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SURFACE DISSOLUTION AND DEGRADATION OF DENTAL RESIN BASED MATERIALS

with Special Emphasis by the Effects of Solvent
Ethanol, Dimethacrylate Monomer Resin and
Catalyst Solution of Ethylene Glycol

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*“Knowledge can only be got in one way, the way of experience; there is no other way to know.” – **Swami Vivekananda***

*To the sweet memories of my Late **Grand Father**, the driving force and the man behind my success for what I am today.*

UNIVERSITY OF TURKU

Faculty of Medicine

Institute of Dentistry

Department of Biomaterials Science

SANTHOSH BASAVARAJAPPA: Surface dissolution and degradation of dental resin-based materials with special emphasis by the effects of solvent ethanol, dimethacrylate monomer resin and catalyst solution of ethylene glycol

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ABSTRACT

In today's modern dentistry, various synthetic materials are used for the replacement or restoration of the missing teeth or parts of teeth structures. These are primarily either polymers or composite materials. The evolution of the synthetic polymers dates back to the use of natural rubbers to *poly*(methylmethacrylate), (PMMA) to the present-day use of cross-linked copolymers and interpenetrating polymer network (IPN). One commonly used polymer is the group of denture base polymers where polymer beads of *poly*(methylmethacrylate) and the monomer of methylmethacrylate (MMA) form multiphase polymer system. During the phase of polymerization, some residual MMA monomers are left unconverted and heat-cured however, auto polymerized denture base polymers differ in this respect. In cross-linked dental resins, monomers are typically *bis*-phenol A-glycidyl methacrylate (*bis*-GMA) and triethylene glycol dimethacrylate (TEGDMA) or epoxies and they on combination with PMMA form IPN polymer. This study aimed to investigate surface crazing and surface dissolving of dental polymer with solvent and disinfectant ethanol by chemical reaction of transesterification. Scanning electron microscopy, infrared spectroscopy, and Nanoindentation were used as the research methods.

The outcomes of the study on various dental polymers suggested that ethanol had a significant influence on affecting the surface roughness, and nanomechanical properties with surface topographical changes of denture base polymers. The effect of ethanol was dependent on time and concentration. Transesterification of the cross-linked *bis*-GMA based substrate was seen on contrary to the epoxy resin, which did not show signs of transesterification. This was explained by the lack of the ester group in the mainly studied epoxy polymer.

KEYWORDS: Acrylic Resin; Adhesive resin; *Poly*(methylmethacrylate); Ethanol; Dissolution; Solvents; Crazing; Fiber reinforced composites; Transesterification; Interpenetrating polymer network; Ester groups; Nanomechanical properties.

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Nykyaikaisessa hammashoidossa käytetään useita erilaisia materiaaleja korvaamaan hampaita ja hampaiden osia. Materiaalit ovat usein muoveja tai muovipohjaisia yhdistelmäateriaaleja. Muovipohjaiset materiaalit ovat kehittyneet luonnon kumista polymetyylimetakrylaatin kautta ristosilloitettuihin kopolymeereihin ja osittaislomittaisverkostomuovirakenteisiin (IPN). Yksi yleisesti käytetty materiaali-ryhmä on proteesien pohjalevymuovit, joissa polymetyylimetakrylaatti (PMMA) -hiukkaset ja metyylimetakrylaattimonomeeri muodostavat monifaasisen muovin. Muovin kovettumisessa osa monomeereista jää reagoimatta ja niin sanotut keittoakryylit ja kylmäakryylit eroavat reagoimattomien monomeerien määrän suhteen. Ristosilloitetut hammashoidossa käytetyt monomeerit ovat usein bisfenoli-A-glysidylimetakrylaatti (*bis*-GMA) ja trietyleeniglykolidimetakrylaatti (TEGDMA) -kopolymeereja, epoksimuoveja ja erilaisia IPN-muoveja, joissa PMMA on osana rakenteessa. Tässä tutkimuksessa tutkittiin hammashoidossa käytettyjen muovien pinnan säröilyä ja liukenemista desinfioidun etanoliliuottimen vaikutuksesta. Lisäksi tutkittiin muovien pinnan hajoamista ns. transesterifikaatioreaktion seurauksena. Tutkimusmenetelminä käytettiin pyyhkäisyelektronimikroskopiaa, infrapunaspektroskopiaa ja pinnan nanomekaanista analysointia.

Tutkimustulokset osoittivat, että etanoliliuotin lisäsi merkittävästi proteesin pohjalevymuovien pinnan karheutta ja vaikutti pinnan mikroskooppiseen topografiaan ja nanomekaanisiin ominaisuuksiin. Etanoliliuottimen vaikutus riippui liuottimen vaikutusajasta ja etanolin pitoisuudesta vedessä. Transesterifikaation vaikutus ristosilloitetun *bis*-GMA -muovien pintaominaisuuksiin havaittiin selvästi toisin kuin tutkimuksessa käytetyn epoksimuovien kohdalla. Transesterifikaatio selitettiin *bis*-GMA -muovissa olevien esterisidosten olemassa ololla.

AVAINSANAT: Akryylimuovi; sidosmuovi; polymetyylimetakrylaatti; etanoli; liukeneminen; säröily; liuotin; kuitulujitteinen muovi; transesterifikaatio; osittaislomittaisverkostomuovirakenne; esterisidos; nanomekaaniset ominaisuudet.

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Abbreviations

AFM	Atomic Force Microscopy
ANOVA	Analysis of Variance
ATR	Attenuated Total Reflectance
<i>bis</i> -EMA	Ethoxylated <i>bis</i> phenol-A-dimethacrylate
<i>bis</i> -GMA	<i>bis</i> -phenol A-glycidyl methacrylate
BPA	<i>bis</i> -phenol A
°C	Celsius
<i>D3MA</i>	1,10-decanediol dimethacrylate
DMAEMA	2-(dimethylamino) ethyl methacrylate
EGDMA	Ethylene glycol dimethyl acrylate
FRC	Fibre Reinforced Composite
FTIR	Fourier Transform Infrared Spectroscopy
GPa	Gigapascal
h	Hour
HEMA	Hydroxyethyl methacrylate
IPN	Interpenetrating Polymer Network
kPa	kilopascals
MARC	Managing Accurate Resin Curing
min.	Minute
mm	Millimeter
MMA	Methylmethacrylate
mN	Millinewtons
mN/s	Millinewtons <i>per</i> second
N	Newtons
n	Number of samples
nm	Nanometre
NMP	Nanomechanical properties
PFC	Particulate-filled composite
PMMA	<i>poly</i> (methylmethacrylate)
R^2	Simple correlation coefficient
R_a	Surface roughness (two-dimensional analysis)

R_p	Maximum peak height
rpm	Revolutions per minute
s	Second
S_a	Surface Roughness (three-dimensional analysis)
SD	Standard Deviation
SEM	Scanning Electron Microscope
semi-IPN	Semi-Interpenetrating Polymer Network
SPSS	Statistical Package for Social Sciences
TEGDMA	Triethylene glycol dimethacrylate
T_g	Glass Transition Temperature
UDMA	Urethane dimethacrylate
wt%	Weight Percentage
δ	Solubility Parameter, $(\text{cal}/\text{cm}^3)^{1/2}$
μm	Micrometre

List of Original Publications

This dissertation is based on the following original publications, which are referred to in the text by their Roman numerals:

- I Basavarajappa S, Al-Kheraif AA, ElSharawy M, Vallittu PK. Effect of solvent/disinfectant ethanol on the micro-surface structure and properties of multiphase denture base polymers. *J Mech Behav Biomed Mater*, 2016;54:1-7.
- II Basavarajappa S, Abdullah Alkheraif AA, Alhijji SM, Matinlinna JP, Vallittu PK. Effect of ethanol treatment on mechanical properties of heat-polymerized *Poly(methylmethacrylate)* denture base polymer. *Dent Mater J*, 2017;36(6):834-841.
- III Basavarajappa S, Perea-Lowery L, Aati S, Abdullah Al-Kheraif AA, Ramakrishnaiah R, Matinlinna JP, Vallittu PK. The effect of ethanol on the surface of the semi-interpenetrating polymer network (IPN) polymer matrix of glass-fibre reinforced composite. *J Mech Behav Biomed Mater*, 2019;98:1-10.
- IV Basavarajappa S, Perea-Lowery L, Alshehri AM, Abdullah Al-Kheraif AA, Matinlinna JP, Vallittu PK. Surface dissolution and transesterification of thermoset dimethacrylate polymer by dimethacrylate adhesive resin and organic catalyst-alcohol solution. *Dent Mater*, 2020;36:698-709.

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1 Introduction

Modern dentistry has evolved with the introduction of new materials such as polymers and composites for restoration and fabrication of teeth along with the replacement of missing teeth. Until the introduction of *poly*(methylmethacrylate) (PMMA) in the late 1930's natural rubber and synthetic polymer were used as denture base material (Sweeney and Caul, 1940), which remains as the standard gold material used for dental prosthesis and appliances. PMMA, from the powder and liquid system, allows for controlling the polymerization shrinkage, and its viscosity allows better handling properties (Vallittu, 1994). The monomer and the polymer, when mixed, go through a series of phases or stage changes. Once the blend reaches the dough stage, the diffusion of the monomer takes place into the polymer. In the dough phase, the undissolved polymer is found suspended in the matrix of the monomer. Before the rubbery stage, the mixture has moulded. Increasing the time after mixing the polymer powder and the monomer liquid and until the monomers start to cure, it allows the dissolving of the monomer beads and the homogeneity of the achieved polymers (Vallittu and Ruyter, 1997). The structure in the interphase of the polymer is a semi-interpenetrating polymer network (semi-IPN), where is the integration of a slightly cross-linked polymer matrix into the polymer structure of the dissolved PMMA beads.

The amount of unconverted or unreacted residual monomer of methylmethacrylate (MMA) present in the polymerized resin decides the mechanical and biological properties of acrylic resin (Melilli *et al.*, 2009). The maximum allowed free monomer in heat-cured and auto polymerized acrylic resin material should be less than 2.2% and 4.5%, respectively (Yilmaz *et al.*, 2003). The acrylic polymer, when treated with solvents/disinfectants containing ethanol, affects their physical properties the flexural strength and hardness along with reduced cytotoxic effect related to the monomer, leached in the oral cavity (Neves *et al.*, 2013). The use of chemical disinfectants for preventing bacterial contamination in dental prosthesis (Cunegatti *et al.*, 2008) also influenced the physical and mechanical properties that affect the denture base resins (Shen *et al.*, 1989) especially by ethanol (Asad *et al.*, 1992). Surface roughness also plays an essential role in the adhering factor for bacterial colonization (Bollenl *et al.*, 1997) and affected significantly by

the chemical disinfectants (Pinto Lde *et al.*, 2010). Some change in the surface roughness of the denture base polymers by crazing is also seen (Schwindling *et al.*, 2014).

Cross-linking thermoset monomers (Bowen, 1963) such as dimethacrylate monomers paved the way for the introduction of IPN like structures in various fields of dentistry, used in denture teeth, fibre-reinforced composites (FRC), denture base polymers and restorative resin composite materials (Garoushi *et al.*, 2008; Vallittu, 2009). Such IPNs are cross-linked polymers (Nowers and Narasimhan, 2006) made up of two or more polymers, formed by a combination of two or more polymer framework in juxtaposition (Sperling, 1994). The inter-network entanglements seen in the IPN polymer are permanent because of their chemical cross-linking (Klemmner *et al.*, 1970), and this prevents the material from being pulled apart and fracturing of the polymer. (Myung *et al.*, 2008). Their ability to dissolve their surface also allows the cover to bind new resin systems to the resin composite of the IPN polymer or IPN polymer matrix (Bell *et al.*, 2005; Lastumäki *et al.*, 2002; Wolff *et al.*, 2012).

Dental resin composite includes five essential components, a cross-linked polymer matrix, inorganic fillers, X-ray opacifiers, initiator system, and a silane coupling agent (Barszczewska-Rybarek and Jurczyk, 2015). In dentistry, the composite resins are usually comprised of *bis*-phenol A-glycidyl methacrylate (*bis*-GMA), triethylene glycol dimethacrylate (TEGDMA), urethane dimethacrylate (UDMA), ethoxylated *bis*phenol-A-dimethacrylate (*bis*-EMA), with *Bis*-GMA being the most commonly used (Luo *et al.*, 2016). Interfacial adhesion of resin composite layers usually occurs by free radical polymerization of incremental composite coatings using oxygen-inhibited layers on the surface of the substrate (Bijelic-Donova *et al.*, 2018; Bijelic-Donova *et al.*, 2015). Without using strong chemicals, high pressure, and temperature, thermoset polymers are difficult to dissolve (Ibarra *et al.*, 2015). FRC is a combination of fibres that are reinforcing component in the matrix of the polymer. To strengthen the dental polymers, Silanized glass fibres (Matinlinna *et al.*, 2004; Matinlinna *et al.*, 2018) are commonly used, and glass fibres are superior from the aesthetic qualities (Vallittu, 1996). The efficacy of fibres in the FRC depends on the resin used, amount, length (Vallittu *et al.*, 1994), form (Ladizesky *et al.*, 1993), direction (Dyer *et al.*, 2004), and the adhesion and impregnation of fibres with the resin (Miettinen and Vallittu, 1997; Vallittu, 1994, 1995). Even though the semi-IPN matrixes in dental resin composites provide improved adhesive properties over the cross-linked polymers of dimethacrylates and epoxies, cross-linked polymers are still the most commonly used in filling composites and root canal posts (Alnaqbi *et al.*, 2018).

The dissolution of polymers by an adhesive or solvent requires diffusion and chain disentanglement. Dental adhesives are usually solvated in different organic

solvents such as ethanol, acetone, *tert*-butanol, tetrahydrofuran (THF), dimethylsulfoxide (DMSO), and water (Ekambaram *et al.*, 2015). Polymer dissolution begins with initial diffusion of the solvent forming two separate interfaces in the polymer, one between the glassy polymer surface and the gel layer, and the second between the gel layer and the solvent. In the absence of the formation of the gel layer, the polymer dissolves or cracks after the induction time has passed (Cooper *et al.*, 1985). Crazing, as an organized crack, appeared on the polymer surface, usually in thermoplastic polymers. This is because of the weaker van der Waals force and a strong covalent bond. In those areas of the polymer surface with higher hydrostatic tension, they are causing localized yielding ending up in microvoids (McLeish *et al.*, 1989).

Polymer dissolution and the dissolution processes are governed by various parameters such as solvent diffusion coefficient, the molecular weight of the polymer, cross-linking density, temperature, and pressure along with the thermodynamic behaviour of the solvent (Binder, 1983). Ethanol, with a solubility parameter of $13 \text{ (cal/cm}^3)^{1/2}$ and *poly*(methylmethacrylate) which has a solubility parameter (Jacques and Wyzgoski, 1979) of $8.9 - 12.7 \text{ (cal/cm}^3)^{1/2}$ indicates that ethanol could dissolve or craze denture base polymers (Kambour, 1973). Another alcohol solution, which dissolved the polymer substrate, is ethylene glycol. Relative to the solubility parameters of epoxy resin (18.2δ) (Mezzenga *et al.*, 2000) and dimethacrylate (18.8δ) the solubility parameters of ethylene glycol (16.30δ) (Luo *et al.*, 2010) suggest that it could potentially dissolve the polymer (Asmussen *et al.*, 1991).

The other mechanism for obtaining monomer diffusion in a cross-linking polymer surface layer, based on the use of transesterification reaction (also called alcoholysis) (Kuang *et al.*, 2018). Cross-linked polymer dissolution by transesterification was of interest from interfacial adhesion and because of its applications in various fields, such as medical and industrial fields in membrane research, plastics recycling, drug delivery control with time-release and tissue regeneration research (Miller-Chou and Koenig, 2003). It has been shown that the transesterification reaction of the epoxy polymer with ester bonds in the chemical structure took place over a reasonable period, but at an elevated temperature of 1800°C with ethylene glycol and accelerator, 1, 5,7-triazabicyclo [4,4,0] dec-5-ene commonly known as triazabicyclodecene. Dissolution or degradation takes place at the surface of the polymer by softening. Hence, the indication of dissolution or degradation is the Nano hardness of the surface. Transesterification requires the presence of ester bonds in chemical structure, and only then, transesterification can take place.

2 Review of the Literature

2.1 Dental polymer resins

Dental polymeric materials should possess specific requirements and performance based on specific clinical applications. The materials that are synthetic resins or plastics, used for various clinical purposes such as impression making, restoration of teeth, and its associated structures. The material selected depends upon the clinical scenario of application, and it should be biocompatible with adequate biomechanical properties. The method of polymerization employed also has an impact on the performance of the final set polymer, which could be either condensation or addition type. In addition, the type of polymerization technique followed as an influence on the polymer to monomer conversion (Xu *et al.*, 2017).

The composition and the structure of a polymer are dependent upon the basic structural units that are repeated to form macromolecules known as the monomers. Few of the monomers most commonly used are methylmethacrylate, *bis*-phenol A glycol dimethacrylate (*bis*-GMA), triethylene glycol dimethacrylate (TEGDMA), urethane dimethacrylate (UDMA), ethoxylated *bis*-phenol A glycol dimethacrylate (*bis*-EMA).

The polymerization process can take place either by condensation or by addition (vinyl) polymerization process, with the technique having an impact on the polymerization process. In the condensation polymerization process, the polymer formed usually contains only a few original atoms of the monomer, whereas, in addition to the polymerization technique, the monomer atoms with repetition make a polymer. Most of the very first polymer materials used in dental restorations and prosthetic appliances were by condensation (Flory, 1946). However, presently used dental polymer systems for denture bases and restorative resin composites and polymerized by free radical polymerization (addition polymerization).

2.1.1 Monofunctional acrylic resins (thermoplastics)

Thermoplastic resins are high molecular compounds, formed from different chemical elements possessing different physical properties. Polyamides, acrylates, polyolefins, polyesters, and thermoplastic acrylic resins are examples of

thermoplastic resins. These resins are made up of linear or fewer branched chains, enabling them to be softened upon heating and solidify once cooled. Tangible property like flexibility and mechanical stability, is determined by the length of the molecule in the resin, defined as the degree of polymerization. Besides, the linear unit gives a high density to the set polymer (Hristov and Yankov, 2017).

Methylmethacrylate monomer (fig 1) based polymers are commonly known as acrylic resins, and they are used in denture bases. *Poly*(methylmethacrylate) (PMMA) is a transparent thermoplastic material with a high molecular mass. It dissolves in a few of the organic solvents other than its monomer of methylmetharylate (MMA). It possesses excellent mechanical strength with high wear resistance and esthetically accepted. Denture based polymers are used in the fabrication removable dentures (complete or partial), and metal framework of removable partial dentures. They usually are based on methylmethacrylate monomer liquid and *poly*(methylmethacrylate) powder. Monomer liquid also contains some amount of cross-linking monomers that are incorporated into the system for improving mechanical properties. The modified forms of denture base polymers based on PMMA are used for direct restoratives, materials used for denture repair, denture teeth fabrication, and as soft liners.

The initiation of a polymerization chain reaction of acrylic resins takes place by free radical addition on exposed carbon atom leading to the formation of a new radical. This newly formed free radical attacks another double bond, which results in the creation of another free radical. This process is propagation. The termination of this chain reaction is dependent on the concentration of free radicals. The MMA will dissolve the PMMA polymer beads entirely or could be restricted only to the surface. The degree of dissolution or swelling depends on the contact wetting time with the monomer liquid. In heat-cured resins, the dough time allows almost the entire PMMA beads to be dissolved. Unlikely in auto-polymerized resins, the initiator and activator are put together, thereby the polymerization rate is rapid. This allows the monomer liquid to penetrate only a few micrometres into the polymer powder. Irrespective of the curing technique, the cross-linking agent in the monomer liquid dissolves the polymer powder and forms a semi-IPN structure in the set polymer and thereby increasing the creep resistance (Oysaed and Ruyter, 1989). Heat-cured polymers have shown better mechanical strength compared to that of the auto polymerized resin. This is attributed to the formation of semi-IPNs in the denture base polymer. Besides, the semi-IPN structure increases the polymer resistance to the effects of various solvents, without any influence on the water sorption by the polymer (Jagger and Huggett, 1990).

In heat-cured acrylic benzoyl, the addition of peroxide to the polymer powder and mixing of the monomer, the benzoyl peroxide dissolves slowly. There is limited dissociation of the benzoyl peroxide at room temperature. The polymer and the

monomer go through a series of phase change from ‘wet sand’ type consistency to a sticky mixture. Even though some polymer dissolves in the monomer, few of the spherical particles seen on the cured-resin representing the original PMMA beads are not affected by the manipulation of the dough. These beads, along with the monomer dissolving the polymer powder, yield a good bond by entanglement.

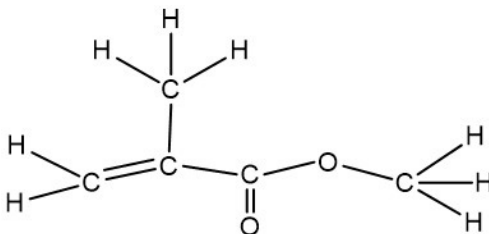


Figure 1: Chemical structure of monofunctional monomer of methylmethacrylate.

The polymerization reaction is usually activated by heat. The initial reaction is exothermic, and the raising of temperature during the curing process accelerates the response further. In autopolymerized, acrylic resins where polymerization takes place at a lower temperature requires the presence of a tertiary amine that reacts with benzoyl peroxide for the generation of free radicals. Tertiary amines are toxic, and it has to be handled with care and the tertiary amine incorporated is *N, N*-dimethylparatoluidine. The amine first forms a salt with benzoyl peroxide to form benzoyloxy, a free radical that acts as an initiator for the polymerization reaction to take place. The degree of monomer conversion of autopolymerized denture base resin is always less as compared to the heat-cured polymer.

The polymerization technique followed influences the homogeneity of the set polymer. Around 5% of ethyleneglycol dimethacrylate (EGDMA) is incorporated in the acrylic resin as a cross-linking agent. The heat-cured polymer is more homogeneous as compared to that of the autopolymerized resin polymer in terms of the semi-IPN structure and also, with the amount of residual monomer present. The PMMA beads in the denture based polymers are attached to the resin matrix by the semi-IPN layer. Besides, unsaturated double chemical bonds are seen to be between the PMMA and MMA during the termination phase of polymerization and the manufacturing of the polymer powder beads (fig 2). The amount of residual monomers in autopolymerized polymers is 4 wt% and in heat-cured is 0.2 wt% (Vallittu *et al.*, 1994). The homogeneity of the semi-IPN structure, the amount of residual monomers, and the polymerization temperature influence the formation of secondary-IPN structures during the repair of denture base polymer and the acrylic resin.

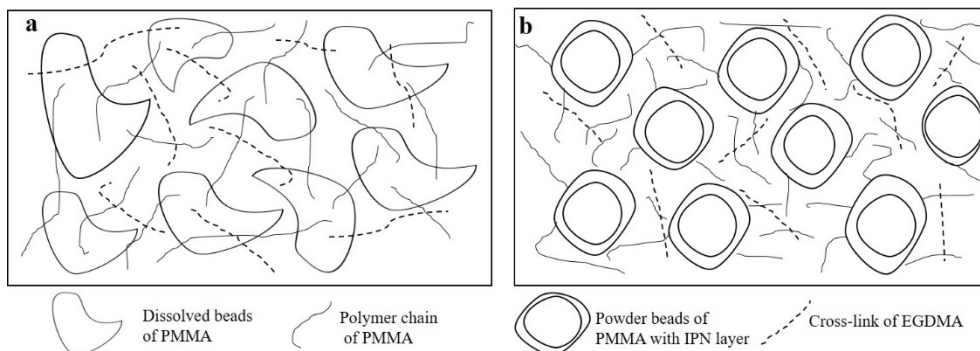


Figure 2: Polymer structure of (a) heat-cured denture and (b) autopolymerized base polymer with their IPN structure.

2.1.2 Bifunctional acrylic resins (thermoset)

Dimethacrylate resins have found a vast use in the field of restorative and prosthetic dentistry for various clinical situations such as adhesives, pit, and fissure sealants, and cementing, veneering and direct restorative materials (Gajewski *et al.*, 2012). The most commonly used bifunctional monomers are bisphenol A glycol dimethacrylate (*bis*-GMA), triethylene glycol dimethacrylate (TEGDMA), urethane dimethacrylate (UDMA), ethoxylated *bis*-phenol A glycol dimethacrylate (*bis*-EMA) as shown in fig 3. The physicochemical properties of the final cross-linked polymer related to the degree of conversion and the network structure depend on the polymerization technique (Asmussen and Peutzfeldt, 1998). Given its high intrinsic reactivity, the presence of hydroxyl groups on the backbone and the interactions provided by the aromatic rings increase the initial viscosity to a point where the homopolymer usually fails to achieve high conversion. Methacrylic acid and diglycidyl ether of *bis*-phenol-A or addition reaction of *bis*-phenol-A and glycidyl methacrylate yield *bis*-GMA. The very high viscosity and low mobility of *bis*-GMA are attributed to the presence of a central phenyl ring with two hydroxyl group. It has high water absorption (Kalachandra and Kusy, 1991) due to the presence of the hydroxyl group. It is the most widely used monomer in the manufacturing of various dental resins. The high viscosity of *bis*-GMA makes it challenging to handle and leads to a lesser degree of monomer conversion (Peutzfeldt, 1997). However, it has lower polymerization shrinkage, reduced toxicity, and higher modulus of elasticity when compared, for example, to PMMA (Pratap *et al.*, 2019). Also, it has a higher refractive index as compared to other commonly used resins in dentistry.

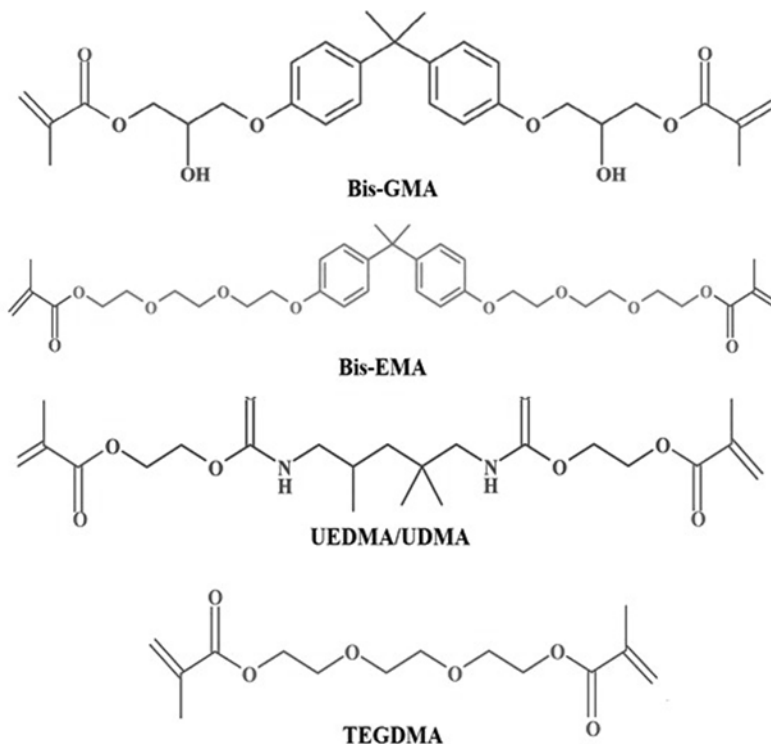


Figure 3: Chemical structure of commonly used bifunctional monomers.

To improve the handling properties and to incorporate inorganic fillers, *bis*-GMA is combined with TEGDMA (Peutzfeldt, 1997). Oxidation and hydration of ethylene yield triethylene glycol. This reacts with methacrylic acid to form TEGDMA. TEGDMA is flexible and has a lower viscosity, and hence it is used as a diluent for *bis*-GMA. However, TEGDMA can decrease the mechanical properties (Goncalves *et al.*, 2010), which affects the colour stability (Janda *et al.*, 2007) along with increasing the water sorption of the set polymer (Sideridou *et al.*, 2007). During polymerization, *bis*-GMA and TEGDMA form highly stable acrylic bonds with inorganic filler particles through the coupling agent, grafted on these filler particles. The formation of a three-dimensional network that possesses good mechanical and chemical characteristics.

Other high molecular weight monomers like urethane dimethacrylate (UDMA) are used along with *bis*-GMA due to its lower viscosity and better flexibility with monomers like *bis*-GMA (Floyd and Dickens, 2006) and UDMA copolymers generally have higher flexural resistance, elastic modulus, and hardness (Tanimoto *et al.*, 2005). The *bis*-GMA ethoxylated is formed, known as *bis*-EMA (ethoxylated bisphenol A-dimethacrylate) with a higher molecular weight, reduced viscosity, and allows the higher degree of conversion with better mechanical

properties (Ogliari *et al.*, 2008). However, the set polymer when it comes in contact with oral fluids undergoes hydrolysis with the leaching of the unreacted monomers and oligomers of low molecular weight (Van Landuyt *et al.*, 2011). Degradation of the filler in the bonding agent (Archegas *et al.*, 2008) eventually leads to material degradation, decreasing the mechanical properties that lead to the failure of the restoration (Berger *et al.*, 2009).

The monomers used in dental composites usually consist of methacrylate group at the ends. Polymerization by chain growth takes place in three sequential processes; initiation, propagation, and termination. During the process of polymer growth, photoinitiators form free radicals. The polymerization process begins with a free radical generation by photoinitiation. The C=C bonds are converted to C-C bonds by the free radical generated in the monomer. The alkene group of the methacrylate group and the free radical donates an electron, while the remaining electron in the alkene group reaches the monomer terminal on the opposite side. This process makes the entire monomer a radical which interacts with the other monomer resulting in a chain reaction and chain growth. Along with the chain growth, the other dimethacrylate monomers present in the composite form a highly cross-linked polymer with increased wear resistance and higher mechanical properties.

Photoinitiators work by two mechanisms; either they have a low energy bond that cleaves upon absorption of light or an excitable group which releases an excitable electron upon absorption of light. The formerly used photo-initiators include diphenylphosphine oxide and benzoyl peroxide (Type-I photo-initiators). They possess low energy bonds, and upon photoinitiated by near-ultraviolet or visible light cleave yielding two radicals that initiate photo-polymerization (Van Landuyt *et al.*, 2007). Type-I photo-initiators does not require the presence of a co-initiator. However, type-II photoinitiators require the presence of a co-initiator for the generation of free radicals. Usually, tertiary amines are used as co-initiators which donate a proton to form free radical. The initiator and co-initiator, upon exposure to visible blue light, exchange of electron takes place, resulting in the formation of a free radical by hydrogen abstraction.

Presently, camphorquinone is the most commonly used photoinitiator, and co-initiators include tertiary amine dimethyl aminoethyl methacrylate. Dimethyl amino ethyl methacrylate has more advantages as compared to other co-initiators as they do not leach out and hence are not cytotoxic. Camphorquinone has a broad light absorbance range between 360–510 nm, with a peak absorbance at 468 nm in visible light spectra. Light curing units with a wavenumber range of 400-500 nm, with blue light-emitting diodes, are commonly used. However, camphorquinone may impart a yellow colour to the set polymer (Pratap and Gupta, 2019). Recently camphorquinone and 1-phenyl-1, 2 propanedione used in the ratio of 1:1 or 1:4 have

shown better polymerization and curing rate, compared when used alone (Van Landuyt *et al.*, 2007).

2.1.3 Other resin systems (IPN systems, epoxies and, dendrimers)

Interpenetrating network, synthesized in juxtaposition. IPNs differ from copolymer or graft polymer, which is chemically bonded (Sperling, 2005). Also, they differ from polymer blend wherein separation can be done by their different phases. In an IPN, polymers are interlaced at a molecular level without covalent bonds, and they cannot be separated without breaking the chemical bonds. In IPNs, they are made up of finely divided phases that are 5-10 nm. IPNs are preferred because of their better-handling properties and toughness with mechanical interlocking with resin adhesives and IPN-like polymer and composites at a nanometer level. This mechanical interlocking plays a crucial role in the clinical success of dental restorative materials like composite resin restorations with the transfer of stresses. In the field of dentistry presently, IPN-like structures are found in denture base polymers and teeth, fibre-reinforced composites, and composite restorative resins (Lastumaki *et al.*, 2003; Vallittu, 2009). Adhesive resins like primers and saline coupling agents and interface formed between the natural and synthetic materials are also similar to IPNs.

If the IPN consists of photo polymerizing dimethacrylate monomers and monofunctional methacrylates, polymerization may occur at the same time, but without the formation of dimethacrylate copolymer and monomethacrylate. The monofunctional methacrylates first have to be prepolymerized in case of photo-induced free radical polymerization. Cross-linking dimethacrylates when mixed with methacrylate, which is monofunctional, a polymer blend is formed without cross-linking. For cross-linking to occur, it requires the dimethacrylate monomers or other solvents to dissolve the monofunctional polymer, which results in the formation of IPN like structure. For the formation of IPN like structure and to dissolve the monofunctional methacrylates, the solubility parameters of the dissolving agent should match the solubility of the polymer phase (Vallittu, 2009).

Presently, IPN like structures are found in denture base resins wherein a cross-linking agent like EGDMA is incorporated at an average of 10% by weight in the monomer liquid. Dissolution of the polymer powder PMMA by the monomer liquid MMA is dependent on the time of contact between them for allowing the complete dissolution of the polymer beads. In heat-cured resin, the degree of dissolution is higher as compared to that of the auto polymerized resin. However, the cross-linking agent like EGDMA is present in the monomer liquid partly or fully dissolves the PMMA polymer beads and the formation of a semi-IPN like structure. This semi-IPN structure in the polymer increases the creep resistance (Oysaed and Ruyter,

1987). Also, the polymer resistance to dissolution to solvents is increased without having any influence on the water sorption of the polymer (Jagger and Huggett, 1990).

Secondary-IPN like structures, formed during the repair of fractured denture resins or when bonding resin composite cement to the IPN polymer matrix FRC, when the fractured fragments are dissolved in a solution of MMA-EGDMA mixture. The three factors govern the formation of secondary-IPN like structures: homogeneity of the semi-IPN structure, amount of residual monomers, and the temperature at which polymerization takes place. Besides, the rate of diffusion of the monomer liquid is related to the T_g of the polymer, wherein the rate of diffusion and time is directly related to a temperature below the T_g of the polymer. Secondary-IPN like structures is formed between the denture teeth at the gingival ridge lap area and the denture base resin. The secondary-ipn structure between the teeth and the denture base depends on the temperature of polymerization. Hence, the heat-cured resin has shown better IPN formation when compared to auto polymerized resin. However, the critical temperature crucial for this adhesion failure to occur is below 550 (Vallittu, 1995).

Epoxy resins were developed in 1940 to overcome few drawbacks of PMMA, related to their coefficient of thermal expansion, colour stability, and adhesion to the tooth surface (Barszczewska-Rybarek and Jurczyk, 2015). *Bis*-phenol-A (BPA) is solid colourless, crystalline. It is an organic and synthetic compound of the *bis*-phenol group and a diphenylmethane derivative, which has two hydroxyl groups. On the other hand, epoxy resin is produced when epichlorohydrin is treated with BPA. Epoxy resins are thermoset resins that cure at room temperature, which have good strength and chemical stability, allowing using the pigments. It is a viscous liquid at room temperature. Upon mixing with a curing agent, the resin becomes more viscous and cures to form an infusible solid (Langer *et al.*, 2019). This is because the cured resin has a high degree of polymerization that is cross-linked between the polymer chains. A thermoset resin like epoxy is generally less affected by solvent chemicals and to heat when compared to thermoplastic resins such as methylmethacrylate (Aazem *et al.*, 2017). The polymerizing process in an epoxy resin occurs by epoxide groups, the oxygen-containing three-membered rings. The ring occurs in a strained and somewhat unstable state in the epoxy group, and is highly prone to opening and combining with compounds with hydrogen present (Su, 2013). The reaction between the epoxy resin and the curing agent is spontaneous at room temperature. As the polymerization reaction, continuous the newly formed hydroxyl radicals form the cross-linking between the polymer chains giving the thermoset characteristics of the cured resin. The water sorption of epoxy resin varies from 0.07%, 0.20% and 0.47% over one day, one week and one month respectively. Besides, the percentage of weight gain when immersed in ethanol was 0.75% after one month. The amount and

type of fillers depend upon the absorption of external solvents or chemicals (Campo, 2008).

However, the dissolution of thermoset anhydrite–epoxy resins could be dissolved by transesterification wherein a mixture of alcohol solution with 1, 5, 7-triazabicyclo [4.4.0] dec-5-ene. Transesterification has enabled the dissolution of the thermoset of resin, coupled with the alcohol-catalyst diffusion process. The formation of the gel, solid swollen and polymer layer had demonstrated the structure of dissolution (Miller-Chou and Koenig, 2003).

Dendrimers (fig 4) are symmetric molecules and are of nano-sized. They have symmetric molecules arranged radially that are homogeneous and monodisperse (Abbasi *et al.*, 2014). They have a compact structure with a higher number of functional groups (Tomalia and Frechet, 2002). Conventionally used monomers in dental resins posed many discontentments due to their properties such as residual monomers, higher polymerization shrinkage and lower mechanical strength (Moszner and Salz, 2001). The structural property of methacrylate functionalized dendrimers is used to overcome the drawbacks mentioned above in the conventional resin monomer system. This could be achieved by lowering the number of methacrylate groups and by adding monomers with large molar volume (Viljanen *et al.*, 2005). Dendrimers improve the mechanical strength of the set polymer, but at the same time, they lead to reduced cross-link density. Despite having high molecular weight, dendrimers structure and its terminal groups have relatively low viscosity (Klee *et al.*, 2001). Various dendrimers based on methylmethacrylate have studied namely, D4, D12, and D24 with a number depicting the number of functional groups. The mixing of D4 dendrimer with MMA is in the ratio of 70:30. The result was that the degree of conversion by photoinitiation achieved in par with that of the dimethacrylate resin at 2% concentration of camphoroquinone.

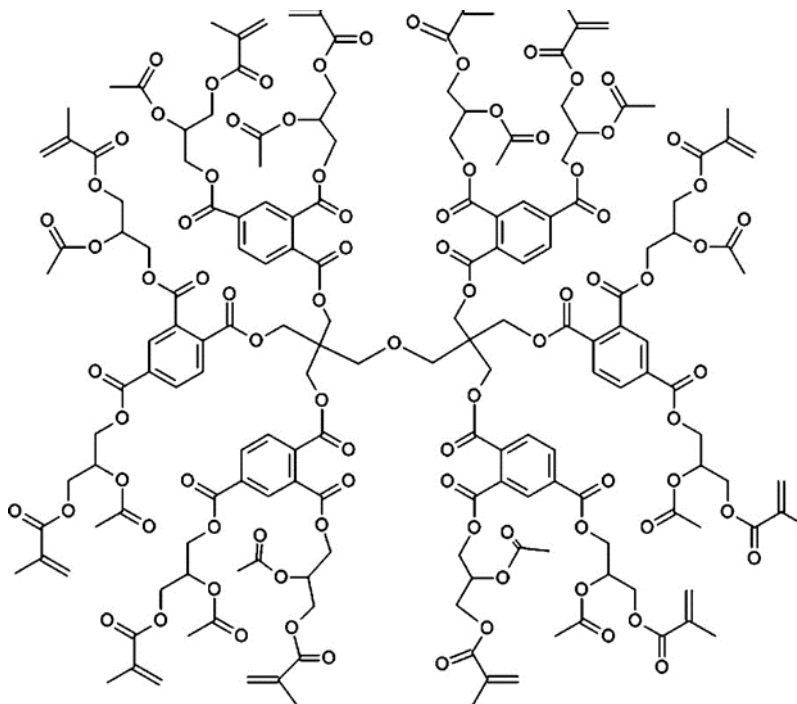


Figure 4: An example of the structure of a dendrimer molecule which has been studied as co-molecule in dental resins. (Copied from: Viljanen *et al.*, 2005).

This suggested that large monomers could use in a newer resin system (Viljanen *et al.*, 2004). Studies on D12 dendrimer of MMA mixed in the ratio of 80:20 by weight showed that the degree of conversion was in par with that of dimethacrylate. However, the functional groups in the dendrimers reacted to photo-initiation, compared to that of MMA, which is not reactive for photo-polymerization. Increasing the photo-initiator in the resin mix showed a higher degree of conversion but reduced mechanical strength (Viljanen *et al.*, 2005). To overcome the problems associated with MMA, other monomers like acetoacetoxyethyl methacrylate have used with D12. This showed an increase in the degree of conversion of the set polymer (Viljanen *et al.*, 2007). However, the amount of residual monomer was not reduced (Viljanen *et al.*, 2006). To overcome the residual monomer content in the set polymer, polymerized by photo-initiation, post-heat polymerization was done. D12, D24 were mixed separately with MMA monomer at different ratios and were light polymerized, and the other group was light and post-heat polymerized. Post heat polymerization increased the degree of conversion was found. Upon comparing the D12 and D24, the D12 showed a better degree of conversion. This was because D24 dendrimer had a higher double bond density led to cyclization. However, at

lower concentrations of MMA in the D24 dendrimer mix, there was an increase in the degree of conversion but lower than that of D12 (Viljanen *et al.*, 2005).

2.1.4 Composite Resins

Particulate filler resin composite (PFC) contains filler particles. The filler particles include quartz, colloidal silica, and silica glass containing strontium, barium, and zirconium (Halvorson *et al.*, 2003). PFC are classified as macro filled, micro filled, hybrid or Nano filled based on the size of filler particles incorporated. The size of the filler particles in PFC varies from 0.1 μm to 100 μm , with 70% to 80 percentage by weight (Beun *et al.*, 2007). PFCs are classified as compact-filled (> 60 vol % fillers) and misfilled composite (< 60 vol % fillers) based on the volume of the filler particles in the resin (Willems *et al.*, 1992). Filler particles incorporated into the resin matrix to reduce the matrix and to enhance the strength of the composite material. Filler integrated composites have shown improved hardness level with lowered wear properties and reduced shrinkage upon polymerization (Azzopardi *et al.*, 2009). Besides, the filler size, morphology, composition, and the distribution determine the physical and mechanical properties of the composite resin. PFCs are usually isotropically, meaning that they have identical mechanical and physical properties in all directions (Vallittu, 2015).

A fibre-reinforced composite (FRCs) represents group non-metallic restorative material, which is a combination of polymer matrix with fibres. Unlike the PFCs, FRCs could be isotropic, orthotropic, or anisotropic, with different physical and mechanical properties in different directions (Vallittu and Özcan, 2017). The fibres are oriented long or short and or continuous or discontinuous in orientation, respectively. The long fibres are oriented uni or bi-directional, whereas the short fibres are randomly incorporated (Vallittu, 2018). These FRCs are widely used in the fabrication of dental prostheses, root canal core, and posts, orthodontic appliances, as restorative resins, periodontal splint fabrication along with surgical applications in implantology and repair of cranial bones (Piitulainen *et al.*, 2017, Posti *et al.*, Shinya *et al.*, 2009, Vallittu, 2018). The properties of FRCs with reduced polymerization shrinkage, improved mechanical properties, lower water sorption, and the brittleness (Vallittu, 1996) and better strength, rigidity, flexural strength and load-bearing capacity has made it superior compared to particulate reinforced fibre composites (Vallittu, 2015). The properties of the FRCs also influenced by the type of fibres that enhances such as the E-glass, S-glass, and S-glass, showing better tensile strength compared to other tissues (Zhang and Matinlinna, 2012). Reinforcement with aramid fibres, carbon/graphite fibres, and ultrahigh molecular weight polyethylene, not recommended due to their lowered performance compared to E- and S- glass fibres.

The resin matrix in composites contains *bis*-GMA, TEGDMA, and UDMA producing cross-linking polymer matrix along with linear polymer like PMMA to aid in the cross-linking of the model. This combination of the direct and the cross-linked matrix forms a semi-interpenetrating polymer network (Vallittu, 2009). The resin matrix is also pre-impregnated with prepregs instead of dry fibres, ensuring a high degree of resin impregnation, which intervenes with the formation of voids and better handling properties (Goldberg and Burstone, 1992). Cross-linking of the polymers is initiated by light activation, however a small portion of unreacted monomers, the residual monomers remain in the polymer matrix, and the polymer structure either could be a linear (thermoplastic) or cross-linked (thermoset). The nomenclature of semi-IPN polymer with a polymer matrix of *bis*-GMA, TEGDMA, and PMMA is called as net – *poly*(methylmethacrylate) – internet – copoly (*bis* – glycidyl – A – dimethacrylate) – tri ethylene glycol dimethacrylate (Vallittu, 2009).

2.2 Chemical stability of polymer surface against solvents

Chemical stability of a polymeric material is its ability to withstand its intrinsic properties when exposed to solutions/chemical reagents. This is governed by various factors such as polymeric molecular structure, fillers, colourants, chemical additives like activators and initiators, along with the time, type, concentration, and temperature at which the solvent interacts with the polymeric material (Brebu, 2020). Also, the stresses moulded-in during processing and stress applied to play a vital role (Devotta *et al.*, 1995). Polymeric materials are affected by the chemical agents by two mechanisms; primarily, the chemical agent behaves like a solvent. Here the solvent dissolves the polymer resulting in loss of physical and mechanical properties, change in the dimensions, degradation, swelling, and eventually leading to the loss of the polymeric mass. Secondly there could be the formation of cracks by the solvent due to reduced resistance of the polymeric material, where the solvent/chemical reagent behaves as stress cracking material (Clough *et al.*, 2017). The type of polymer bonds, degree of crystallinity, branching, bonding distance, along with the energy needed to cleave the bonds determines the chemical stability of the polymer to solvents/chemical reagents (Campo, 2008).

Dental adhesives (dentin primers) are solutions used for adhesion between tooth structures and resin composite blocks of cement or filling materials. They contain the resin monomers making the resin and the dental substrate interaction to achieve. The monomers in adhesive resins and the composite restorative materials are nearly the same. The adhesive resin system contains a hydrophilic group, which enhances the wettability to the dental hard tissues, and a hydrophobic group to undergo copolymerization with the restorative material. Initiators, inhibitors or stabilizers,

solvents, and inorganic fillers are incorporated into the resin adhesive system (Van Landuyt *et al.*, 2007). The monomers that are included in the adhesive resin usually comprise of hydroxyethyl methacrylate (HEMA), TEGDMA, UDMA, and *bis*-GMA. HEMA is incorporated as it is miscible in water and enhancing the polymerizing wettability property of the resin. On the other hand, *bis*-GMA is hydrophobic, absorbing only 3% of water, and it is the main monomer present. TEGDMA can be used due to its hydrophilic nature along with *the Bis-GMA* monomer. Adding the Solvents such as water, ethanol, and butyl alcohol as thinning agents, which enhances the polymerizable monomer for better wetting, spreading and penetration into the resin composite and the dentin substrate (Sofan *et al.*, 2017).

Dental resins absorb water or chemicals, and this process of sorption or desorption can produce some deleterious effect on the resin. There can be volumetric changes taking places, such as plasticization or softening of the resin along with some chemical changes due to oxidation or hydrolysis. The water sorption values for the various resin are *bis*-GMA (3.73wt %), TEGDMA (6.23wt %), UDMA-resin (3.39wt%), *bis*-EMA(2.02wt%) and the 1,10-decanediol dimethacrylate (*D3MA*) (0.58wt %).

The water sorption values of the resin TEGDMA (6.23wt %) and *bis*-GMA (3.73wt %) have a larger value difference as+ compared to the water sorption values of the same monomers with TEGDMA (2.74wt %) and *bis*-GMA (2.35wt %) (Kalachandra and Kusy, 1991). Given that the hydrophilic nature of the resin with *bis*-GMA and TEGDMA is due to the different physical structure of TEGDMA as it is more heterogeneous than *bis*-GMA with spaces between the polymer clusters which can accommodate a larger volume of water. This also allows for the higher flexibility of TEGDMA resin compared to that of the *bis*-GMA (Sideridou *et al.*, 2002).

The chemical composition of the restorative material along with the environment, when exposed to various organic solvents or oral fluids influences the mechanical properties. The deleterious effect on the polymeric network of the restorative material, due to leachable components mainly comprising inorganic ions or filler particles, affects the chemical or physical modification in the structure. Filler particles with metallic ions have an enhanced effect on hydrolytic degradation (Martos *et. al.*, 2013). Restorative materials contain various monomers with varying cytotoxicity. The cytotoxic effects of different monomers commonly used increases as follows: HEMA<TEGDMA <UDMA<BisGMA (Gupta *et. al.*, 2012).

The dissolving process of solvents on the resin polymer is instantaneous, depending on the external mass transfer resistance through the liquid layer adjacent to the solid-liquid interface. An uncrosslinked, amorphous, glassy polymer when in contact with the solvent, the diffusion of the solvent takes place quickly. The dissolution of the polymer by the solvent takes place by its diffusion and chain disentanglement as shown in fig 5 below.

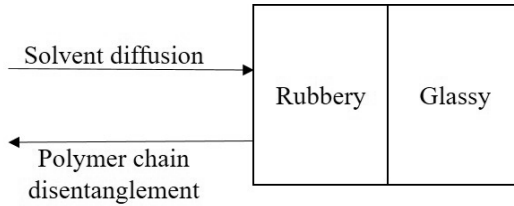


Figure 5: Dissolution process of polymer. (Modified from: Miller-Chou and Koenig, 2003).

2.2.1 Surface crazing

Cracking occurs in polymers, and it usually precedes by crazing. Craze represents that region of the polymer where localized yielding is seen, wherein the polymers are aligned and pulled apart from the adjacent unaffected material into microscopic fibrils (Bazhenov, 2011). It is growing at the free surface level in two directions: propagating outwards and downward direction, and traversing to the area of tensile stress. During the yielding process, the fibrils carry a specific load. Propagation of crazing takes place until the fibrils can no longer be drawn, finally leading to a break in the fibrils, causing fracture or crack in the polymer (van Krevelen and te Nijenhuis, 2009).

Chain drawing in the polymers results in plastic deformation. The picture of the fibrils due to the results of the tensile forces in the formation of a larger volume or void; however, the intermolecular forces oppose this increase in size (Pawlak, 2007). If this happens in a smaller area, the amount formed remains constant. In larger sections, the surrounding unchanged polymer tries to prevent the lateral contraction. It results in the formation of tensile stresses, which run in the perpendicular direction of the drawing directions (Hossain *et al.*, 2009). The stresses thus formed separate the aligned polymer resulting in the void formation and causing crazing, as shown in fig 6.

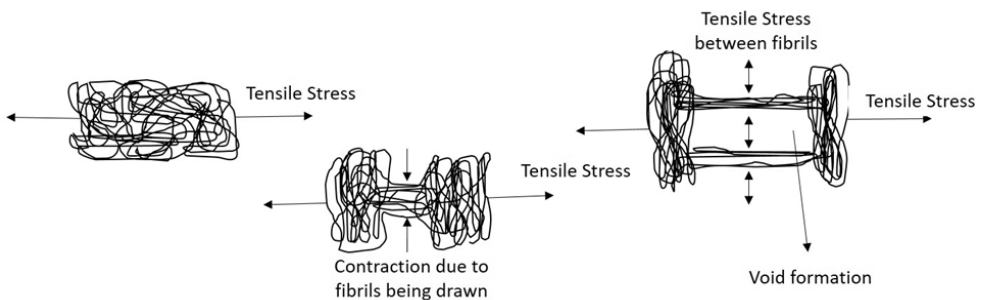


Figure 6: Stages in crazing formation in a polymer. (Modified from: Darvell, 2009).

As the stretching of the fibrils continues, newer and newer voids are formed, and the crazing process continues. The weak van der Waals forces between the polymeric chains make it easier for the resultant tensile stress to pull apart the polymer fibrils. During this process, few of the polymer fibres are drawn apart from the polymer surface. This is known as a craze, and it differs from the crack, as it contains some solid material that connects the drawn fibrils and the aligned fibrils in the polymer. As the crazing process continues, the fibrils are drawn apart until it reaches its end stage where it can be no more drawn. At that point, of time the fibrils tear apart while transferring the load to the adjacent fibrils and the process continues until the release of stresses. This tearing or breaking of the fibrils is known as cracking (Darvell, 2009).

2.2.2 Surface swelling, dissolving and degradation

a. Formation of surface layer and dissolution mechanism

The solvent initially pushes the swollen polymer substrate resulting in the creation of a dilute layer towards the solvent. This process of penetration of the swollen layer increases the swollen layer until it reaches a quasistationary stage wherein further diffusion of the solvent has no effect on the swelling of the polymer layer (Moreaur *et al.*, 2016). The surface layer is seen from the solvent to the polymer, includes different stages or layers formed by the polymer diffusion, as shown in fig 7 below. The polymer contains free voids resulting in a number of channels or pores through which the diffusion of the solvent takes place (Kozanecki *et al.*, 2016).

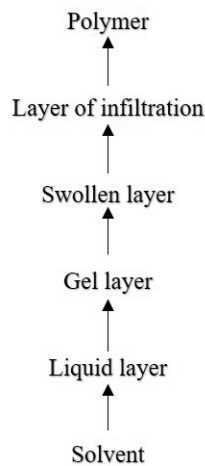


Figure 7: Different phases between polymer and solvent. (Modified from: Miller-Chou and Koenig, 2003).

The dissolution of the polymer takes place by two processes, namely normal diffusion by the formation of a gel layer or without the formation of a gel layer. Normal diffusion involves a different stage, as shown above (Ueberreiter, 1968). The dissolution of the polymer without the formation of a gel layer usually occurs in PMMA. This phenomenon took place when the PMMA which showed normal dissolution at the glass transition temperature, T_g , but, once the temperature was lowered below the T_g the thickness of the gel layer formed also reduced finally resulted in the formation of the cracks. The formation of the cracks was related to the release of stresses that were freezing-in in the polymer at the T_g (Miller-Chou and Koenig, 2003).

b. Molecular weight and polydispersity on polymer dissolution

The molecular weight of the polymer has a profound effect on its dissolution process, with molecular weight being inversely proportional to the dissolution rate. PMMA films have shown a non-linear behaviour between the $\log M_n$ (number of average molecular weight) and the dissolution rate (Cooper *et al.*, 1985). The dissolution rate was also affected by the polydispersity of the polymer, wherein polydispersity polymer materials dissolved twice faster compared to monodisperse polymer (Manjkow *et al.*, 1987). Polymers at a certain level of lowered molecular weight the dissolution resulted in the formation of cracks. It showed that the molecular weight and crazing effect has a direct relation with lowered molecular weight causing crazing at a higher level. Higher molecular weight polymers have higher levels of chain disentanglement, showing a higher degree of swelling before the actual dissolution process begins (Papanu *et al.*, 1989).

c. Polymer structure and composition

The chain chemistry and composition also affect the dissolution process along with the molecular weight. Polymer dissolves by the formation of a swollen layer or by the formation of cracks depending on the pressure stress build up in the polymer. The tacticity of the polymer also plays a role in the type of polymer dissolution. Formation of cracks was seen in tactic PMMA, whereas, in isotactic PMMA it was absent. Moreover, the solubility rate of isotactic PMMA was much higher than that of syndiotactic and heterotactic stereo forms (Ouano and Carothers, 1980)

d. Effect of solvent and its additives on polymer dissolution

The type of solvent used also has a profound impact on the rate of dissolution of the polymer. Smaller molecules containing solvents like methyl acetate and

tetrahydrofuran have shown to be better than bulkier solvents like methyl isobutyl ketone. These materials induced cracks in the polymer due to their ability to faster diffusion rates and swelling power. Sudden rapid drying of a polymer at a higher temperature leaves a larger void facilitating the solvent diffusion easily (Ouano, 1982). The addition of non-solvent molecules significantly increases the dissolution rate of the solvent. This is due to the plasticizing effect of the polymer, allowing for rapid and faster diffusion of the solvent molecules. Water, ethanol, and methanol enhanced the dissolution process, whereas higher alcohols decreased the dissolution rate. Non-solvent molecules enhancement effect on dissolution was lower in low molecular weight polymers (Cooper *et al.*, 1986).

e. Environmental factors, radiation and processing conditions.

Temperature and agitation influence the dissolution process. The dissolution velocity increases with the agitation and stirring frequency of the solvent because of a reduction in the thickness of the surface layer. The dissolution rate approaches a limiting value if the solvent pressure against the polymer surface is increased. In the absence of agitation, a gel layer is formed due to the penetration of the solvent, whereas when agitated the gel layer is absent due stripping of the layer by the stirring process (Pekcan *et al.*, 1997). Dissolution levels are highly sensitive to molecular weight distribution, softback refrigeration process and temperature of dissolution (Manjkow *et al.*, 1987). Radiation leads to a drastic reduction in all homo- and copolymer molecular weights (Parsonage and Peppas, 1987). The dissolution process is a function of the radiation dose and the process starts with the swelling of the glass polymer with water followed by the dissolution by chain disentanglement. That said, the swelling rate exceeds the dissolution rate with the thickness of the gel layer increasing linearly with the square root of time, and vice versa, if the dissolution rate was higher compared to the swelling rate, it resulted in the reduction of the gel thickness (Drummond *et al.*, 1990).

f. Solubility parameters of polymer and solvent

In practice, solubility parameters are predictors of polymer compatibility, chemical resistance, solvent swelling of cured elastomers, solvent permeation rates, and for characterization of the fibre, and filler surfaces (Grulke, 1999). Solubility parameters of the solution have a connection with various physical properties such as wettability and surface tension (Gardon, 1963). The dissolution of a polymer by a solvent largely depends on its chemical structure, and those solubility parameters, which are not far off the polymer dissolves easily. The Hildebrand solubility parameter (δ) provides a numerical approximation of the degree of interaction between materials, and a good

indicator of solubility, particularly for polymers. Materials with identical δ values interact with each other resulting in solvation, miscibility or swelling. For polymers, the internal pressure, swelling data, refractive index, intrinsic viscosity, inverse phase gas chromatography (Zeng et al., 2007), could calculate the solubility parameter. Solubility parameters of ethylene glycol and ethanol, when compared to the solubility parameters of epoxy resin, dimethacrylate, *poly*(methylmethacrylate), indicate that these solvents could potentially dissolve the polymer (Brandrup, 1975).

g. Transesterification

Transesterification is the exchange mechanism between the organic group R'' of an ester and the organic group R' of alcohol. By donating a proton to the carbonyl group, strong acids catalyze the reaction, making it a more potent electrophile. In contrast, bases catalyze the reaction by removing a proton from the alcohol, making it more nucleophilic (Otera, 1993). We can get Esters with larger groups of alcohol from high purity methyl or ethyl esters by heating and evaporating the mixture of ester, acid/base, and large alcohol. Solvolysis or alcoholysis reaction is the reaction of a pure alcohol triglyceride, such as methanol or ethanol, to the fatty acid methyl or ethyl esters, and glycerol (Anastopoulos *et al.*, 2009).

3 Aims

The current series of studies were designed to evaluate the effect of various solvents on the dental resin-based composite and polymer materials at different concentrations and at different time intervals at the level of the surface structure level. The specific aims and working hypothesis were:

1. This study aimed to evaluate the solvent crazing and dissolving effect of ethanol, a solvent/disinfectant on autopolymerized and heat-cured denture base polymers at different concentrations and different treatment intervals. Nanomechanical properties, surface topographic analysis, and surface roughness were analyzed. The hypothesis was that ethanol is known to cause some damage to the denture base polymer. The study results would evaluate the level and the extent at which the damage occurs on the surface microstructure of the multiphase denture based polymers.
2. The goal of this study was to evaluate by comparing and contrasting the findings on the nanomechanical properties of solvents such as ethanol, surface topographic analysis, and surface roughness of heat-cured acrylic resin. The moulding and polymerization of resin done at different post-dough stages, *i.e.*, 0 min, 15 min, and 30 min past the dough stage and treated with different concentrations and different treatment times. The hypothesis for this research was that crazing could be seen in resins, leading to micro-voids or cracks that are induced by solvent/disinfectant materials based on their solubility parameter. The study results would be useful in understanding the polymerization process for attaining better mechanical properties and the solvent effect on the topography of the surface.
3. The aim was to evaluate by comparing and contrasting the effect of ethanol on the nanomechanical properties, surface topographic analysis, and surface roughness along with chemical characterization on dental fibre with a reinforced composite of the semi-interpenetrating polymer network. The hypothesis was based on the effect of ethanol, causing crazing on the *poly*(methylmethacrylate) dental polymer, with similar

composition present in the interpenetrating polymer network systems induced in the dental fibre-reinforced composites. The study results would help in developing newer dental adhesive resins and primers.

4. The fourth aim was to evaluate the effect of a dental adhesive resin and an organic mixture of ethylene glycol and 1,5,7-triazabicyclo [4,4,0] dec-5-ene on the surface of a dimethacrylate polymer and diepoxy polymer surface, used as a control surface. The hypothesis for this study was based on a transesterification reaction wherein a hydroxyl group of ethylene glycol reacts with the ester group of the epoxy polymer resulting in cross-linked polymer dissolution. The molecular dissolution mechanism was studied by analyzing the characterization of the chemical structure by surface profile peak and the effect at different intervals of time on the polymers nanomechanical properties. The study results would help in understanding the behaviour and developing newer dental adhesive resins and primers.

4 Materials and Methods

Commercially available denture base polymers and dental restorative resin-based materials were used in the study. The effect of ethanol (Medical Grade) and an organic catalyst-alcohol solution on the resin-based polymers were evaluated.

4.1 The complete list of materials used in the series of studies

Table 1: List of Chemicals.

Materials	Composition	Manufacturer	Study
Interacryl Hot®	Heat-curing, cadmium-free, methylmethacrylate-based artificial material. Polymer (powder) and monomer (liquid).	Interdent, Opekarniska, Slovenia	I, II
Orthoresin®	Methylmethacrylate, Ethylene glycol dimethacrylate, N, N-dimethyl-p-toluidine	DeguDent, Hanau, Germany	I
EverStick® C&B	Glass fibre impregnated with <i>bis</i> -GMA, PMMA	StickTech-GC, Turku, Finland	III
Component A Biresin® U1419	4,4'-Methylenedi(Cyclohexyl Isocyanate)	SikaAG, Germany	IV
Component B Biresin® U1458	6-Methyl-2,4- <i>bis</i> -(methylthio) phenylene-1,3-diamine diethylmethylbenzenediamine	SikaAG, Germany	IV
Initiator	Camphoroquinone	09003AQV, product code: 124893, Aldrich	IV
Stick Resin®	<i>bis</i> -GMA, TEGDMA	StickTech-GC, Turku, Finland	IV
Ethylene Glycol®	Ethylene glycol anhydrous, 99.8%	Sigma-Aldrich, Belgium	IV
TBD®	1,5,7 triazabicyclo[4,4,0]dec-5-ene, 98%	Sigma-Aldrich, Belgium	IV
Ethanol	Absolute Ethanol, Medical Grade	ACS, Reag. PhEur, 2814 batch 15762402	I, II, III
<i>Bis</i> -phenol-A-glycidyl dimethacrylate	<i>bis</i> -GMA	X9500000/P20, lot: 804-65, Esschem Europe	IV
Tri(ethyleneglycol) dimethacrylate	TEGDMA	X9437446/P5, lot: 807-256, Esschem Europe	IV
2(Dimethylamino) ethylmethacrylate	DMAEMA	BCBP5648V, product code: 234907, Aldrich	IV

Key: *bis*-GMA-bisphenol-A-glycidyl dimethacrylate, TEGDMA – tri (ethyleneglycol) dimethacrylate, DMAEMA – 2 – (dimethylamino) ethylmethacrylate, PMMA-*poly*(methylmethacrylate).

4.2 Specimen preparation and distribution

4.2.1 Specimen preparation and distribution for evaluation of heat and autopolymerized denture base polymers (Study-I)

A total of 200 specimens measuring in 10 mm x 10 mm x 3 mm of both heat cured and autopolymerized acrylic resin were prepared. A ratio of 3:1 for the polymer to monomer was used for both the heat-cured and autopolymerized resin. The curing time for heat-cured resin was 90 min at a temperature of 74 °C with 30 min boiling at 100 °C. Autopolymerized acrylic resin was cured in a pressure flask at 45 °C – 50 °C at a pressure of 207 KPa for a time period of 9 min as recommended by the manufacturer. The surfaces were wet ground and polished to obtain uniform smoothness, with the removal of any gross nodules or surface irregularities using a lathe mounted acrylic bur and 360-grit sandpaper. Final polishing was done by using a 600-grit disc of silicon carbide for a period of 30 s, the load of 13 N pressure at 100 rpm using an automated polishing machine. Both the heat-cured and autopolymerized acrylic resin were treated with an ethanol concentration of 99.9%, 70% and 40% ethanol for 30 s, 60 s and 120 s. The sample distribution for heat-cured and autopolymerized acrylic resin specimens is shown in fig 8.

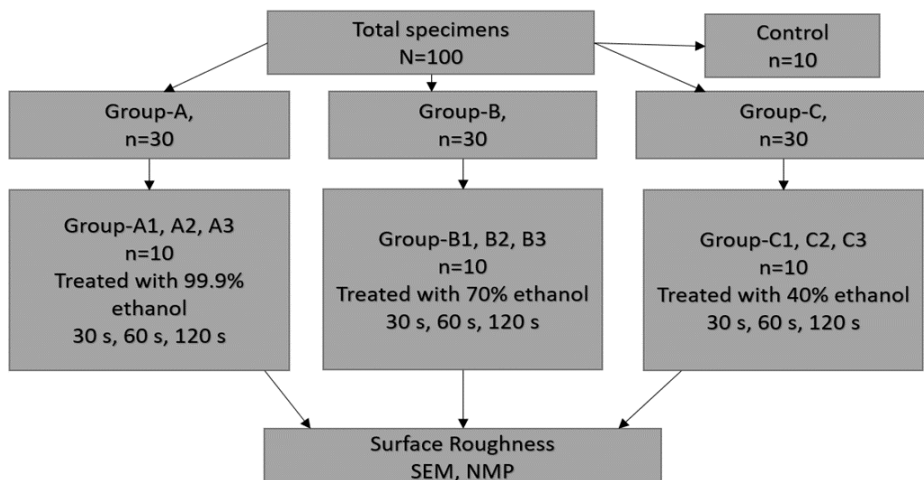


Figure 8: Specimen distribution for heat cured and autopolymerized acrylic resin for analysis of S_a , NMP and SEM.

The specimens were completely immersed with solvent in the crucible, for the specific treatment at a given time at ambient room temperature of 23 ± 1 °C. Further, the specimens were rinsed with tap water and air dried and subjected to analysis.

Specimens in group A1, B1 and C1, were treated for 30 s, specimens in group A2, B2 and C2 were treated for 60 s and specimens in group A3, B3 and C3 were treated for 120 s and were subjected to analysis of surface roughness, surface topographic analysis by (SEM) and nanomechanical (NMP) properties.

4.2.2 Specimen preparation and distribution of heat-polymerized *poly*(methylmethacrylate) acrylic resin cured at the different post dough stage (Study-II)

A total of 200 each specimen was prepared from heat polymerized acrylic resin measuring in 10 mm x 10 mm x 3 mm in size, wherein the packing of the resin was done at three different time intervals past the dough stage, 0 min, 15 min and 30 min. The monomer to polymer ratio was in the ration of 1:3. The specimens were prepared at a room temperature of 23° C and 30% relative humidity. Polymerization was done for 90 min at 74° C, followed by a further 30 min boiling at 100° C as recommended by the manufacturer. The surfaces were wet ground and polished using a rag wheel and pumice. One group of specimens was prepared where the resin was packed immediately after reaching the dough stage 0 min, another at 15 min past dough stage and the last group at 30 min past dough stage. The specimens in each group were treated with an ethanol concentration of 99.9%, 70% and 40% ethanol for 30 s, 60 s and 120 s. The specimen distribution is shown in fig 9.

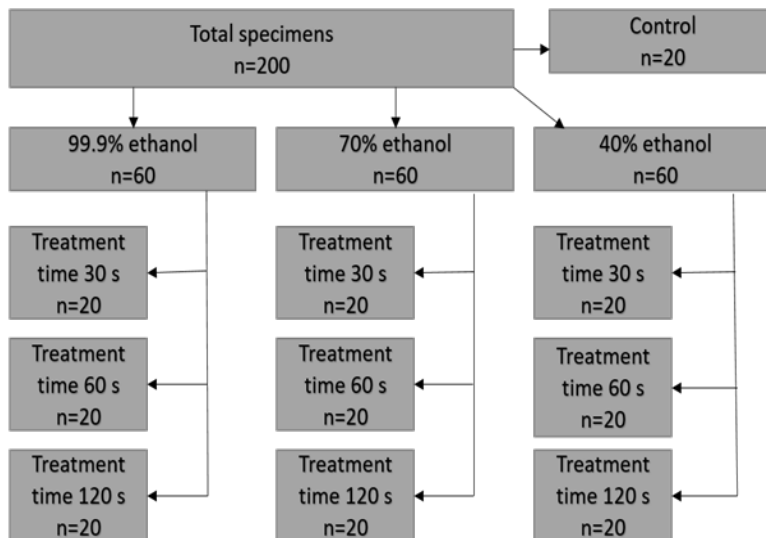


Figure 9. Specimen distribution for each group (0 min, 15 min and 30 min post dough stage) for analysis S_a , NMP and SEM.

The specimens were completely immersed with solvent in the crucible, for the specific treatment at a given time at ambient room temperature of 23 ± 1 °C. Further, the specimens were rinsed with tap water and air dried and subjected to analysis. The specimens in each group (n=20) were treated with different concentrations of ethanol for different time period as mentioned in fig 12 above. In all the groups 15 of the specimens (n=15) were used for the analysis of surface roughness (S_a), and nanomechanical property analysis (NMP) and 5 specimens (n=5) were used for the analysis by scanning electron microscope (SEM). The data was then compared with that of the control group.

4.2.3 Specimen preparation and distribution of semi-interpenetrating polymer network polymer matrix of fibre reinforced composite (Study-III)

A total of 240 specimens of semi-IPN fibre reinforced composites (EverStick C&B) were prepared using a silicone putty (Affinis Putty, Coltene/Whaledent, Altstätten, Switzerland) for preparing and standardizing the size and shape. The specimens were cut off and placed inside the silicone mould. This was pressed against two glass plates for obtaining an even and a flat surface. The specimens were polymerized for 40 s by a handheld polymerizing unit with an irradiance output of 1150 mW/cm² (Elipar S10; 3M ESPE, USA). The irradiance output was measured on a Spectro radiometrically calibrated NIST-referenced USB 4000 spectrometer, Managing Accurate Resin Curing (MARC) device.

The prepared specimens were randomly divided into two groups of 120 each, light-cured and post-heat-cured group. The light-cured and post-heat-cured group were further heat-cured in the oven for 25 min at 95^o C (Targis Power, Ivoclar, Vivadent, Schaan, Lichtenstein). The specimens were polished by using a 1200 grit silicon carbide grinding paper under running water for obtaining a uniformly flat surface and to expose the glass fibres and the matrix in between. All the specimens were washed with deionized water in an ultrasonic bath (Quantrex 90; L&R Ultrasonics, USA) for 10 min and were later dried at an ambient laboratory temperature ($23^{\circ}\text{C} \pm 1^{\circ}\text{C}$) for 60 min. Before the specimens were grouped, 10 randomly selected specimens were analyzed for surface roughness (S_a), Scanning electron microscope (SEM), Fourier Transform Infrared (FTIR) spectroscopic and nanomechanical property analysis (NMP). The specimens were later grouped, as shown in fig 10.

The specimens were completely immersed with solvent in the crucible, for the specific treatment at a given time at ambient room temperature of 23 ± 1 °C. Further, the specimens were rinsed with tap water and air dried and subjected to analysis. The specimens were treated with different ethanol concentrations with varying times of treatment. They were evaluated for surface roughness (S_a), scanning electron

microscope (SEM), Fourier Transform-Infrared (FTIR) spectroscopy and nanomechanical property analysis (NMP). These were then compared and contrasted with the control group.

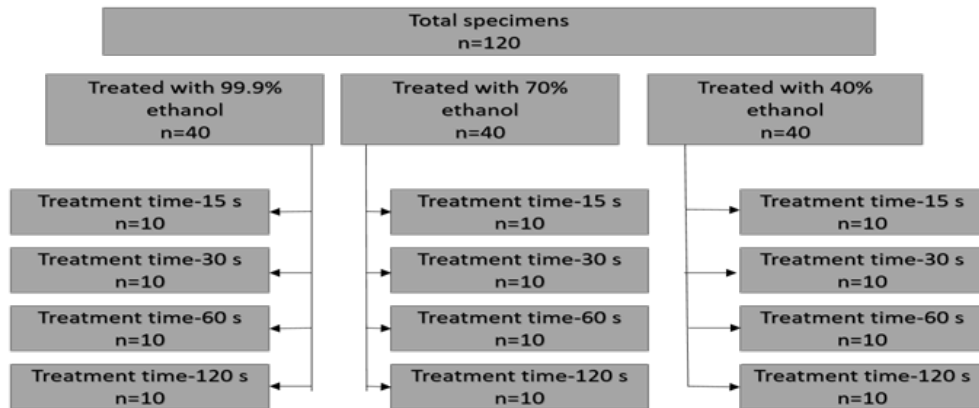


Figure 10. Specimen distribution for each light-cured and light-cured and post heat-cured group for analysis of S_a , NMP, FTIR and SEM.

4.2.4 Specimen preparation and distribution for evaluation of dimethacrylate polymer and epoxy resin (Study-IV)

A total of 200 specimens (10 mm × 5 mm × 3 mm) of epoxy resin and dimethacrylate polymer were prepared. A mixture of 70% *bis*-phenol-A-glycidyl dimethacrylate (*bis*-GMA), 30% tri(ethylene glycol) dimethacrylate (TEGDMA), 0.7% 2-(dimethylamino) ethyl methacrylate (DMAEMA), 0.7% camphoroquinone, were placed into moulds and pressed against two glass plates to achieve an even and smooth 3 mm thick surface. The mixture was first light-healed for 40 s with a hand-held light polymerizing unit (Elipar S 10; 3 M ESPE, Minnesota, USA), and then post-healed for 25 min in an oven (Targis Energy, Ivoclar, Vivadent, Schaan, Lichtenstein) at 95 °C. The samples were ground to achieve a smooth, flat surface using a 1200 grit silicon carbide grinding paper under running water. Next, the specimens were washed for 10 min with deionized water in an ultrasonic bath (Quantrex 90; L&R Ultrasonics, Kearny, New Jersey, USA) and allowed to dry for 60 min at ambient laboratory temperature (23 °C ± 1 °C).

Control substrate specimens of bisphenol-based diepoxy resin were prepared by mixing 100 parts by weight of an elastomeric casting resin (Component A Biresin® U1419, Sika AG, Germany) and 16 parts by weight of an amine (Component B Biresin® U1458, Sika AG, Germany) which were mixed by manual stirring in a beaker. The amine accelerator used to cure epoxy monomers results in the polymer without

ester bonds, and thus the epoxy polymers acted as a negative for transesterification to take place. A polyvinyl siloxane putty (Affnis Putty, Coltene/Whaledent, Altstätten, Switzerland) material was used to prepare and standardize the size and shape of a mould for preparing the substratum specimens. The mixture was then placed in a degas vacuum for 10 min, then poured into polyvinyl siloxane moulds and pressed against two glass plates to obtain a flat, even surface of 5 mm thick. The mixture was then cured for 8 h at 80 °C. The specimen distribution is shown in fig 11. The specimens in both the groups were treated with both adhesive Resin (SR) and, ethyleneglycol+1,5,7-triazabicyclo [4,4,0] dec-5-ene mixed in the ratio of 3:1 for 5 min and 24 h. The specimens were completely immersed with solvent in the crucible, for the specific treatment at a given time at ambient room temperature of 37 ± 1 °C. Further, the specimens were rinsed with tap water and air dried and subjected to analysis. Scanning electron microscope (SEM), surface profile peak (R_p), Fourier Transform Infrared (FTIR) spectroscopy and nanomechanical property analysis (NMP) was done and compared with the control group.

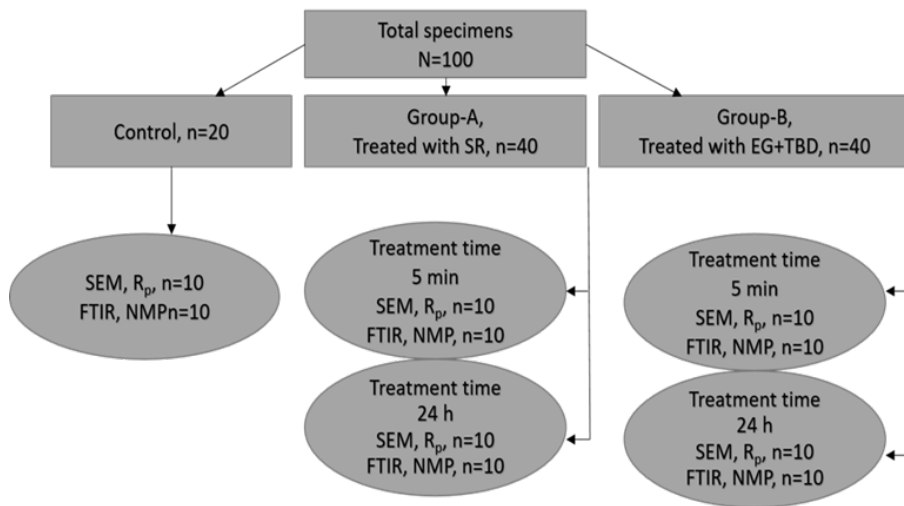


Figure 11. Specimen distribution for each material (epoxy and dimethacrylate resin) for analysis of R_p , NMP, FTIR and SEM.

4.3 Methodology

4.3.1 Surface assessment (S_a -study I, II, III and R_p study IV)

Surface roughness frequently referred to as roughness representing the surface texture. It is quantified from its ideal form by the deviations in the direction of the normal vector of a real surface. Larger deviations meaning the surface texture is

rough or else smooth. High-frequency, short-wavelength portion of a measured surface is typically considered as roughness. Surface roughness is the average value of the absolute value of the profile height over a given specific area. It is represented by R_a for two-dimensional and S_a for three-dimensional analyses. R_p represents the maximum peak height.

A non-contact optical profilometer (Bruker, Contour GT, Tucson, AZ, USA) was used to assess the surface topography for surface roughness (S_a) and surface profile peak (S_p or R_p). A nano lens AFM module with a fully automated turret and platform which can be programmable in X, Y and Z axis is used. Laser light is delivered by the profilometer to guide the operator for the selection of a particular area on the specimen for evaluation. Randomly selected five areas were analyzed for the surface roughness (Study I, II and III) and profile peak (Study IV). The specimens were placed on a platform in a perpendicular direction to the optical beam. The long and short cut off wavelength was 0.08 and 0.25 mm in X and Y directions was used. The images were captured in a 3x optical zoom integrated into "vision 64" software. Moreover, the profile peak data (R_p) were correlated with FTIR analysis to check the effect of solvents on the specimen

4.3.2 Scanning electron microscope analysis (Study I–IV)

The gross surface topographical changes at a microstructural level were assessed before and after the treatment with the solvents and adhesive resins were analyzed using SEM (JSM-6360LV, JEOL, Tokyo, Japan). Analysis of the specimens was performed at different magnifications. Original magnification of 1000 x was used in study I and II, 250 x and 700 x in study III and IV respectively. The width of the affected layer by ethanol on autopolymerized resin in a study I was also measured on the SEM image.

4.3.3 Nanoindentation (Study I–IV)

Nanoindentation is a viable test for identifying the quantitative mechanical properties of materials. In the field of dentistry, nanoindentation is used for analysis and evaluating the mechanical properties of various biomaterials and dental hard tissues. The mechanical properties of the specimen are determined by the load-displacement response involving the application of load at nanoscale for indenting a specimen with continuous documentation of the load and displacement (Fujisawasa, 2007). It also facilitates the accurate assessment of load and depth of indentation. The data obtained indicate that the load required for indenting a specimen and for the elastic recovery of the specimen depends upon unloading. The nanomechanical properties were assessed using a nano-indenter (Bruker, Tucson, AZ, USA)

equipped with a three-sided Berkovich diamond indenter tip. Modulus of elasticity and surface nano hardness was assessed for all the specimens before and after treatment with solvents at different time intervals and concentration. Tests were performed at a controlled temperature of 23°C and low noise conditions. The loading and unloading rate of 0.5mN/s was used and 10 s of resting period at maximum load and varying the maximum load between 1 and 50 mN in study I and II. Loading and unloading values of 0.01mN/s and 0.02mN/s respectively with a maximum load of 20mN and a resting period of 10 s was employed in study III. Loading and unloading values of 0.2 mN/s and 0.2 mN/s respectively with a maximum load of 50 mN and resting time of 10 s, was employed in study IV.

4.3.4 Fourier Transform Infrared spectroscopic analysis (Study III–IV)

Fourier Transform Infrared Spectroscopy (FTIR), is a technique used for analysis and identification of various organic and inorganic polymers wherein infrared light is used to scan the specimens for observation of the chemical properties. Infrared radiation with the wavenumbers from 10,000 to 100 cm^{-1} is passed through the specimens, wherein some radiations are absorbed, and some passed through. Rotational and vibrational energy results from the amount of absorbed radiation by the specimens ranging from 4000 cm^{-1} to 400 cm^{-1} , which is fingerprint area that represents particularity for each specimen. This makes FTIR analysis an excellent tool for chemical characterization of each specimen. The absorption intensity is correlated to the quantity of the functional group present in the specimen. However, in specimens with typically less than 5% of the overall constituent, very little information could be gathered. The earlier only transmission was the analysis technique available which made the samples to be translucent for analysis. This drawback was overcome with the introduction of reflectance techniques known as the ATR (Attenuated Total Reflectance), for observing the energy of each functional group in a non-translucent material to introduce and observe the energy.

FTIR (Thermo Scientific, iD7 ATR, Canada) was used to perform a surface chemical characterization of the specimens. In the wave-number range 750–4000 cm^{-1} , Attenuated Total Reflection (ATR), the most common sampling technique for FTIR analysis was employed. The specimens were subjected to ATR element made of diamond, in which the infrared (IR) beam enters the ATR crystal at an angle of 45° which is fully reflected the specimen interface at the crystal. In Studies III and IV, the IR spectrum was plotted as wavenumber versus reflectance.

4.3.5 Statistical analysis

Statistical analysis was performed using SPSS (Statistical Package for Social Sciences) version 23 (IBM, USA) in study I and II and version 20.0 (SPSS, Chicago, IL, USA) in study III and IV.

In the study, I: Results were statistically analyzed using a one-way ANOVA and Scheffe post-hoc test at a mean level of 5 percent for comparison of mean S_a values, time interval dissolution of the polymer, and specimen NMP properties. Linear regression analysis was used to determine a correlation between the length of ethanol treatment and the dissolved area's estimated thickness for autopolymerized resin at the p -value less than 0.05 was considered as significant.

In study II: The findings of S_a and NMP (nano-hardness and elasticity modulus of Young) with ethanol treatment for groups of 0 min, 15 min, and 30 min doughing time at different time intervals were statistically evaluated by two-way and three-way ANOVA and Tukey's post-hoc HSD measures. A regression analysis was performed for groups of 0 min, 15 min, and 30 min with a dependent variable (x-axis) as the treatment time by ethanol, and an independent variable (y-axis) as the nano hardness (GPa) between the treatment time and nano hardness. The p -value less than 0.05 was considered as significant.

In study III: Two-way ANOVA and Tukey's post hoc tests were applied. The regression analysis was performed at different concentrations of ethanol and at different time intervals for surface roughness and nanomechanical properties. The p -value less than 0.05 was considered as significant.

In study IV: One –way ANOVA and the Tukey's post hoc tests were applied. For NMP, linear and nonlinear regression analyzes were performed at different time intervals for the two solvents. The p -value less than 0.05 was considered as significant.

5 Results

5.1 Effect of ethanol on the micro-surface structure and properties on heat and autopolymerized denture base polymers (Study-I)

The mean values for the S_a measurement showed that ethanol affected the S_a , which varied between the acrylic resins of heat-cured and autopolymerized treated at different ethanol concentrations. Statistically significant and non-significant changes for both the heat-cured and auto-polymerized resins were seen at different ethanol concentrations and different time intervals, as shown in table 2 and 3.

Table 2: Surface roughness (S_a) (μm) of heat-cured polymerizing acrylics. (Adapted from original publication I).

ETHANOL CONCENTRATION	CONTROL	30 S	60 S	120 S
99.9%	0.164 ^a ±0.01	0.171 ^a ±0.01	0.169 ^a ±0.01	0.178 ^a ±0.01
70%	0.145 ^a ±0.005	0.145 ^a ±0.003	0.146 ^a ±0.005	0.164 ^b ±0.005
40%	0.185 ^a ±0.002	0.212 ^a ±0.007	0.192 ^a ±0.009	0.195 ^a ±0.009

A different superscript letters in the same row indicate statistically significant ($p < 0.01$).

Table 3: Surface roughness (S_a) (μm) of autopolymerized acrylics. (Adapted from original publication I).

ETHANOL CONCENTRATION	CONTROL	30 S	60 S	120 S
99.9%	0.245 ^a ±0.006	0.243 ^a ±0.001	0.267 ^b ±0.005	0.291 ^c ±0.003
70%	0.219 ^a ±0.003	0.210 ^a ±0.003	0.214 ^a ±0.003	0.209 ^a ±0.003
40%	0.199 ^a ±0.003	0.207 ^a ±0.005	0.203 ^a ±0.005	0.207 ^a ±0.01

A different superscript letters in the same row indicate statistically significant ($p < 0.01$).

Nanomechanical properties were also affected with maximum nano hardness seen at 70% ethanol treatment for 30 s treatment time in both the heat-cured and auto

polymerized resins as shown in table 4 and Young modulus of elasticity as shown in table 5. Also, the thickness of dissolving and crazing increased with increasing the period of contact seen at the interface between the polymer bead and the matrix, as shown in table 6. Regression analysis showed a correlation with R^2 value of 0.83 between the time of treatment and the extent of the thickness of the affected layer width in autopolymerized acrylic resin, as shown in fig 12.

Table 4: Nanohardness (GPa) of heat-cured (HC) and autopolymerized (AP) acrylics. (Adapted from original publication I).

ETHANOL CONCENTRATION	CONTROL		30 S		60 S		120 S	
	HC	AP	HC	AP	HC	AP	HC	AP
99.9%	0.286 ^{AC}	0.044 ^a	0.232 ^B	0.123 ^a	0.155 ^{AB}	0.150 ^a	0.194 ^C	0.074 ^a
70%	0.242 ^{AD}	0.069 ^a	0.332 ^A	0.134 ^{abc}	0.272 ^{BC}	0.093 ^b	0.313 ^D	0.077 ^c
40%	0.241 ^A	0.053 ^{ab}	0.201 ^B	0.129 ^{ab}	0.188 ^{AC}	0.078 ^a	0.246 ^C	0.099 ^b

Different superscript small and capital letters in the same row indicate statistically non-significance at $p < 0.05$.

Table 5: Young's modulus of elasticity (GPa) of heat-cured (HC) and autopolymerized (AP) acrylics. (Adapted from original publication I).

ETHANOL CONCENTRATION	CONTROL		30 S		60 S		120 S	
	HC	AP	HC	AP	HC	AP	HC	AP
99.9%	2.072 ^{AB}	0.618 ^a	1.915 ^{CD}	2.070 ^a	0.982 ^{AC}	1.899 ^a	1.211 ^{BD}	1.323 ^a
70%	2.988 ^A	0.533 ^{ab}	3.010 ^B	1.191 ^a	2.585 ^{ABC}	1.193 ^b	2.940 ^C	1.012 ^{ab}
40%	3.054 ^A	0.410 ^{ab}	2.028 ^A	1.326 ^b	1.533 ^A	1.282 ^a	2.752 ^A	1.578 ^a

Different superscript small and capital letters in the same row indicate statistically non-significance at $p < 0.05$.

Table 6: Affected width of measurements (μm) by ethanol concentration and treatment time on autopolymerized acrylics. (Adapted from original publication I).

ETHANOL CONCENTRATION	30 S	60 S	120 S
99.9%	2.44 ^a ±0.07	3.42 ^b ±0.06	5.6 ^c ±0.1
70%	2.49 ^a ±0.07	3.61 ^b ±0.1	5.87 ^c ±0.06
40%	3.69 ^a ±0.05	4.6 ^b ±0.09	6.4 ^c ±0.1

Different superscript number in the same row indicate statistically significant at $p < 0.01$.

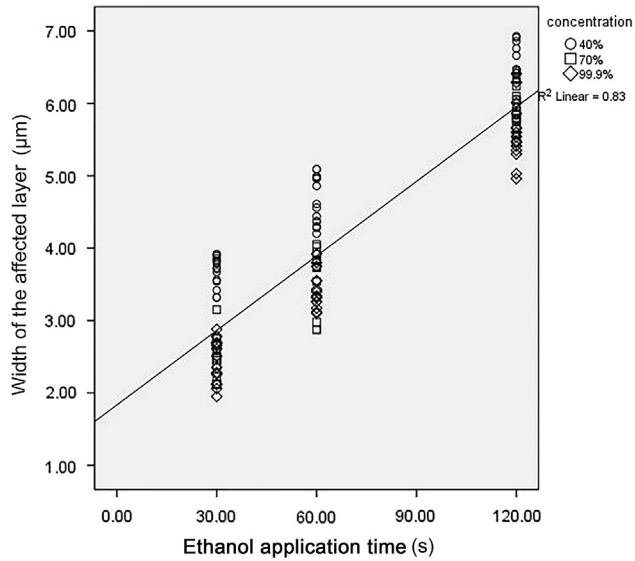


Figure 12: Representative curve for regression correlation between the affected width of by ethanol concentration and treatment time on autopolymerized acrylics. (Adapted from original publication I).

Autopolymerized resins showed surface topographic changes due to dissolving and crazing effects of ethanol which was absent in heat-cured resins.

The changes were shown by SEM surface topographic imaging, as shown in fig 13.

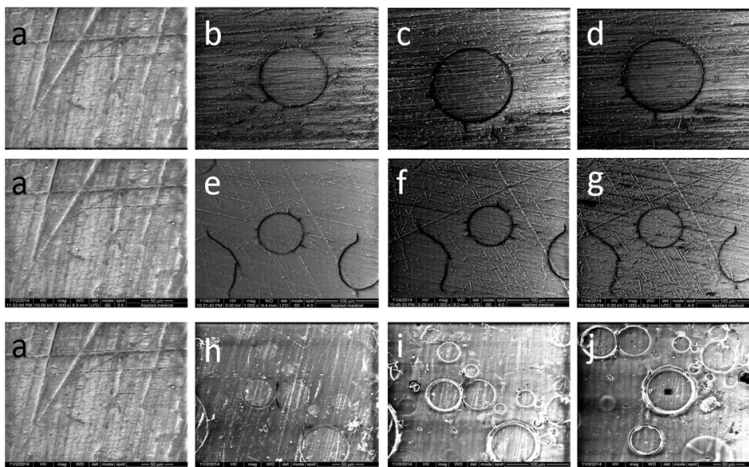


Figure 13: Representative SEM images of autopolymerized acrylic resin treated with 40% ethanol (30 s, 60 s and 120 s, - fig. **b, c, d**). 70% ethanol (30 s, 60 s and 120 s, - fig. **e, f, g**) and 99.9% ethanol (30 s, 60 s and 120 s, - fig. **h, i, j**) with control (**a**) with original magnification of 1000 x. (Adapted from original publication I).

5.2 Effect of ethanol on heat-polymerized poly(methylmethacrylate) acrylic resin cured at the different post dough stage (Study-II)

Surface roughness and nanomechanical properties were affected upon treatment with ethanol which varied based on its concentration and treatment time on specimens prepared at different post dough time, as shown in table 7.

Table 7: Surface roughness (μm) and nanomechanical properties (GPa) of heat-cured resin treated with ethanol at different concentrations and period. (Adapted from original publication II).

		0 min			
		CONTROL	30 s	60 s	120 s
40%	Surface roughness, S_a	0.163 ^{a A}	0.158 ^{a A,B}	0.148 ^{a, AB}	0.155 ^{a AB}
	Nanohardness, GPa	0.183 ^{a A}	0.185 ^{a A}	0.193 ^{a A}	0.215 ^{a A}
	Young's modulus	2.349 ^{a A}	2.670 ^{a B}	3.937 ^{b B}	4.138 ^{b C}
70%	Surface roughness, S_a	0.162 ^{a A}	0.172 ^{a A}	0.175 ^{a A}	0.168 ^{a, A}
	Nanohardness, GPa	0.182 ^{a A}	0.148 ^{b B}	0.188 ^{a A}	0.206 ^{a B}
	Young's modulus	2.479 ^{b A}	1.501 ^{a A}	3.024 ^{c A}	3.428 ^{c B}
99.9%	Surface roughness, S_a	0.164 ^{a A}	0.134 ^{b B}	0.138 ^{b B}	0.132 ^{b, B}
	Nanohardness, GPa	0.181 ^{a A}	0.175 ^{a A}	0.167 ^{a A}	0.173 ^{a B}
	Young's modulus	2.669 ^{a A}	2.693 ^{a B}	2.509 ^{a A}	2.281 ^{a A}
		15 min			
		CONTROL	30 s	60 s	120 s
40%	Surface roughness, S_a	0.167 ^{a A}	0.147 ^{a A}	0.152 ^{a A}	0.154 ^{a A}
	Nanohardness, GPa	0.175 ^{a A}	0.144 ^{b A}	0.186 ^{a A}	0.192 ^{c A}
	Young's modulus	2.447 ^{a A}	3.622 ^{b A}	2.190 ^{a A}	2.642 ^{a A}
70%	Surface roughness, S_a	0.165 ^{a A}	0.162 ^{a A}	0.164 ^{a A}	0.166 ^{a A}
	Nanohardness, GPa	0.175 ^{a, b A}	0.187 ^{a A, B}	0.14 ^{b B}	0.179 ^{a B}
	Young's modulus	2.572 ^{a A}	3.618 ^{b A}	2.230 ^{a A}	2.649 ^{a A}
99.9%	Surface roughness, S_a	0.143 ^{a A}	0.148 ^{a A}	0.144 ^{a A}	0.147 ^{a A}
	Nanohardness, GPa	0.179 ^{a A}	0.196 ^{a B}	0.187 ^{a A}	0.193 ^{a A}
	Young's modulus	2.581 ^{a A}	3.689 ^{b A}	2.766 ^{a B}	2.968 ^{a, b A}
		30 min			
		CONTROL	30 s	60 s	120 s
40%	Surface roughness, S_a	0.187 ^{a A}	0.186 ^{a A}	0.191 ^{a A}	0.198 ^{a A}
	Nanohardness, GPa	0.172 ^{a A}	0.147 ^{a A}	0.184 ^{a A}	0.174 ^{a A}
	Young's modulus	2.403 ^{a, b A}	1.827 ^{a A}	3.116 ^{b A}	2.520 ^{a, b A}
70%	Surface roughness, S_a	0.169 ^{a A}	0.17 ^{a A, B}	0.17 ^{a A, B}	0.17 ^{a B}
	Nanohardness, GPa	0.171 ^{a A}	0.186 ^{a A}	0.199 ^{a A}	0.179 ^{a A}
	Young's modulus	2.327 ^{a A}	3.523 ^{b B}	3.149 ^{a, b A}	2.370 ^{a A}
99.9%	Surface roughness, S_a	0.164 ^{a A}	0.161 ^{a B}	0.156 ^{a B}	0.159 ^{a B}
	Nanohardness, GPa	0.175 ^{a A}	0.162 ^{a A}	0.165 ^{a A}	0.219 ^{b B}
	Young's modulus	1.994 ^{a A}	1.700 ^{a A}	1.779 ^{a B}	4.204 ^{b B}

Different capital letters in the same column and different small letters in the same row indicate statistically significant ($p < 0.05$)

SEM images showed minor topographical changes in the resin caused by ethanol. They did not reveal the presence of polymer beads, both in control and after ethanol treatments seen in autopolymerized acrylic resin. Correlation between ethanol treatment time and post dough time for nanohardness was shown by regression analysis for specimens prepared at different dough time, as shown in fig 14.

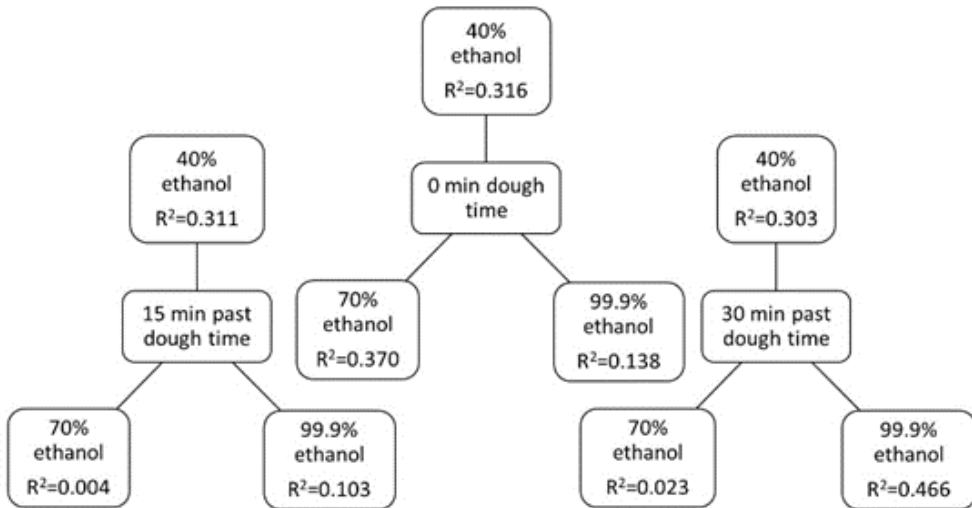


Figure 14: Regression analysis correlation values for ethanol concentration and treatment time intervals.

5.3 Effect of ethanol on semi-interpenetrating polymer network polymer matrix of fibre-reinforced composite (Study-III)

Surface roughness analysis for both the light-cured and light-cured and post-heat-cured FRC's were affected by ethanol treatment. In the light-cured group as the concentration of ethanol and treatment time was increased, it also increased the S_a , however in the light-cured and post-heat-cured group, less variation was seen. The light-cured group treated with 99.9% ethanol for 120 s showed the highest roughness value of $0.733 \mu\text{m}$. Each concentration of ethanol showed a statistically significant difference based on the treatment time at $p < 0.05$, as shown in table 8.

Table 8: Surface roughness (S_a) (μm) of light-cured (L) and light-cured and post heat-cured (LH)-FRC. (Adapted from original publication II).

ETHANOL CONCENTRATION	CONTROL	15 S	30 S	60 S	120 S
	L-Group				
99.9%	0.325 ^a	0.535 ^b	0.540 ^b	0.624 ^c	0.733 ^d
70%	0.226 ^a	0.225 ^a	0.253 ^b	0.275 ^b	0.328 ^b
40%	0.158 ^a	0.157 ^a	0.158 ^a	0.203 ^b	0.255 ^c
LH-Group					
99.9%	0.142 ^a	0.145 ^a	0.173 ^b	0.189 ^b	0.222 ^d
70%	0.140 ^a	0.146 ^a	0.152 ^a	0.189 ^b	0.202 ^b
40%	0.134 ^a	0.143 ^a	0.159 ^a	0.160 ^a	0.159 ^a

Different superscript small letters in the same row indicate statistically significant at $p < 0.05$.

Table 9: Statistical results of surface nanohardness (GPa) of light-cured (L) and light-cured and post heat-cured (LH)-FRC. (Adapted from original publication II).

ETHANOL CONCENTRATION	CONTROL	15 S	30 S	60 S	120 S
	L-Group				
99.9%	0.108 ^a	0.424 ^b	0.655 ^b	1.139 ^c	1.296 ^c
70%	0.108 ^a	0.649 ^b	0.835 ^b	1.245 ^c	1.292 ^c
40%	0.108 ^a	0.369 ^b	0.517 ^b	1.021 ^c	1.383 ^d
LH-Group					
99.9%	0.301 ^a	0.586 ^b	1.081 ^c	1.669 ^d	1.908 ^e
70%	0.301 ^a	0.647 ^b	1.065 ^c	1.734 ^d	1.895 ^d
40%	0.301 ^a	0.727 ^b	1.149 ^c	1.189 ^c	1.579 ^d

Different superscript small letters in the same row indicate statistically significant at $p < 0.05$.

Table 10: Statistical results of modulus of elasticity (GPa) of light-cured (L) and light-cured and post heat-cured (LH)-FRC. (Adapted from original publication II).

ETHANOL CONCENTRATION	CONTROL	15 S	30 S	60 S	120 S
	L-Group				
99.9%	4.856 ^a	8.648 ^b	9.894 ^b	14.329 ^c	14.663 ^c
70%	4.856 ^a	11.855 ^b	15.754 ^c	15.797 ^c	16.863 ^c
40%	4.856 ^a	8.687 ^b	9.893 ^b	12.946 ^c	16.568 ^d
LH-Group					
99.9%	8.882 ^a	12.592 ^b	16.006 ^c	19.516 ^d	20.533 ^d
70%	8.882 ^a	11.090 ^b	12.615 ^b	19.937 ^c	21.217 ^c
40%	8.882 ^a	11.371 ^b	13.059 ^b	17.811 ^c	22.798 ^d

Different superscript small letters in the same row indicate statistically significant at $p < 0.05$.

Nanomechanical properties were affected upon treatment with ethanol at different concentrations and time period. Specimens which were light-cured and additionally posted heat-cured showed better nanohardness compared to specimens that were only light cured. 1.91 GPa was the highest nanohardness value measured for specimens treated with 99.9 % ethanol at 120 s and modulus of elasticity was the highest (22.79 GPa) for the group treated with 40 % ethanol at 120 s seen in specimens which were heat cured post light curing. Both light-cured and light-cured and post-heat-cured group specimens showed statistically significant difference at different concentrations and treatment time intervals at $p < 0.05$, as shown in tables 9 and 10.

Regression correlation between ethanol treatment time for surface roughness and nanomechanical properties for the light-cured and light-cured and post heat-cured treated at varying concentrations of ethanol is shown in fig 15 and 16, respectively.

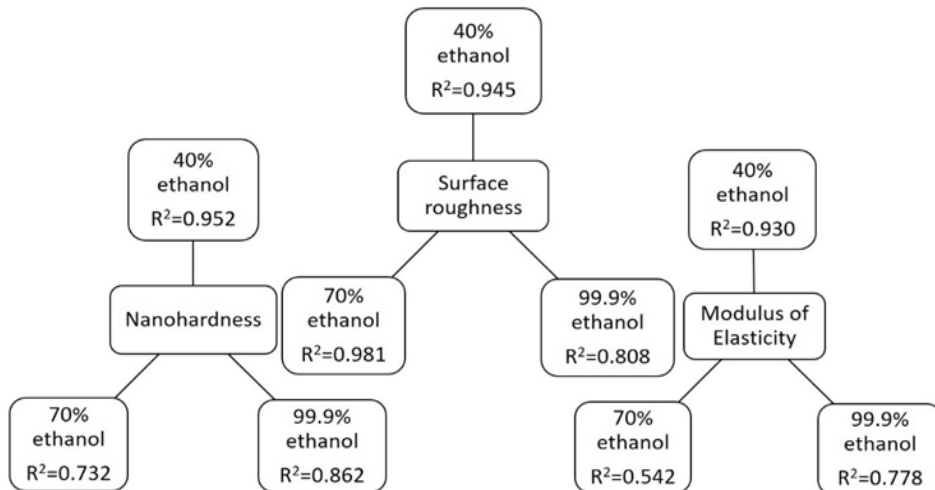


Figure 15: Regression analysis correlation values for ethanol concentration and treatment time intervals of light-cured FRC.

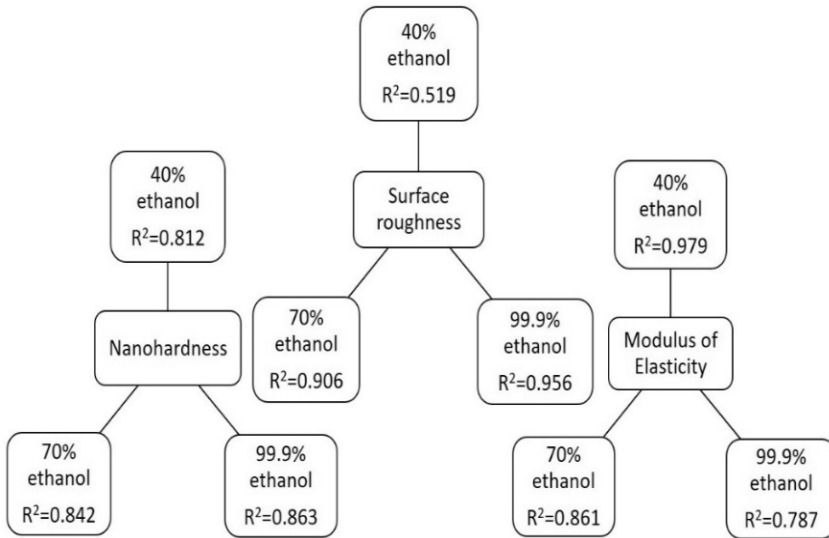


Figure 16: Regression analysis correlation values for ethanol concentration and treatment time intervals of light-cured and post heat-cured FRC.

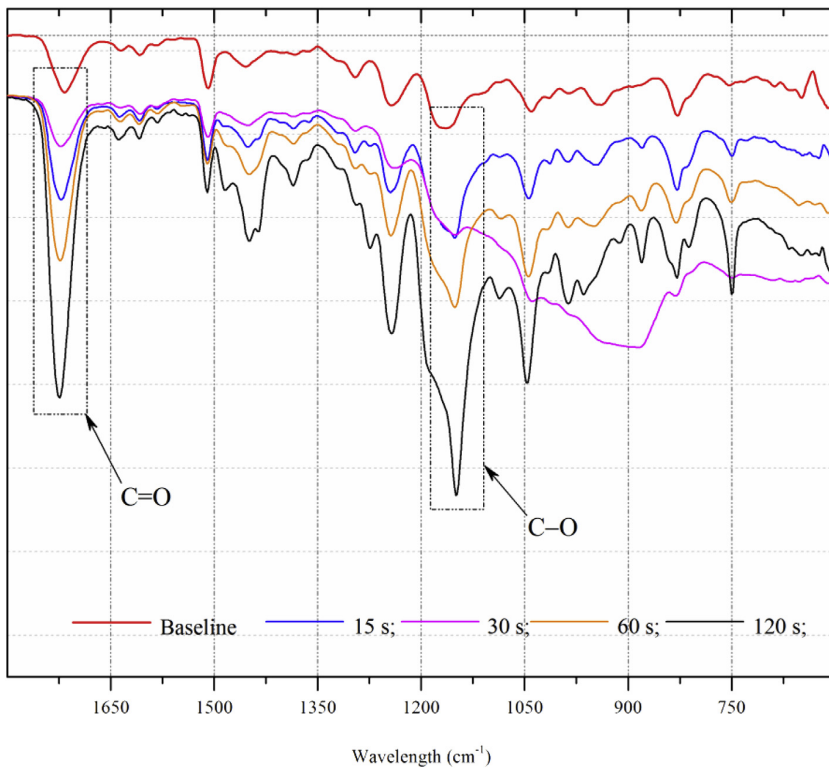


Figure 17: FTIR spectrum depicting the elongation of the carbonyl groups in light-cured and post heat-cured FRC. (Adapted from original publication II).

The FTIR analysis showed the variation of peaks in the wavenumber of 1650 – 1750 cm^{-1} as shown in fig 17. SEM images showed of light-cured specimens showed topographical changes caused by ethanol which varied based on the treatment time and different concentration groups, as shown in fig 18.

5.4 Effect of an organic-catalyst solution and adhesive resin on dimethacrylate polymer and epoxy resin (Study-IV)

Surface profile peak analysis of the epoxy substrate showed higher values compared to the dimethacrylate polymer at the baseline without any trend in the change of its values at different points of time. Dimethacrylate polymer showed a significant reduction in the R_p values at the end of 24 h when treated with both the solution. However, some statistical significance was seen, as shown in table 11.

Nanohardness and modulus of elasticity of the epoxy resin substrate showed a minor increase at the end of 24 h, unlike the dimethacrylate substrates which showed a decrease by prolonging the treatment time up to 24 h as shown in the tables 12 and 13, respectively.

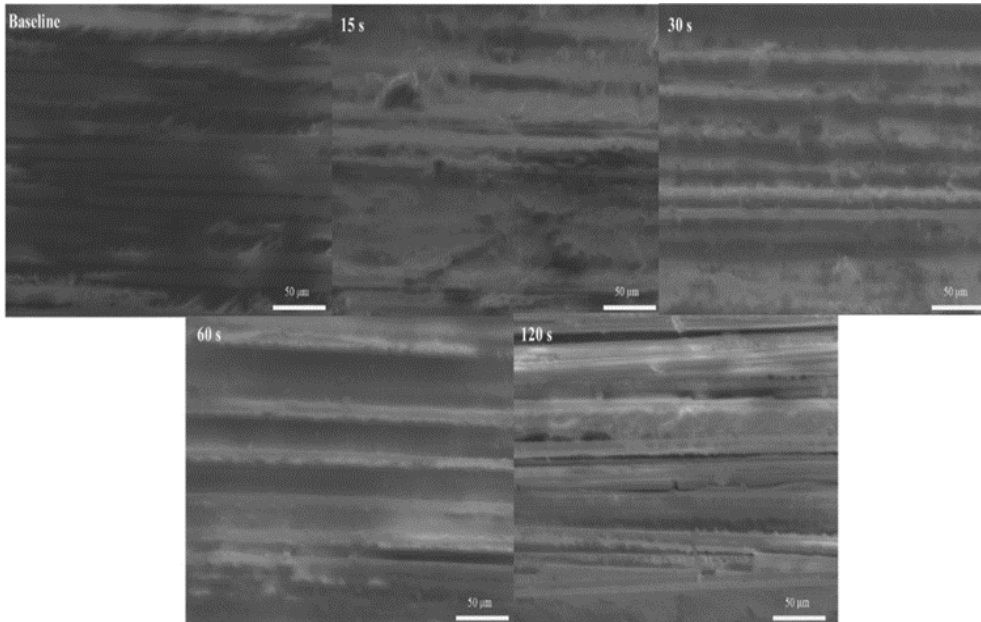


Figure 18: SEM images of light cured FRC (L-Group) treated with ethanol 99.9% concentration at different time intervals. (Adapted from original publication II).

Table 11: Surface profile peak (R_p) values (μm) of epoxy resin and dimethacrylate polymer treated with an adhesive resin (SR), Ethyleneglycol+1,5,7-triazabicyclo [4,4,0] dec-5-ene (EG+TBD). (Adapted from original publication IV).

EPOXY RESIN	CONTROL	5 MIN	24 H
SR	56.94 ^{a, A}	63.17 ^{b, A}	48.84 ^{c, A}
EG+TBD	56.94 ^{a, A}	55.11 ^{b, B}	55.87 ^{b, B}
DIMETHACRYLATE POLYMER			
SR	41.47 ^{a, A}	47.52 ^{b, A}	36.33 ^{c, A}
EG+TBD	41.47 ^{a, A}	54.61 ^{b, B}	32.65 ^{c, B}

Different superscript small letters in the same row and different superscript capital letters in the same column indicate statistically significant for each group at $p < 0.05$.

Table 12: Statistical results of nanohardness (GPa) and Young’s modulus of elasticity (GPa) of epoxy resin treated with an adhesive resin (SR), Ethyleneglycol+1,5,7-triazabicyclo [4,4,0] dec-5-ene (EG+TBD). (Adapted from original publication IV).

NANO HARDNESS	CONTROL	5 MIN	24
SR	0.202 ^{a, A}	0.171 ^{a, A}	0.312 ^{c, A}
EG+TBD	0.202 ^{a, A}	0.324 ^{b, B}	0.327 ^{b, A}
YOUNG’S MODULUS OF ELASTICITY			
SR	3.433 ^{a, A}	3.878 ^{a, A}	6.427 ^{b, A}
EG+TBD	3.433 ^{a, A}	6.742 ^{b, B}	6.434 ^{b, A}

Different superscript small letters in the same row and different superscript capital letters in the same column indicate statistically significant for each group at $p < 0.05$.

Table 13: Statistical results of nanohardness (GPa) and Young’s modulus of elasticity (GPa) of dimethacrylate polymer treated with an adhesive resin (SR), Ethyleneglycol+1,5,7-triazabicyclo [4,4,0] dec-5-ene (EG+TBD). (Adapted from original publication IV).

NANO HARDNESS	CONTROL	5 MIN	24 H
SR	0.389 ^{a, A}	0.308 ^{b, A}	0.342 ^{b, A}
EG+TBD	0.389 ^{a, A}	0.328 ^{b, A}	0.310 ^{b, A}
YOUNG’S MODULUS OF ELASTICITY			
SR	6.714 ^{a, A}	6.033 ^{b, A}	5.963 ^{b, A}
EG+TBD	6.714 ^{a, A}	5.797 ^{b, A}	6.121 ^{b, A}

Different superscript small letters in the same row and different superscript capital letters in the same column indicate statistically significant for each group at $p < 0.05$.

Surface topographical changes were seen in the dimethacrylate polymer (fig 19) substrate, with epoxy resin (fig 20) showing no changes upon treatment with the two solvents at the end of 24 h as shown in the SEM images

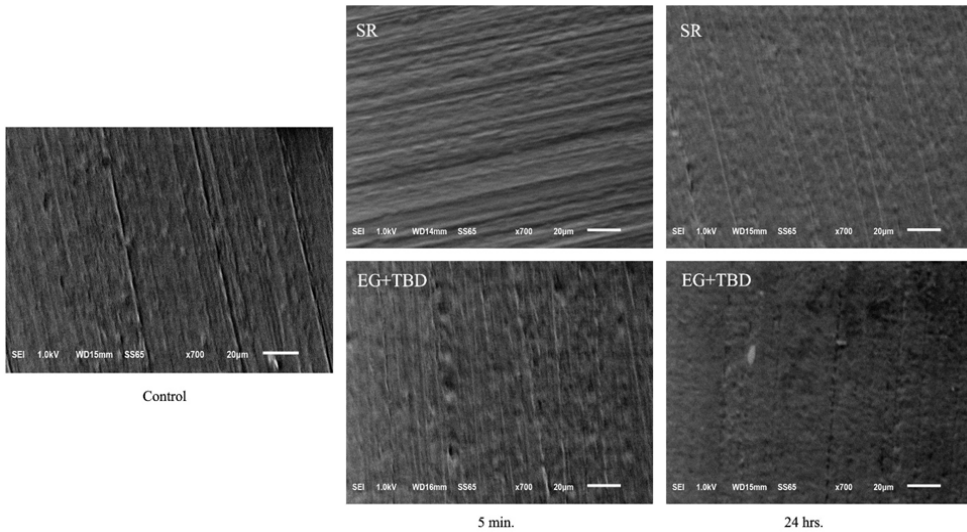


Figure 20: SEM images for specimens of dimethacrylate polymer at baseline (control), 5 min, and 24 h treated with an adhesive resin (SR), Ethyleneglycol+1,5,7-triazabicyclo [4,4,0] dec-5-ene (EG+TBD). Original magnification x700. (Adapted from original publication IV).

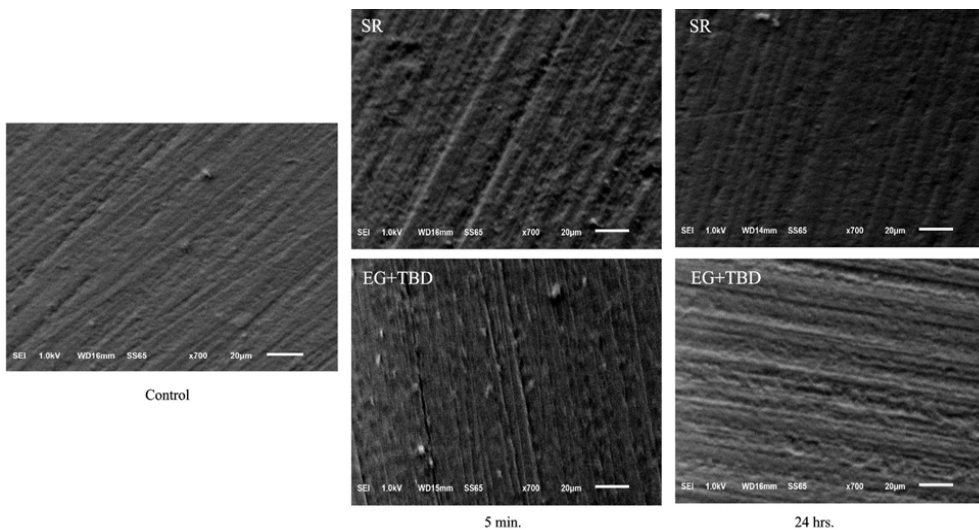


Figure 21: SEM images for specimens of epoxy resin at baseline (control), 5 min, and 24 h treated with an adhesive resin (SR), Ethyleneglycol+1,5,7-triazabicyclo [4,4,0] dec-5-ene (EG+TBD). Original magnification x700. (Adapted from original publication IV).

Analysis of linear regression for nanohardness, modulus of elasticity with treatment time for epoxy resin with SR (fig 21(a)) were $R^2=0.96$, $p<0.05$ and $R^2=0.98$, $p<0.05$. The non-linear regression analysis, the value of $R^2=-0.28$, $p<0.05$ for hardness and $R^2=-0.49$, $p<0.05$ for modulus of elasticity were seen, when treated with

ethyleneglycol +1, 5, 7 – triazabicyclo [4,4,0] dec – 5 – ene (fig 21 (b)). Analysis of non linear regression for nano-hardness and modulus of elasticity with treatment time for the dimethacrylate substrate with adhesive resin fig 22(a) were $R^2=-0.89, p<0.05$; $R^2=0.20, p<0.05$ respectively. The value of $R^2=0.03, p<0.05$ & $R^2=-0.79, p<0.05$ for nano-hardness and modulus of elasticity were calculated on treatment with ethyleneglycol+1,5,7 – triazabicyclo [4,4,0] dec – 5 – ene, as shown in fig 22 (b).

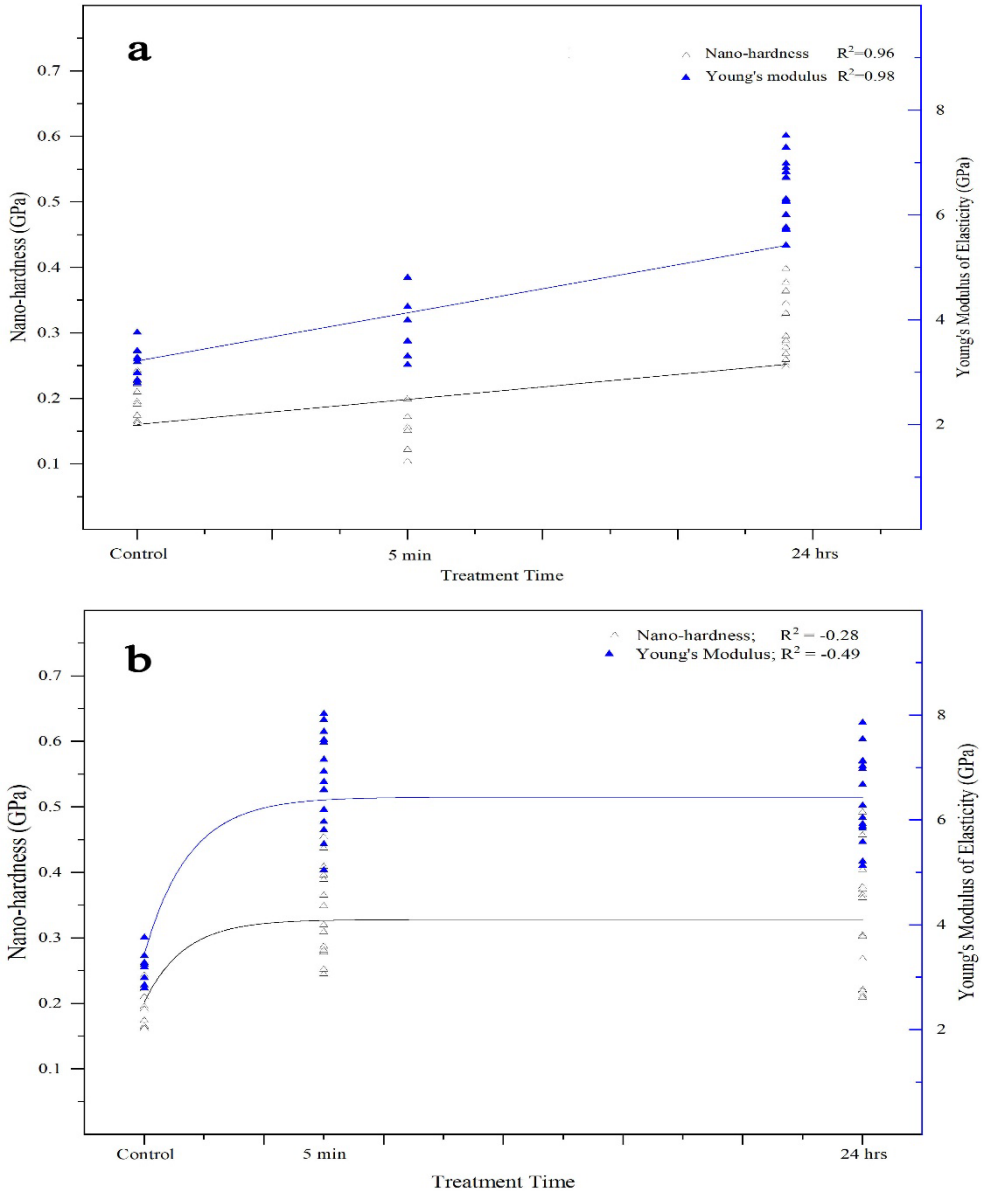


Figure 22: Linear and non-linear regression analysis of epoxy resin with adhesive resin and ethyleneglycol+1,5,7-triazabicyclo [4,4,0] dec-5-ene. (Adapted from original publication IV).

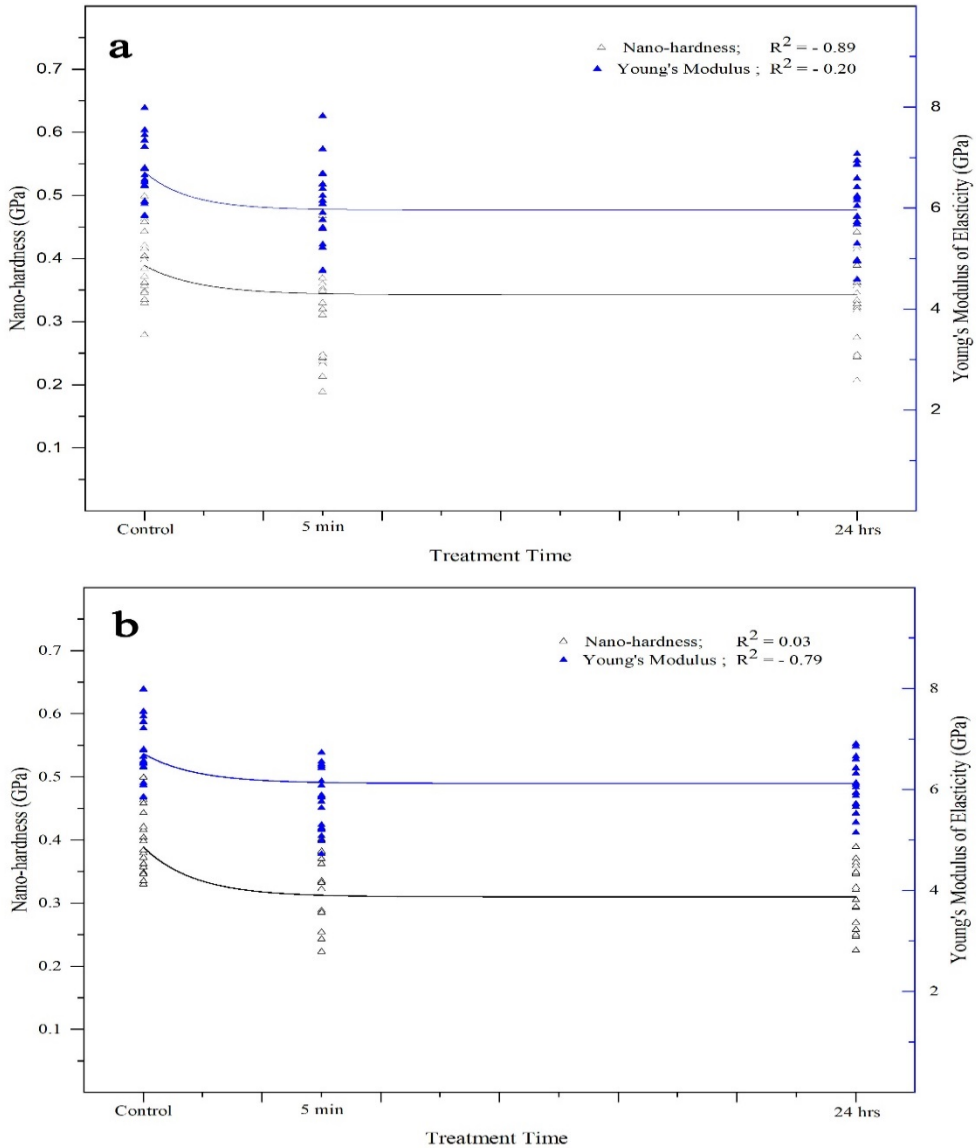


Figure 23: Non-linear regression analysis of dimethacrylate polymer with with adhesive resin and ethyleneglycol+1,5,7-triazabicyclo [4,4,0] dec-5-ene. (Adapted from original publication IV).

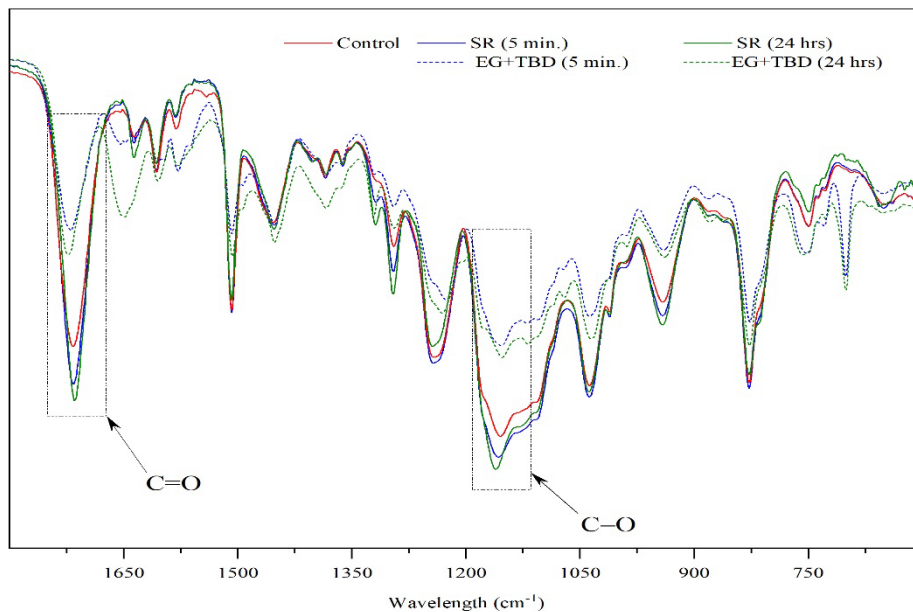


Figure 24: FTIR spectrum of dimethacrylate polymer substrate treated with adhesive resin (SR) and ethyleneglycol+1,5,7-triazabicyclo [4,4,0] dec-5-ene (EG+TBD). (Adapted from original publication IV).

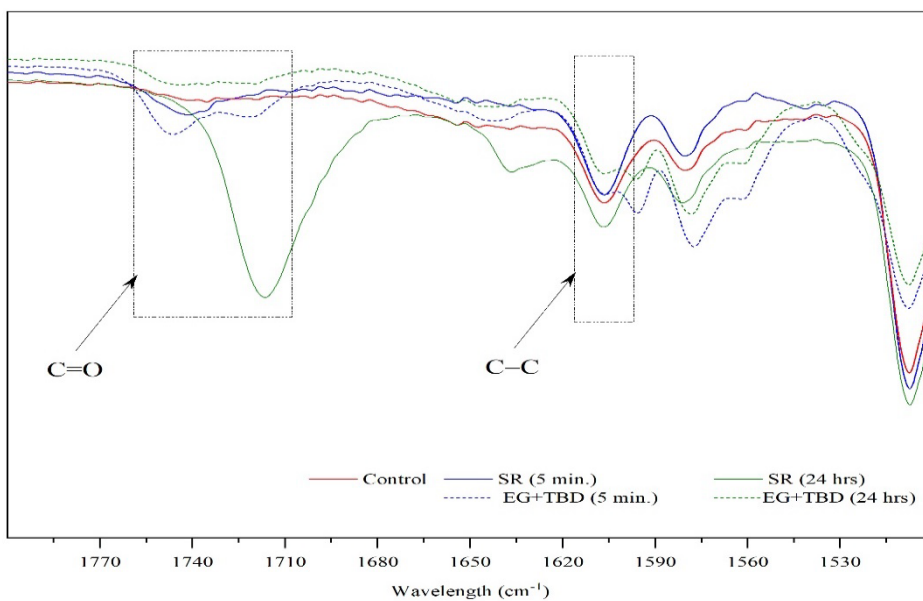


Figure 25: FTIR spectrum of epoxy resin treated with adhesive resin (SR) and ethyleneglycol+1,5,7-triazabicyclo [4,4,0] dec-5-ene (EG+TBD).

FTIR analysis of dimethacrylate substrate showed a lowered peak heights of C=O ($1650-1750\text{ cm}^{-1}$) and C-O ($1141-1271\text{ cm}^{-1}$) when the specimens were treated with ethyleneglycol+1,5,7-triazabicyclo [4,4,0] dec-5-ene whereas not much changes in the peak height were seen by the treatment with SR resin at C=O and no change seen in the peaks of C-O as shown in fig 23.

On the other hand, epoxy resin showed no effect upon treatment with both SR and blend of ethyleneglycol+1,5,7-triazabicyclo [4,4,0] dec-5-ene. However, a significant peak was seen at a wavenumber of 1720 cm^{-1} when treated with SR for 24 h as shown in fig 24.

6 Discussion

The process of polymer dissolution with solvents starts with the creation of a surface layer into which the solvent invades and resulting in the formation of the swollen polymer layer. This dissolution cycle is gated by the disentanglement of the polymer chain and by the diffusion of the polymer chain adjacent to the interface between solvent and polymer. Organizing various layers from the pure solvent to the pure polymer involves a liquid bed, a gel bed, a solid swollen layer and an infiltration layer (Ribar *et al.*, 2000). The solvents' infiltration into the polymer increases the swollen polymer layer until getting a quasistationary state. crazing, as organized crack, occurs ideally on the surface of materials on the thermoplastic polymers. This is because of the weaker Van der Waals force and a strong covalent bond. Usually, crazing in the polymer material is present in those regions represented with high hydrostatic tension. Localized yielding occurs in those regions resulting in the formation of microvoids (Doi and Edwards, 1978). The reflections of light from the fibrils that form the backbone of the polymeric chain demonstrate crazing. The polymers, used in the field of dentistry are mainly composite resins, which are cross-linked polymers, and the denture base resins with various modifications like the addition of ethylene glycol dimethacrylate and rigid-rod polymers (Gajewski *et al.*, 2012). Crazing relates to the ability of solvents to dissolve the polymer, and thus factors that influence the solubility of the polymers may play an insane role (Bazhenov, 2011). There are generally two types of dissolution of any thermoset polymer: controlled reaction rate (polymer-solvent diffusion rate above reaction rate), and controlled diffusion rate (diffusion rate slower than reaction rate). Temperature influenced the process of dissolution. A drop in temperature as shown reduced gel layer formation leading to stress build-up, resulting in crack formation (van Krevelen and te Nijenhuis, 2009). Of the several factors regulating the polymer dissolution rate, molecular weight and polydispersity played a significant role (Miller-Chou and Koenig, 2003).

6.1 Effect of ethanol on the structure and properties of heat an autopolymerized denture base polymers (Study-I)

The present study evaluated and compared the effect on the mechanical properties on heat-cured and auto polymerized acrylic dental resins when treated with solvent/disinfectant containing ethanol at different concentrations and at varying time intervals. Structural change in the resin (Cunegatti *et al.*, 2008 and Shen *et al.*, 1989) and surface damage (Ma *et al.*, 1997), shown in contact with various chemical disinfectants.

In this current study, the dissolution of the PMMA resin was attributed to the formation of water and hydrogen bonding at absolute ethanol concentration and 40%, and it was due to the formation of water cages. Besides, at 70%, both the factors played an equal role in the dissolution of the PMMA polymer. The imbibed water molecules into the resin polymer cause irreversible damage by hydrolytic degradation depending on the period of contact of the resin and formation of surface cracks by the polymer scission (Pinto Lde *et al.*, 2010). The chemical structure of the acrylic resins is polar, and this causes to absorb water from ethanol at varying concentrations of 40% and 70%. This absorbed water molecule intrudes into the polymer chain that affects the physical properties induced by swelling of resin polymer network and stress relaxation (Takahashi *et al.*, 1998 and Yiu *et al.*, 2004).

The results showed that S_a was affected by ethanol at varying concentrations, with significant changes seen in auto polymerized acrylic resins. The form of acrylic resin (heat-cured vs auto polymerized) plays a major role in deciding the degree of surface modification (Lira *et al.*, 2012). The process of diffusion of the solvent is governed by the presence of uncrossed link monomers in a stable solvent, with higher the presence of the latter more favourable for the diffusion process. The degree of surface modification by a solvent is due to the conversion of monomer to polymer, with less residual monomers in heat-cured acrylic resins (Zissis *et al.*, 2008) when compared to auto polymerized acrylic resins resulting in greater elution in it (Koda *et al.*, 1989). In the heat-cured acrylic resin, no cracks or surface crazing was seen because the contact time of the ethanol with the resin was not more than two minutes, which is the desired period of contact for the dissolution of the polymer to occur. Unlikely in the auto-polymerized acrylic resin due to the presence of the non-cross linked monomers cracks or surface crazing was evident. For auto polymerized acrylic resins statistically significant dissolution was seen at varying concentrations of ethanol with higher dissolution seen at 40% compared to others. The dissolution of the polymer depends on the molecular weight of each material and poly or monodispersed within each material (Manjikow *et al.*, 1987). Also, the solubility parameter of PMMA and ethanol are near closer and hence making ethanol an excellent solvent for PMMA.

Surface topographical analysis of the resin by SEM confirmed the same. It noticed that the semi-IPN layer between the polymer bead and the polymer matrix was mainly affected by the solvent/disinfectant ethanol. This advocated that the core of the polymer bead or the slightly cross-linked polymer matrix was less vulnerable to dissolution compared to the semi-IPN layer. The interface with the semi-IPN structure was swollen by the methylmethacrylate monomers and could not resist dissolution or crazing compared to the polymer beads of PMMA that are syndiotactic polymer in nature. In the heat-cured, PMMA crazing or dissolution was not seen, attributed to the MMA monomers that penetrate through the polymer beads of PMMA during doughing. This results in a homogeneous polymer structure, and more resistant to crazing and dissolving by the solvent ethanol.

The solvent materials replace the residual monomer present in the polymer results in an increased plasticizing nature of the polymer affecting the NMP properties of the polymer (Ferracane, 2006 and Pedreira *et al.*, 2009). Assessment of the NMP of the heat-cured and auto polymerized acrylic resins post-polymerization at different concentrations of ethanol and different periods, it was found that hardness and modulus of elasticity were affected significantly in auto-polymerized acrylic resins. In heat-cured acrylic resins, there was no significant change in the NMP, and this was due to the lower quantity of residual monomers that were present when compared to that of the auto-polymerized acrylic resin. From the findings of this study, we could conclude that disinfectants containing ethanol could cause the dissolution of the denture base polymers depending on its concentration and time, and hence not recommended.

6.2 Effect of ethanol on heat-polymerized *poly*(methylmethacrylate) acrylic resin cured at the different post dough stage (Study-II)

In this study, a heat-cured denture base polymer was selected to evaluate the effect of ethanol on the surface of heat-cured acrylic resin dentures. The heat-cured polymer has more a more homogeneous structure compared to that of the auto-polymerized polymer. This is attributed to the longer period contact of the monomer liquid with the polymer beads and dissolves them over a longer period (McCabe *et al.*, 1975; Mutlu *et al.*, 1992). The extent of damage to the polymer is also influenced by the curing technique followed (Lira *et al.*, 2012), which as an influence on the monomer to polymer conversion ratio: with better conversion, the amount of elution is a higher and less residual monomer (Zissis *et al.*, 2008). The dissolution of solvent into the polymer occurs by a diffusion process, causing salvaging of the polymeric chain. The diffusion of the solvent is directly proportional to the number of monomers present in the polymeric resin resulting

in the formation of a swollen gel layer, occurring between the gel layer and the glassy polymer and along with the solvent and the gel layer. This results in initial plasticizing and the latter resulting in crazing and cracks. In this study, the focus was to evaluate the nanomechanical properties of the heat-cured acrylic denture base resin treated with different concentrations of ethanol on resin moulded and cured at differing post dough stage, immediate, 15 min and 30 min post dough stage. Also, assessment of surface roughness, with nanomechanical properties after exposure to ethanol at varying concentrations. Of the many factors determining the post-polymerization effect, the chemistry of the solvent and the type of monomers (Ferracane and Condon, 1990), plays a vital role with the former influencing the solubility of the monomers. The inter-relationship between the effect of the solubility of the solvent and the monomer is influenced by the Hildebrand parameter (Barton, 1983) (δ) and solubility parameter. The solubility parameter of ethanol is $13 \text{ (cal/cm}^3\text{)}^{1/2}$ and for denture base resins is $8.9 - 12.7 \text{ (cal/cm}^3\text{)}^{1/2}$ and the δ value of the monomer is $\sim 16.0 \text{ MPa}^{1/2}$, δ value of $26.0 \text{ MPa}^{1/2}$ for ethanol and δ value of water is $47.9 \text{ MPa}^{1/2}$. The δ value of ethanol is closer to monomeric methylmethacrylate when compared to that of water, explaining the effect of ethanol to be directly proportional to its concentration. The monomer MMA discharged from the polymer is in linear relation with the ethanol concentration (Bettencourt et al., 2002). Also, the solubility parameters of PMMA and ethanol that are closer to each other, allowing ethanol to dissolve the polymer linearly related to its concentration. Denture base polymers also contain cross-linking monomers, like EGDMA, which improves the resistance of the polymer against solvent-induced dissolution/crazing (Jagger and Huggett, 1990).

The addition of a cross-linking monomer like EGDMA improved the crazing resistance but did not influence reducing the water sorption of the polymer. The results of the study showed that the nanomechanical properties and surface roughness were consistent. However, there is a certain effect of ethanol treatment on surface hardness and modulus of elasticity. In addition, the molecular weights of the materials and poly or monodisperse within the same materials influence the dissolution of the (Manjkow et al., 1987). In this laboratory study, no detectable polymer beads were seen even with short doughing time in the polymer specimens. Light microscopic examination of the heat-cured denture base polymer has shown the presence of polymer beads (Vallittu and Ruyter, 1997; Vallittu and Ruyter, 1997). Interestingly, PMMA beads and the semi-interpenetrating polymer network were detectable in auto-polymerized denture base polymer. The dissolving effect of ethanol in auto-polymerized denture base polymer seen between the polymer matrix and polymer bead in the IPN layer. The magnitude of surface topographical changes was lesser in heat-cured denture base polymer compared to that of the auto-polymerized polymer. Besides, the use of ethanol in various concentrations can

deteriorate the denture base polymers topographically, which could be significant at varying concentrations and time.

PMMA becomes dissolvable in the mixture of ethanol and water, wherein it is indecipherable in either water or alone (Jewrajka *et. al.*, 2004). Water cages are found to be formed around the ethanol molecules at 40-50 vol. % and hydrogen bonds seen around the ester moieties in the polymeric resin (Piccarlo, S. & Titomanlio, G, 1982.). The dissolution behavior is influenced by the molecular weight of the PMMA and the cross-linking monomer. The solvent affected primarily the semi-IPN layer between the polymer matrix and the polymer bead. This suggested that the semi-IPN layer was prone for dissolving compared to the polymer bead core or the cross-linked polymer. PMMA polymer beads are syndiotactic polymer and hence resisted dissolving and crazing more effectively compared to that of the semi-IPN structure. In this present study, results for the nanomechanical properties and surface roughness were consistent and suggested that the use of ethanol in various concentrations could deteriorate denture base polymers topographically which could be significant at different concentrations and at varying time period.

6.3 Effect of ethanol on the structure and properties of semi-interpenetrating polymer network polymer matrix of fibre-reinforced composite (Study-III)

IPN resin matrix is used in dental FRCs for better handling properties of fibre preppers and for attaining adhesion at the interface between the FRC and the resin composite at the outermost layer. The present study evaluated the degree of effect of ethanol on FRCs affecting NMP, S_a and FTIR analysis on light-cured and light-cured and post heat-cured. It was found that the NMP and S_a were affected at different concentrations and treatment time by ethanol on both light-cured and light-cured and post heat-cured groups which varied based on the time of exposure and treatment time. This was likely associated with the swelling and solidification of the polymer surface between the glass fibres, which are not influenced by ethanol. This was associated with solvent lured crystallization (Andjelic and Scogna, 2015). At times, the solvent take-up causes expanding of the polymer surface is non-Fickian due to polymer chain segmental relaxations. Solidification of the solvent following evaporation, crystallization might take place leading to solidification on the surface (Aly, 2015). The tactility of the PMMA has been appeared to identify with the crystallizing process supporting the conclusions for the recommended crystallization with syndiotactic PMMA (John *et al.*, 1989). Nanometer-scale surface solidifying after a momentary presentation to ethanol has been shown likewise in our past studies I & II.

Further examinations are expected to affirm and research the conceivable crystallization of the PMMA in the wake of being uncovered with ethanol. At this point when the cross-linked polymer network is considered from the viewpoint of solvent disintegration, it is established that the dental dimethacrylate resin composite frameworks respond with solvents complex and they are identified with the synthetic structure of the resin (Ferracane, 2006). Nevertheless, it is in the demonstration that various components of the resin matrix, for example, *bis*-GMA, UEDMA, TEGDMA, have contrasted in their dissolvability percentile with ethanol and water at different concentrations (Sideridou and Karabela, 2011). Fundamentally, higher the *bis*-GMA based resin composite is polymerized; it is generally impervious to dissolvable effect by ethanol (Asmussen, 1984). Moreover, the polymer structure of IPN polymer assimilates various types of intermolecular forces holding the polymer chains together. The dominating ones are the covalent bonds of cross-link (phase of copolymer *bis*-GMA-TEGDMA), with lower hydrogen bonds and van der Waals bonds (a.k.a. London forces) between the polymer chains of the non-cross-connected PMMA chains. Considering the various factors, in the disintegration procedure, there are two phases: polymer swelling and the disintegration stage itself. The presentation time of 120 s begins the swelling stage. After the dissipation of ethanol, the polymer chains of PMMA of the swelled layer are arranged, the second time and forming a structure with a strong polymer layer. Polymer chains of the rearranged PMMA in the superficial layer of the FRC may have even shaped solidified locales by which the surface hardness and modulus of elasticity increased. Increasing the ethanol contact time, the dissolving stage would have mainly occurred. This has been accounted for PMMA based dental resin polymer base in the wake of dissolved by ethanol for 30 days (Regis *et al.*, 2009). FTIR analysis of the light-cured and post-heat-cured group showed that the peaks for carbonyl group (C=O) at the wavenumber scope of 1650-1750 cm^{-1} got higher (progressively escalated) when exposed to ethanol. This may be identified with conceivable crystallization of the furthest layer of the polymer matrix and advancement of linear polymer to the surface alongside with better recognition of the methacrylate groups of the polymer network by the removal of the debris by ethanol. The findings have given newer options to modify the crystallization of the polymer surface.

6.4 Effect of an organic-catalyst solution and adhesive resin on the surface characteristics and properties on dimethacrylate polymer and epoxy resin (Study-IV)

The use of the present study was to ascertain a new technique for improving adhesion at the interface between resin luting cement, composites used for core-build-up and composite veneers with thermoset cross-linked resins. The main point of this study

was the interfacial adhesion by dissolving the substrate by the process of transesterification, used in the recycling of plastics (Miller-Chou and Koenig, 2003). For the transesterification reaction, the chemical structure in the polymer should have an ester group. Among the most commonly used monomer systems, *bis*-GMA-TEGDMA contain ester groups and hence selected for the transesterification to break down the surface layer—an epoxy polymer widely used as a restorative material and selected without an ester group in it.

FTIR analysis, to confirm the presence or absence of the ester group. The surfaces of dimethacrylate and epoxy polymer were evaluated for physical and chemical observations related to the perceptions of polymer swelling and dissolution upon treatment with adhesive resin and an organic-catalyst solution blend ethylene glycol and 1, 5, 7-triazabicyclo [4,4,0] dec-5-ene.

The results showed a decrease in surface nano hardness of the dimethacrylate polymer when treated with an adhesive resin, which was due to the swelling of the substrate surface by the process of diffusion of monomers of TEGDMA and *bis*-GMA. Evaluation of the nanomechanical properties and SEM micrographs also demonstrated softening. Topographic changes of the polymer surface were similar to those seen in thermoplastic resins like *poly*(methylmethacrylate) and solvent methylmethacrylate (Vallittu *et al.*, 1994). Polymer dissolution is also influenced by the diffusion rates and swelling power of the solvent. The addition of a non-solvent to a solvent has shown to contribute to increasing the dissolution process of the solvent by increasing the plasticizing nature of it (Cooper *et al.*, 1986). Moreover, other factors such as wettability, solubility parameter and surface tension of the solvent are other important criteria that influence the polymer dissolution process. If the solubility parameters of the polymer and the solvent do not have a more significant difference, then the dissolving process takes place quickly.

Surface softening of the polymer surface was evident only in the first few minutes of time exposure and no further softening was seen even after a prolonged exposure time of 24 h. This could be possible due to some degree of polymerization, which would have halted the dissolution and swelling process, or evaporation of lower viscosity monomer like TEGDMA. We found that thermoset polymer (epoxy resin) required 24 h to show microscopically visible changes unlike the thermoplastic polymer (dimethacrylate resin) which demonstrated dissolution patterns within one-minute of treatment time. Compared to cross-linked thermosets, thermoplastic polymers and semi-IPN polymers have shown better bonding characteristics (Kallio *et al.*, 2003; Lastumäki *et al.*, 2002; Lastumaki *et al.*, 2003). Dimethacrylate polymer structure could have undergone the formation of few crystallized regions on the surface layer by the reorganized polymer chain (Andjelic and Scogna, 2015). This contributed to a higher value of surface hardness and elastic modulus (Aly, 2015). The actual dissolution stage would have taken place in the polymer if the

exposure time was prolonged by alcoholysis if the time was for more than 30 days (Regis *et al.*, 2009). FTIR analyzes of dimethacrylate polymer have suggested that polymer softening was likely due to transesterification after treatment with adhesive resin and ethyleneglycol+1,5,7-triazabicyclo [4,4,0] dec-5-ene.

The FTIR results showed no significant changes of dimethacrylate polymer surface upon treatment with adhesive resin, in the spectra. Therefore, the softening of the polymer surface was more likely due to surface swelling and not because of dissolution. However, upon treatment with ethyleneglycol+1,5,7-triazabicyclo [4,4,0] dec-5-ene reduction in the surface hardness with a change in the FTIR spectra was seen about the alteration in the chemical structure. There was a reduction in the height of the peak in the wavenumber region of 1650-1750 cm^{-1} , suggesting that transesterification had occurred. A mixture of ethyleneglycol+1,5,7-triazabicyclo [4,4,0] dec-5-ene was used for dissolving the polymer because, 1,5,7-triazabicyclo [4,4,0] dec-5-ene dissolves thoroughly in ethylene glycol compared to other catalysts (Shi *et al.*, 2016). Ethyleneglycol used alone without any catalyst increased the mass of the epoxy resin by diffusion (Yu *et al.*, 2016). Due to the absence of the ester group in epoxy resin, the dissolution of resin by transesterification was not possible with ethylene glycol. The adhesive resin caused the polymer layer to swell and softened it. The above mechanism applies to epoxies containing ester groups and the mechanism could be considered to occur in other polymer ester groups, such as *bis*-GMA-TEGDMA.

A characteristic peak in the wavenumber of 1730 cm^{-1} was seen when the dimethacrylate polymer was dissolved in a blend of ethyleneglycol+1,5,7-triazabicyclo [4,4,0] dec-5-ene (Ahmed and Gai, 2017). This peak disappearance was due to the alcoholysis reaction in which there is a release of functional ester groups by the cleavage of the bonds. Depolymerizing of the epoxy resin by catalytic degradation is demonstrated by the action of ethyleneglycol+1,5,7-triazabicyclo [4,4,0] dec-5-ene. This takes place first on the ester by attacking the carbonyl group on the di-substituted nitrogen and forms betaine as intermediate. After this, the protonated nitrogen drives the 1, 5, 7-triazabicyclo [4, 4, 0] dec-5-ene amide transition compound and releases the alcohol. This process of releasing alcohol into the polymer network and spreading the ethyleneglycol+1, 5, 7-triazabicyclo [4,4,0] dec-5-ene solution causes depolymerization at a faster rate (Pratt *et al.*, 2006). Epoxy resin showed a significant peak at a wavenumber of 1720 cm^{-1} when treated with adhesive resin 24 h attributed to the aldehyde group.

We noted that the treatment agent's influenced peak surface profile (R_p), associated with the polymer surface swelling and solidification. Also, leaching out of residual monomers from the polymer matrix, have a minor effect on the polymer matrix dimensions (Polydorou *et al.*, 2009). From clinical and dental technology, the current results have an impact on knowing the interfacial adhesion of resin

composites of various kinds for a better understanding of the effects of commonly used dental adhesives.

Dendrimers belong to the group of multifunctional reactive macromolecules, which form a highly cross-linked polymer. Dendrimers do have high potential to use as dental resin although high viscosities have hindered their practical use as far. However, from the chemical structure point of view and by considering high molecular weight, dendrimers could be used as low polymerization shrinkage macromolecules are dental resins and resin composites (Viljanen *et al.*, 2005). From the perspective of dissolution, the dendrimers, which have been tested as dental materials, do have several ester bonds in the polymer structure and can potentially, be degraded by the transesterification reaction in a similar manner than dimethacrylate polymer studied in the experimental part of this thesis. There is a need for Further to confirm surface dissolution and degradation behaviour of dendrimer origin polymers.

7 Conclusions

The effects of various solvents and organic-catalyst solutions on denture base polymers, fibre-reinforced composites and polymer resins like epoxy and dimethacrylate were studied. Following conclusion were drawn, based on the current laboratory studies and findings and stated hypothesis,

1. Denture base polymers, particularly auto polymerized, are prone to surface crazing and the solvent/disinfectant dissolving effect of ethanol. The effect of ethanol was dominant in the interphase region between the PMMA polymer and the matrix of the polymer. This research first demonstrated that a 40% concentration of solvent/disinfectant ethanol deteriorates the surface of multiphase denture polymers between the polymer bead interface with the polymer matrix.
2. Heat-polymerized denture base polymers are also prone to alterations in the mechanical properties and surface topography induced by ethanol at varying concentrations and treatment time. The degree of change that affected the heat polymerized denture base polymer was slightly less than that previously observed for auto-polymerized resins. The doughing time affected the resistance to ethanol concentration and period of contact.
3. Exposure to ethanol influenced the surface roughness, nanomechanical properties and the chemical surface characterization of both the light-cured and light-cured with heat post-cured fibre-reinforced composite with an interpenetrating polymer matrix at varying levels. Short-Term Exposure to ethanol improved the surface nano hardness and elasticity modulus of the resin.
4. The epoxy substrate without ester bond in the chemical structure was not affected by surface softening effect upon application of adhesive resin and mixture of an organic solvent with a catalyst solution of ethylene glycol and 1,5,7-triazabicyclo [4,4,0] dec-5-en. However, the dimethacrylate polymer substrate decreased its surface nanohardness within 5 min of treatment time. The softening of the dimethacrylate surface was mainly associated with the reduction of ester groups in the polymers.

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