# Evaluation of Some Properties of Two Types of Bonding Agents After Modification with Ethanolic Extract of Egyptian Propolis

*Thesis submitted to the Biomaterials Department*
*Faculty of Dentistry*
*Ain-Shams University*

*In partial fulfillment of the requirements for the Doctor of philosophy (PhD) in Biomaterials Science*

***By***

**Mennatullah Mohammed Lutfy Khalil**

**B.D.S. Cairo University (2007)**
**M.D.Sc. Cairo University (2013)**
**Assistant Lecturer of Biomaterials**
**Faculty of Dentistry**
**Fayoum University**

**Biomaterials Department**
**Faculty of Dentistry**
**Ain-Shams University**
**2017**

# Supervisors


## Professor Dr. Tarek Salah El-Dine Hussein

*Professor of Biomaterials*

*Faculty of Dentistry*

*Ain-Shams University*

## Professor Dr. Dina Hassan Mostafa

*Professor of Biomaterials*

*Faculty of Oral and Dental Medicine*

*Cairo University*

## Professor Dr. Ahmed G. Hegazi

*Professor of Microbiology and Immunology*

*National Research Center*

# *Dedication*

*I would like to dedicate this work to the soul of my beloved father, who has always encouraged me and pushed me forwards.*
*To my loving and supportive mother and husband, I could have never done it without you.*
*Thank you.*

# *Acknowledgments*

*I would like to express my sincere gratitude and respect to my supervisor Dr. Tarek Salah, Professor of Biomaterials, Former Head of Biomaterials Department and Former Dean of the Faculty of Dentistry, Ain-Shams University for his guidance, patience, motivation, time, trust and support. I could not have imagined having a better mentor; I am remarkably grateful and cannot thank you enough.*

*I am honored to express my deepest appreciation and gratitude to Dr. Dina Mostafa, Professor of Biomaterials, Biomaterials Department, Faculty of Oral and Dental Medicine, Cairo University, for her help, generosity, understanding and care. Thank you for having faith in me and supporting me unconditionally.*

*I would like to express my thankfulness and appreciation to Dr. Ahmed Hegazy, Professor of Microbiology and immunology, National Research Center, for his valuable guidance, help and support.*

*Finally, I would like to cordially thank all staff members of Biomaterials Department, Faculty of Dentistry, Ain- Shams University, for their friendly support and cooperation.*

# List of Contents

# List of Figures

# List of Tables

# Introduction

In recent years resin-based composites have become the material of choice for cavity restorations. They mainly bond to the tooth surface micromechanically using adhesive systems [(1)].

The primary cause of failure of these restorations is secondary caries that results from residual bacteria left behind in the cavity or microleakage that occurs at the tooth-restoration interface [(2)]. Replacing failed restorations accounts for 50% to 70% of all restorations performed [(3)].

Elimination or reduction of bacteria at the tooth-restoration interface would be expected to influence the caries incidence and reduce failure rates. Therefore, giving adhesive systems antibacterial properties is attractive to promote the longevity of restorations. Several attempts have been made at giving resins antibacterial properties [(4-6)].

Propolis (bee glue) is a natural resinous plant-based material collected, digested, and modified by bees. Propolis has been used in folk medicine for centuries because it has a wide range of biological actions including antibacterial, antifungal, antiviral, anti-inflammatory and antioxidant activity. Ethanolic extract of propolis (EEP) is a low-wax propolis extract rich in biologically active compounds and can be used directly to employ antibacterial activity [(5-7)]. Recently, the use of propolis has extended to the dental field and is incorporated in some commercial and experimental materials [(8-14)].

Accordingly, this study is designed to modify bonding agents with EEP and evaluate their properties.

# Review of Literature

The world health organization (WHO) considers dental caries as one of the two major oral diseases besides periodontal disease. A vast majority of people suffer from loss of tooth structure due to tooth decay caused by dental caries, especially in developing countries. Other causes that contribute to the loss of tooth structure including; fracture due to dental traumas and surface loss due to abrasion, abfraction, and erosion. To avoid the negative impact these factors can have on people's lives such as; pain and loss of function; dental restorations are needed to restore the lost tooth structure [(15)].

The basic function of dental restorations is to restore the tooth anatomically and functionally, but recently this has extended to include and satisfy patients' rising esthetic demands. The need for invisible restorations along with an increasing awareness of the environmental implications of mercury in dental amalgam has caused a shift of the request from conventional silver-colored dental amalgam to tooth colored restorations [(16-18)].

Among the direct tooth-colored restorations are resin-based composites which provide acceptable mechanical properties, as well as, an ability to replace biological tissues anatomically, functionally, and aesthetically. Resin-based composites bond to the tooth structure and any existing resin-based composite restorations through adhesive systems [(18-20)].

The evolution in restoring tooth structure using resin-based composite restorations and adhesive systems, along with a better understanding of the caries process and its prevention has led to a

change in treatment strategies. Today's restorative treatments are conservative and understand the importance of preserving the natural tooth structure through 'minimally invasive' or 'minimum intervention' care. These treatments focus on removing and replacing only the diseased or lost tissue by directly bonding restorations to the remaining sound tissue. For even further conservation 'maintenance and repair of restorations' is promoted, rather than replacing entire restorations (exhibiting marginal discolorations and defects). These treatment strategies have further boosted the use of adhesive techniques in diverse applications of everyday clinical practice [16, 19, 21].

# 1. Resin adhesive systems (Bonding systems)

## 1.1. Composition of resin adhesives

Resin adhesives are composed of five main components: resin monomers, solvents, fillers, initiators, and inhibitors.

### 1.1.1. Resin monomers

Resin monomers are a key component of resin adhesives. Upon polymerization, they form covalent bonds and construct the backbone of resin adhesives known as the resin matrix. The properties of the formed resin matrix greatly depend on the quality of the resin monomer. Resin monomers are usually composed of three parts; cross-linkers, functional monomers and spacers [22].

#### 1.1.1.1. Cross-linking monomers

They contain two polymerizable groups (vinyl groups or - C = C -), on curing it forms a cross-linked polymer. Cross-linkers have

shown to provide better mechanical properties to the polymer i.e. reinforce resin adhesives and enhance hydrolytic stability. Commonly, cross-linking monomers have high molecular weight and exhibit hydrophobic properties. Therefore, they are less likely to infiltrate into the hydrophilic demineralized dentin and are usually incorporated in the bonding resin rather than the primer. Examples of cross-linking monomers are bisphenol A-diglycidyl methacrylate (Bis-GMA), urethane dimethacrylate or 1,6-di(methacryloyloxyethylcarbamoyl)-3,30,5-trimethylhexaan (UDMA), triethylene glycol dimethacrylate (TEGDMA), and polyethylene glycol dimethacrylate (PEGDMA) [22].

1.1.1.2. Functional monomers

They contain only one polymerizable group, which exhibits a particular chemical group that imparts the monomer with a specific function. Once cured it forms a linear polymer that exhibits hydrophilic properties. Some of the functions they exhibit are: enhancing wetting of dentin, demineralization (etching monomer), releasing fluoride, giving the monomer antibacterial properties and improving the bond strength of adhesive to dentin (adhesion promoters) [22].

2-hydroxyethyl methacrylate (HEMA) is the most common functional monomer. Its popularity is primarily because of its biocompatibility in the cured state. Rakich et al. in 1998 [23], investigated the effects of 4 components of dentin bonding agents on the mitochondrial activity (MTT assay) of macrophages which are important in wound healing and inflammatory reactions. The cytocompatibility of 2-hydroxyethyl methacrylate (HEMA), 4-

methacryloyloxyethy trimellitate anhydride (4-META), bisphenol A-glycidyl methacrylate (Bis-GMA) and urethane dimethacrylate (UDMA) were evaluated, and HEMA showed the best biocompatibility followed by 4-META then Bis-GMA and finally UDMA. Another important characteristic of HEMA is its hydrophilicity which enhances wetting of the dentin surface and promotes adhesion of the monomer improving bond strength. The problem with HEMA is that, both in uncured and cured state, it will readily absorb water. In an uncured state, this can lead to inhibition of polymerization reaction. While in a cured state, it will lead to water sorption, hydrolytic degradation and discoloration thereby reducing mechanical properties, bond strength and durability [22, 24, 25].

The most common functional groups have an etching ability which varies according to its acidity i.e. sulfonic acid, phosphonic, phosphoric, carboxylic and alcohol. Acidic functional monomers are used in self-etch adhesives. Pentamethacryloyloxy-ethyl-cyclo hexa-phosphazene monofluoride (PEM-F) is a functional monomer that releases fluoride upon mixing with water. This fluoride acts as a calcium scavenger intensifying the demineralization process rather than remineralizing the tooth tissue. 4-methacryloyloxyethy trimellitate (4-MET) is a frequently used functional monomer; it was originally used as an adhesion promoter and later it was found to act as a demineralizing monomer. N-methacryloyl 5-aminosalicylic acid (5-NMSA), Phenyl-P and methylene diphosphonate (MDP) were originally used to promote adhesion and were also found to inhibit bacterial growth[22, 24, 26].