Salem Awfi *et al*., 2022).

The percentage of solubility was determined as follows:

$$\text{solubility (\%)} = \frac{W1-W2}{W1} \times 100.$$

FTIR Spectroscopy: The chemical reaction between plasticizers and PMMA of the acrylic-based soft liner was assessed using Fourier Transform Infrared Spectroscopy (FTIR) analysis (PLATINUM ATR, Bruker, Germany) at FTIR spectra in the wavenumber range of 4,000 cm^{-1} to 400 cm^{-1}. Every type of material can be positively identified using infrared spectroscopy; this phenomena can be utilized to qualitatively identify compounds (Shaikh & Agrawal, 2014). A small number of control and experimental samples were scratched and stored in water for two periods 24 hours and 14 days then tested using FTIR (Hong *et al*., 2012).

This work implemented an extensive calibration routine for FTIR spectrometers. A method for the accurate characterization of the instrumental line shape from open path measurements was presented. In order to verify the invariability of the instrumental characteristics and to derive inter-calibration factors, side-by-side observations were carried out. The drifts were smaller than 0.005 and 0.035 %, respectively and uncorrected biases were smaller than 0.01 and 0.15 % a common calibration factor was derived in this study. The high level of stability of the spectrometers was demonstrated in this work (Frey *et al.*, 2015).

3. Results

Surface hardness: Table 2 showed significant differences (P-value < 0.05) between the testing and control groups. Duncan's multiple range test for the additives of plasticizers showed that the control group and group B (glycerol 2%) were significantly higher mean (64.57,64.82) followed by group C (glycerol 5%)(61.8) and the group D (DEHP2%) were the lowest mean value (53.7) followed by group E (DEHP 5%) with mean value (56.42) (Figure 4).

Table 2. A hardness of modified soft liner

	Sum of squares	df	Mean Square	F	Sig.
Between Groups	1097.412	4	274.353	56.665	0.0001
Within Groups	246.925	51	4.842		
Total	1344.337	55			

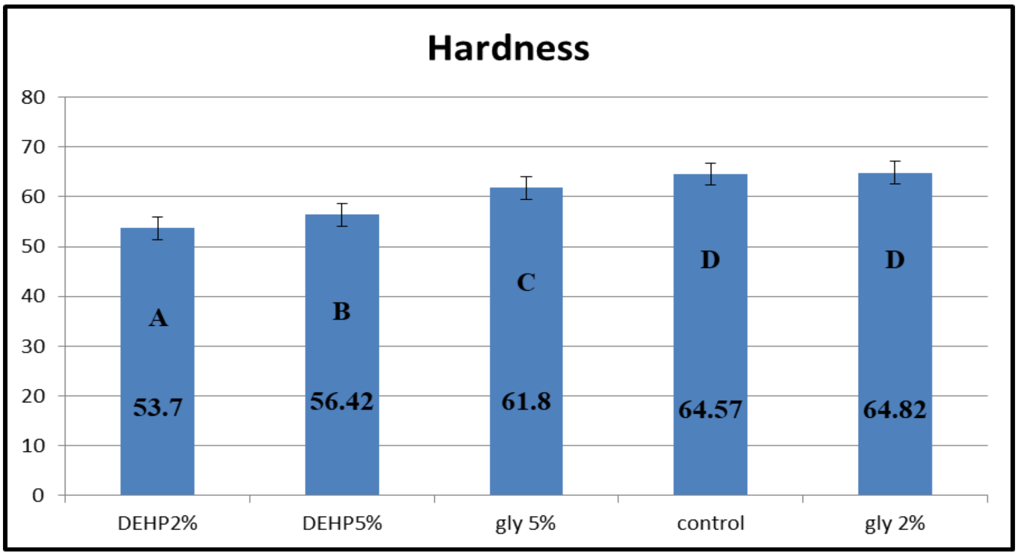

Figure 4. Mean and Duncan's multiple range test of shore A hardness of modified soft liner

Table 3. ANOVA of elastic modulus of modified soft liner

Source of variance	Sum of squares	Df	Mean square	F	significance
Between Groups	1.225	4	0.306	32.297	0.0001**
Within Groups	0.379	40	0.009		
Total	1.604	44			

The Elastic Modulus: Analysis of variance (One-way ANOVA) is a significant difference (p < 0.001) in the modulus of elasticity (Table 3). Duncan's multiple range test for interaction between different variables shows that the samples with 5% DEHP additives with a mean value of (0.6060) was significantly higher mean of the elastic modulus while samples of DEHP 2% additives have significantly the lowest mean (0.1760) (Figure 5).

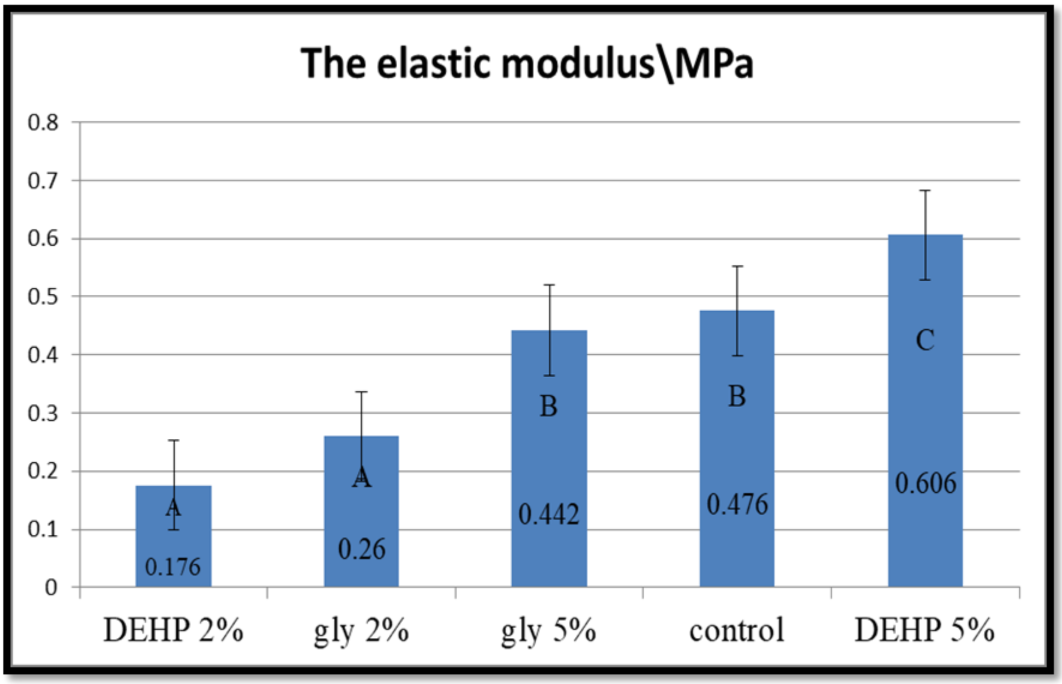

Figure 5. Duncan's multiple range test for elastic modulus

Water Solubility: ANOVA shows no statistically significant difference in the amount of water solubility of the control group when compared to that of experimental groups at $p \leq 0.05$ (Table 4).

Table 4. ANOVA of water solubility of soft liner

Source of variance	Sum of Squares	Df	Mean Square	F	Significance
Between Groups	8.980	4	2.245	1.969	0.118
Within Groups	45.616	40	1.140		
Total	54.596	44			

Fourier Transform Infrared Spectroscopy (FTIR) Results: The modified acrylic-based soft liner showed no chemical interaction with plasticizers at different concentrations with different periods of time for storage in water that was analyzed by the FTIR device (Figure 6). Furthermore, as demonstrated by the FTIR test in this study, there was no chemical interaction between the plasticizers and the lining material; this indicates that a physical rather than chemical relationship exists between the two. The great material resilience and low hardness values can be explained by this physical link (Bodaghi, 2020).

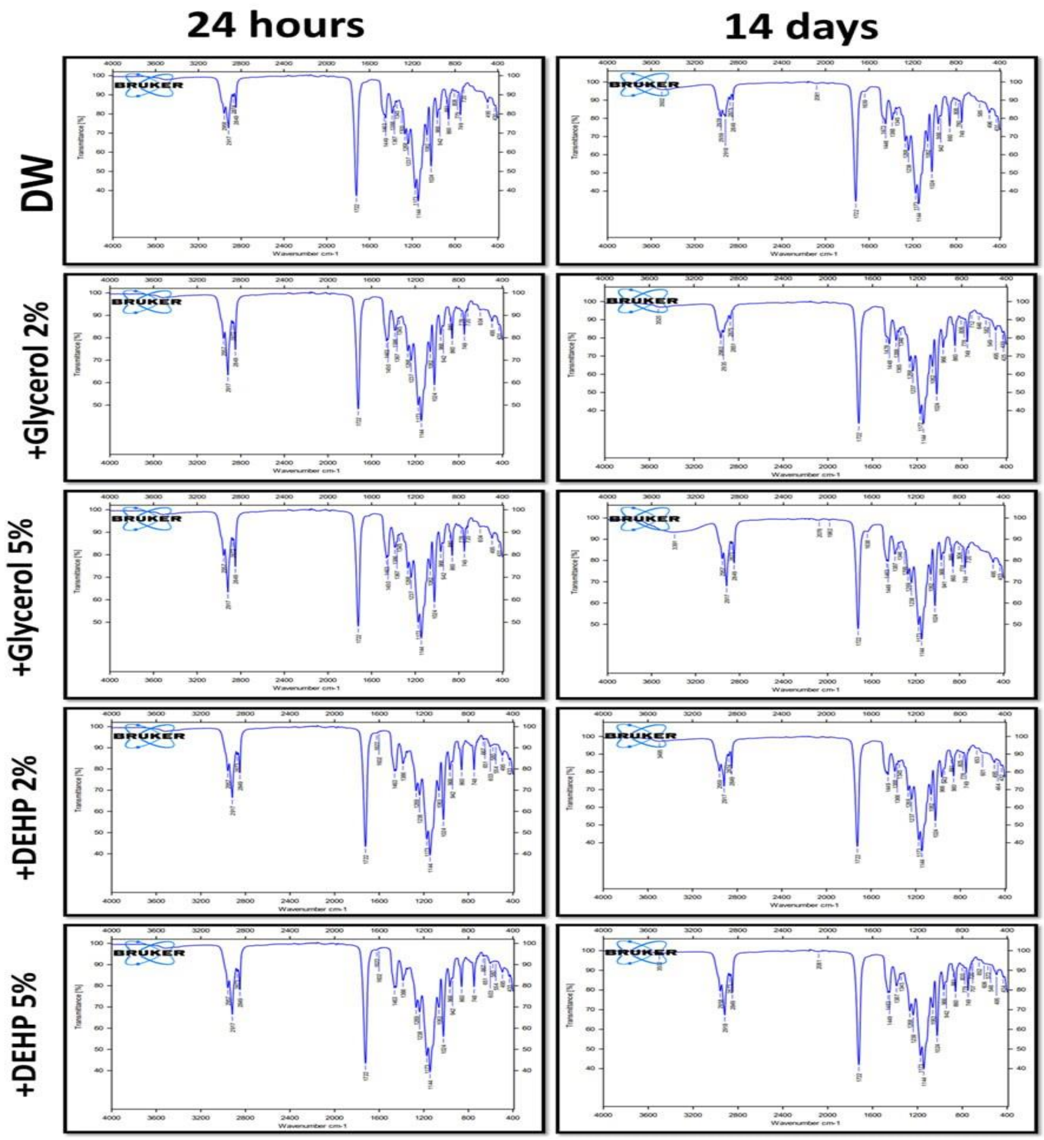

Figure 6. FTIR analysis for soft liner samples after 24 hours and 14 days of storage in distilled water

4. Discussion

When using these materials in clinical settings, the most frequent problems that occurred were resilience loss, hardness, water sorption, growth and adherence of microbe, color change and detachment from the base of a denture (Dorocka-Bobkowska *et al*., 2017). Chemical disinfectants may have a negative impact on the chemical and physical characteristics of acrylic resin, such as leaching, color change, surface roughness and flexural strength (AlHamdan, 2022). Research findings indicate that acrylic resilient experience problems with durability as a result of water absorption and component leaching, causing them to become rigid (Perchyonok, 2017).

The shore A following the addition of DEHP plasticizers, a hardness statistical analysis revealed a significantly substantial drop in the mean values mainly at 2% concentration with a mean of (53.7) and DEHP 5% concentration with a mean of (56.4) in contrast to the control group (64.57). Plasticizers are frequently caused by a decrease in the resin's strength, hardness and softening temperature. For example, soft, cushioning denture liners are made using both internal and external plasticizers (Anusavice *et al*., 2012).

According to Nakhaei et al. (2019), who found that ozone and correga tablet mean hardness values were substantially lower than those of the control and NaOCl groups, the results of this investigation regarding the impact of plasticizers on soft liners' hardness are in agreement with these findings (Abbas & Mahmood, 2023). This investigation's results are different from those of Abbas and Mahmood (2023), who stated that soft lining material's surface hardness increased significantly at 0.5% MMTNPs but that the hardness was still acceptable at 0.25% (Nakhaei *et al*., 2019).

Viscoelasticity is the quality of a material that allows it to behave both viscous and elastically or to put it another way, when stress is applied, it deforms elastically if it is removed quickly but plastically if it is applied over an extended length of time (Stavreva, 2021). Plasticization prevents the formation of chemical bonds. The lubricating theory of plasticization states that plasticizers act as molecular lubricants to facilitate the movement of polymer chains in plastics under force. Certain portions of the plasticizer molecule were strongly attracted to the polymer, whereas other portions of the molecule can protect the polymer chain and serve as a lubricant. The decrease in van der Waals or intermolecular interactions between the polymer chains increased the polymer's flexibility, softness and elongation (Godwin, 2017).

Yang et al. (2015) observed that after 28 days of immersion in water, the novel hyperbranched polyester group and acetyl tributyl citrate demonstrated more stable viscoelastic capabilities than other traditional tissue conditioners. Furthermore, the biocompatibility of the novel hyperbranched polyester and acetyl tributyl citrate groups was identical to that of the control group. Thus, acetyl tributyl citrate combined with new hyperbranched polyester have the potential to be a new tissue conditioner.

Solubility refers to the loss of the submersion component. Elution of leachable compounds might occasionally irritate the tissue surrounding dentures. The gradual release of plasticizers and monomer residues from the denture liner caused certain clinical problems (Ergun *et al*., 2022). According to Palasuk et al. 2019, silicone-based soft liner (Soft Liner ToughM®) is more stable than acrylic-based soft liners in terms of water sorption, water solubility and color stability irrespective of cleaning solutions and time. Maciel et al. (2019) state that the smaller the plasticizer's molecular weight and the higher the concentration of this molecule and ethyl alcohol in a robust material, the larger the plasticizer's weight loss and percentage of solubility during water storage. Garg and Shenoy (2016) have discovered in their investigation that the water solubility of acrylic-based self-curing soft denture liners was highest in distilled water, followed by Shellis artificial saliva and lowest in 5.25% sodium hypochlorite.

In educational labs and the workplace, FTIR spectroscopy were widely employed for qualitative and quantitative research, primarily for structural analysis and molecular level interactions (Kumar *et al*., 2019). Given that neither the soft liner nor the plasticizers contain functional groups, the results suggest that only physical changes occurred between the soft liner and plasticizers. Most plasticizers are composed of esters, which physically interact with polymers to produce a homogenous physical unit by processes including swelling, dissolving or other actions (Shaikh & Agrawal, 2014).

The results in this study are consistent with the findings of Hasan and Ali's (2018) study, which discovered that the presence of other oxygen atoms in the Alumina in Halloysite Nanotubes (HNTs) even in the case of coordinated bonds between Alumina

(Al_2O_3) and Carbonyl ester, prevented any chemical reaction between the HNT nanoparticles and the soft lining from occurring (Abbas & Mahmood, 2023).

Clinical implications and societal impact of the study represented as, soft denture liner materials have been used in dentistry for more than a century, with the earliest soft liners being natural rubbers. The International Standard Organization (ISO) in 1999 defined soft denture lining material as a soft resilient material bonded to the fitting surface of a denture to reduce trauma to the supporting tissues. Although the properties of soft lining materials have been much improved, they still have several drawbacks. Soft denture liners have several problems associated with their use, such as, a loss of softness, and a gradual hardening due to plasticizer leaching out, which are the main drawbacks of plasticized acrylics. In this study, plasticizers were added to the soft liner in order to enhance the softening property of soft liner (Hashem, 2015).

5. Conclusion

In conclusions within the constraints of this research, FTIR analysis for soft liner showed the soft liner made of acrylic and the plasticizers did not react chemically (glycerol & DEHP) it resulted in physical change only, the hardness of a modified acrylic based soft liner material with plasticizers was decreased. The future scope of this research is to study more bio-based plasticizers (less toxic) made from vegetable oils, citrates and sugar derivatives able to plasticize the soft liners and other polymers.

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