

**Chemical degradation of dental composites**

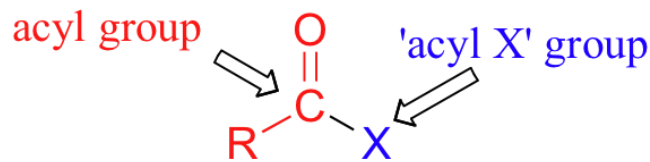
To learn about the quality of dental composites and to avoid the failure of this item, dental student must have knowledge about the biodegradation of dental composites in the oral cavity after light cure resin based composites

Starting from the important definitions:

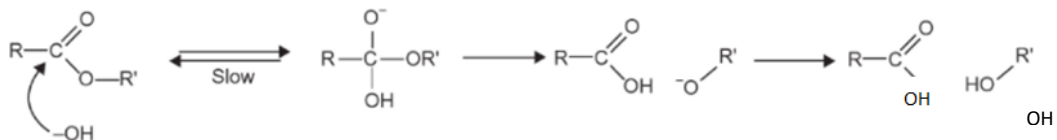
**Hydrolysis:**

It is a common form of a chemical reaction where water is used to break down the chemical bonds that exist between a particular substances. It is one of the most common drug degradation reactions in the presence of moisture and the most common substrates are those that contain the acyl group such as the compounds shown in the following table:

$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{X} \end{array}$	X
Ester	-OR'
Thioester	-SR'
Amide	-NHR'
Acid chloride	-Cl
Acid anhydride	-OCOR'
Imide	-NHCOR'



An example to the mechanism of ester hydrolysis is shown in the following figure



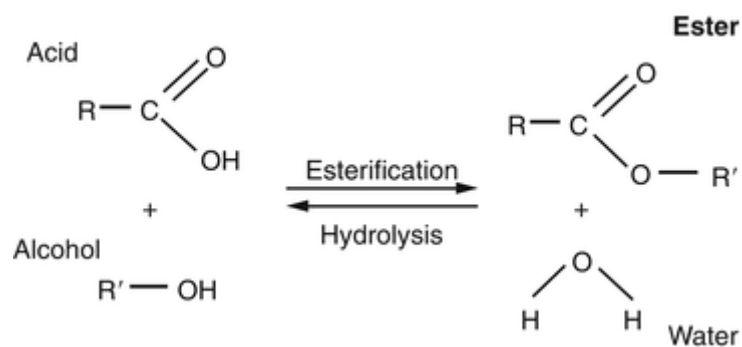
*Specific base catalyzed ester hydrolysis in aqueous solution.*

### **Hydrolase:**

It is a class of hydrolytic enzymes that are commonly used as biochemical catalysts utilizing water to break a chemical bond in order to divide a large molecule into two smaller ones.

### **Esterification:**

The chemical reaction between alcohols and carboxylic acids to produce esters



### **Esterase:**

Is a hydrolase enzyme that breakdown esters into an alcohol and acid in a chemical reaction with water called hydrolysis.

Hydrolytic reaction can be catalyzed or facilitated by acids, bases and also different enzymes (when taking about enzymatic degradation).

The susceptibility to degradation largely depends on the material composition. In the first instance it is determined by silanated filler fraction, as highly filled composites show a higher resistance to the biodegradation than composites with a lower filler content. In highly filled composites a smaller matrix surfaces is exposed to the activity of enzymes

In addition, susceptibility to degradation is determined by the resin matrix chemistry, as certain types of resin monomers are more prone to hydrolysis than others. Ester bonds, which are present in most of the currently used monomers, are particularly susceptible to degradation. However, the presence of other chemical groups on monomer molecules and their interactions can affect their stability considerably

Human saliva has been shown to contain a different hydrolase enzymes, hydrolases and esterases are the most important in relation to restorative resins. These esterases split the ester linkages in many common dental resins, accelerating the biodegradation of these materials.

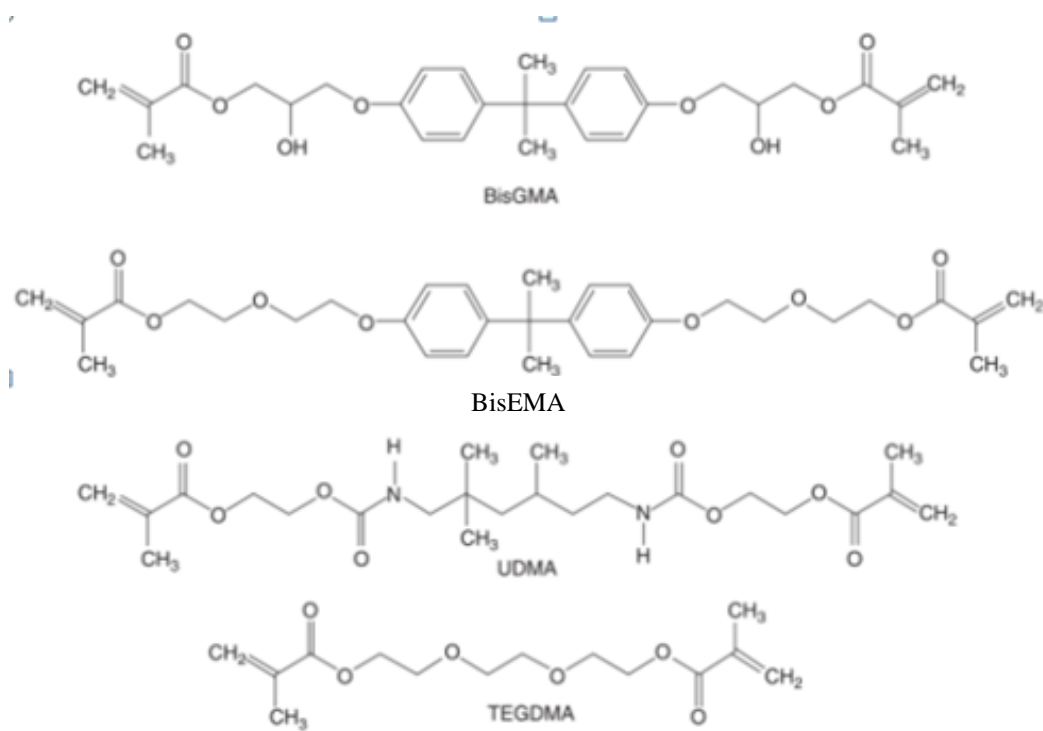
The potent esterase present in human saliva has been characterized as:

- 1- Cholesterol esterase (CE).
- 2- Pseudocholinesterase (PCE).

These two esterases are released by normal as well as inflamed gingiva. These two esterases show strong ability to degrade bisGMA, TEGDMA, HEMA, and other ester-containing monomers in dental resins.

The ester bonds in several common dental resin monomers, such as bisGMA, TEGDMA, and urethane dimethacrylate (UDMA), are sensitive to hydrolysis in saliva. This degradation cause a loss of material mass, decreased surface hardness, and increased wear

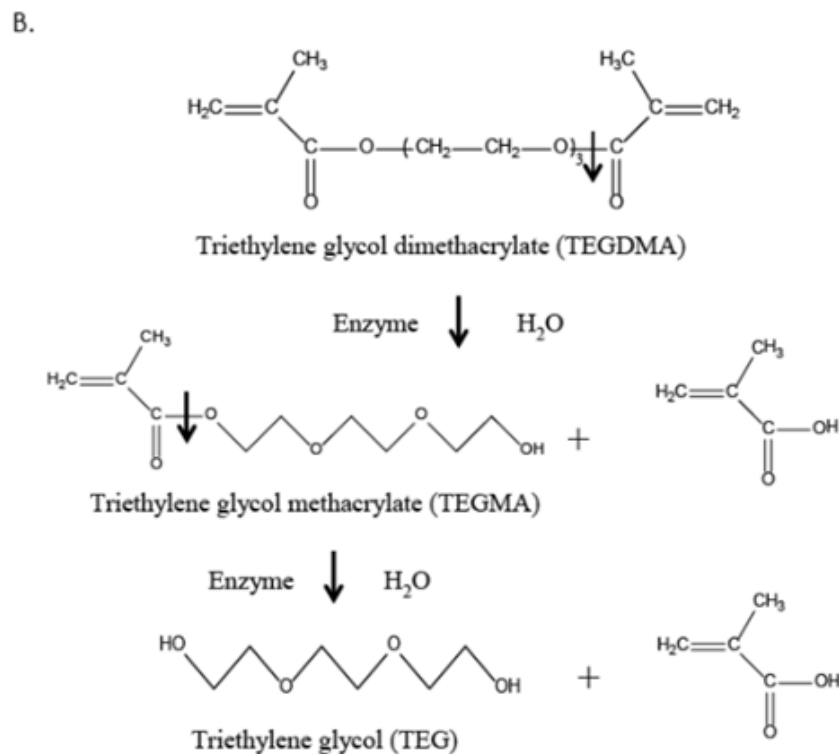
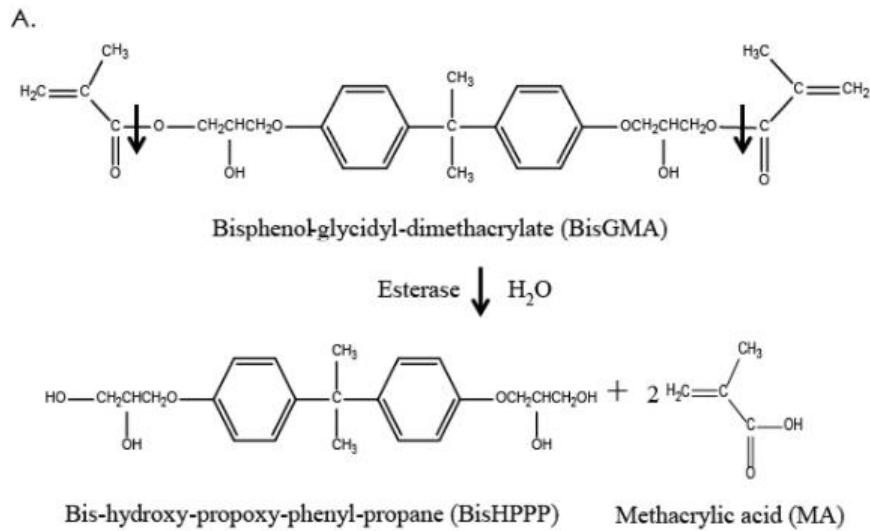
Among most commonly used resin monomers, which are presented in the following figure, triethylene glycol dimethacrylate (TEGDMA) seems to be the most susceptible to degradation.



A possible reason for this is the presence of ethylene glycol segments, which attract water molecules and increase the water uptake leading to a higher chance for hydrolysis. Aromatic cross-linking monomer bisphenol A-glycidyl methacrylate (BisGMA) and its ethoxlated version (BisEMA) are more stable than (TEGDMA) due to the presence of hydrophobic aromatic rings in their backbone, which partly protect polar groups from water and hydrolysis. The authors showed that aromatic

methacrylate derivatives were more resistant to enzyme attack than aliphatic derivatives.

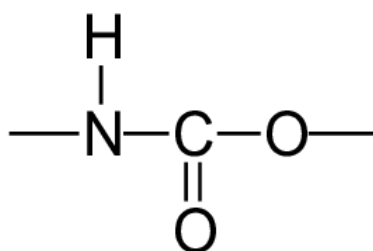
Structure and hydrolysis of the common dimethylacrylate monomers: (A) BisGMA and (B) TEGDMA are shown in the following figure



. Water sorption of typical dental dimethacrylate homopolymers.

Monomer	Water Sorption ( $\mu\text{g}/\text{mm}^3$ )
Bis-GMA	32.18
UDMA	23.85
TEGDMA	66.93

On the other hand, monomers containing urethane groups, such as urethane dimethacrylate (UDMA), show considerably lower susceptibility to degradation compared to other monomers present in contemporary composite materials.



Urethane group

Urethane groups can form hydrogen-bonded structure which can restrict the access of enzymes to the cleavage sites, thereby delaying enzymatic reaction and protecting ester bonds in their vicinity from the hydrolysis. In addition, the elimination of hydroxyl groups by the formation of urethane links in urethane-modified BisGMA leads to an increased hydrophobicity of the monomer and a higher resistance to hydrolytic attack

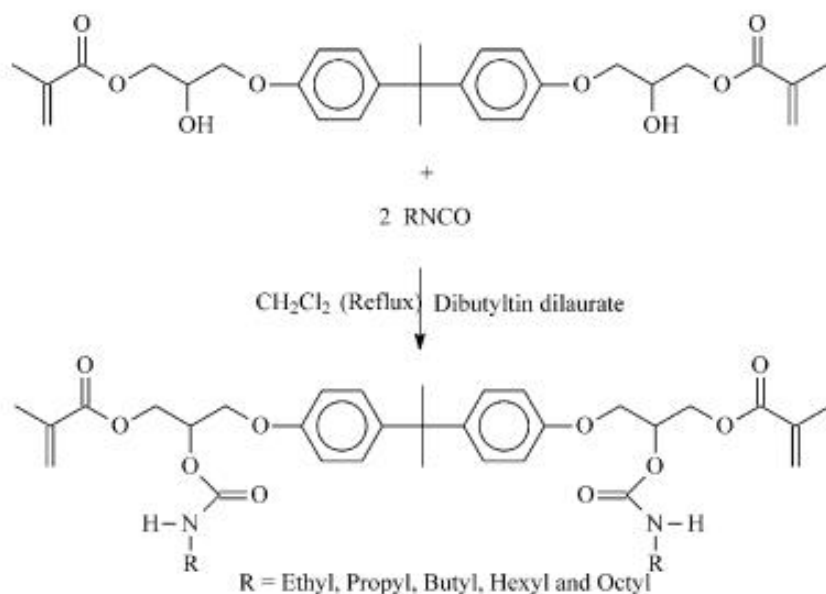
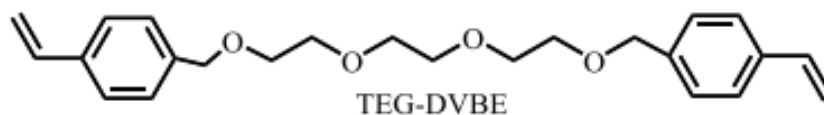


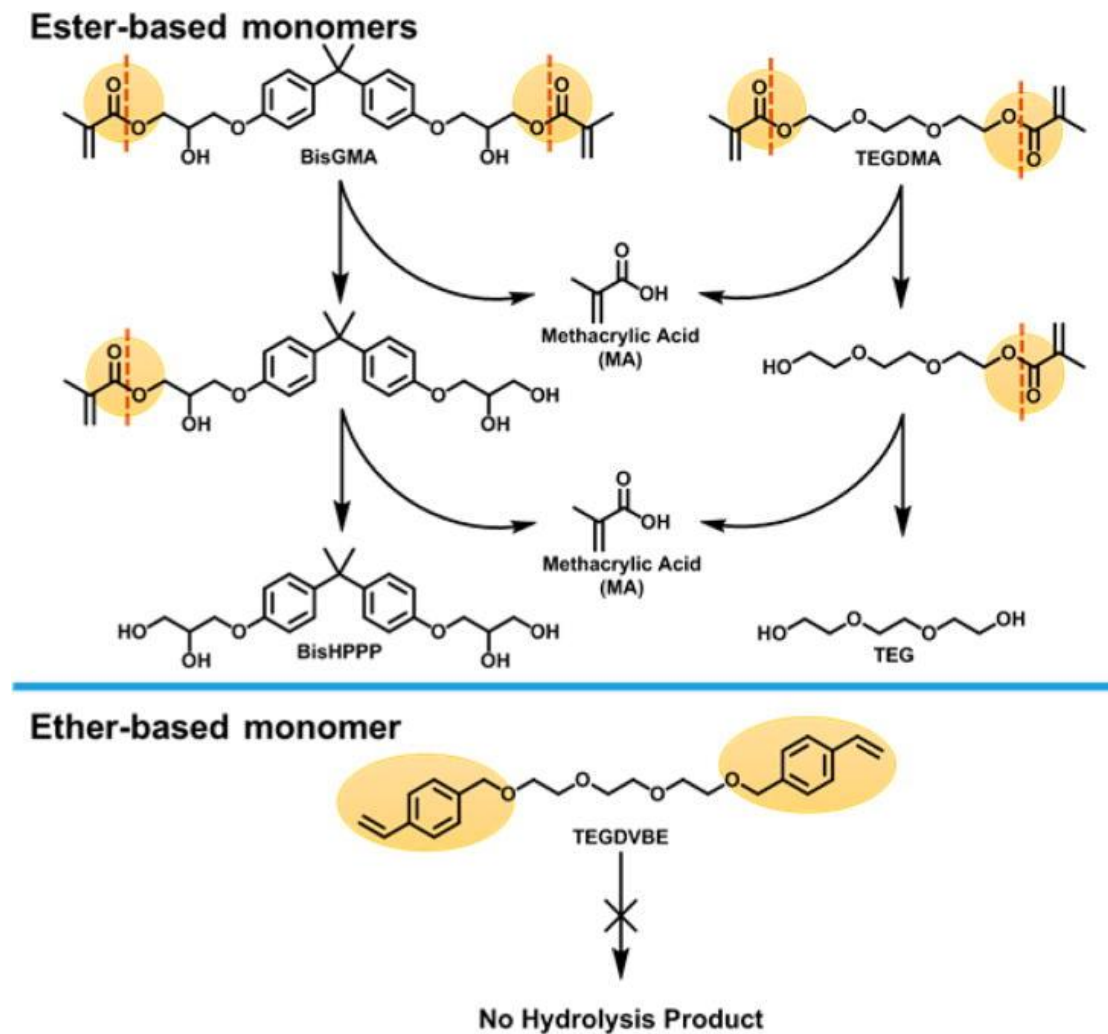
Fig. 1. Synthesis of urethane modified Bis-GMA.

In the last years, much research has been devoted to designing new monomers with different chemistries, which would have a higher resistance to biodegradation in oral cavity. Several studies reported quite promising results with experimental monomers for composites. Ether based monomer triethylene glycol divinylbenzyl ether (TEG-DVBE) which showed no signs of degradation in cholesterol esterase (CE) and pseudocholeline esterase (PCE) solutions, compared with BisGMA and TEGDMA which degraded at different levels



TEG-DVBE is stable to hydrolysis and esterase degradation because of the ether-based chemical structure

The following figure show the comparison between the stability of the ester based monomers and ether based monomers. It is very clear that there is no any degradation in the new dental materials (ether based monomers)



Esterases are the most extensively studied class of enzymes against resin composites. This class of enzymes is derived from many different biological sources including salivary glands, inflammatory responses, microorganisms, and mononuclear phagocytic cells such as macrophages and monocytes that are commonly found in both normal and inflamed gingival tissues.



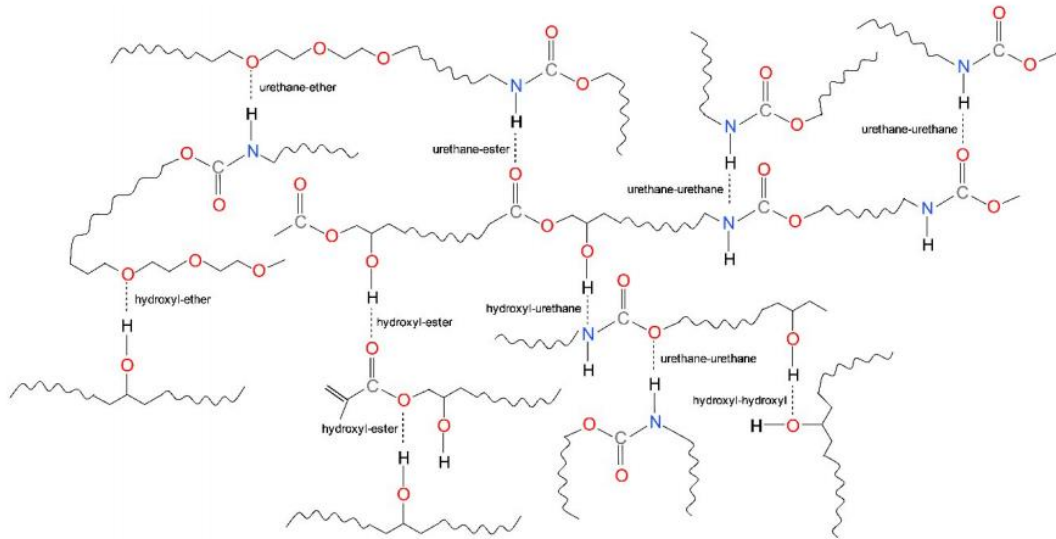
Cholesterol esterase was capable of degrading the resin composites Z250 and Z100 and TPH XL. The latter, TPH XL, was found to have the highest stability (ten fold fewer degradation by-products were produced) uBisGMA was more hydrophobic and more stable against hydrolysis in comparison to BisGMA. Composites containing higher quantities of BisGMA attracted a greater amount of water, and would therefore be more prone to degradation. In addition, the traditional BisGMA composite may have also experienced greater amount of water uptake due to the larger quantity of TEGDMA in its formulation, 45% weight fraction of TEGDMA in comparison to 10–20% weight fraction in the uBisGMA composites. Urethane modified BisGMA molecules were found to have the greatest stability and resistance to salivary hydrolysis

The Z100 resin system consists of BIS-GMA and TEGDMA while in Z250 restorative, the majority of TEGDMA has been replaced with a blend of UDMA and Bis-EMA. In TPH, urethane-modified BisGMA is present in addition to other compositions

**Table 1 – Composition of commercial resins specified by the manufacturer.**

Material	Filler type	Filler (wt%)	Monomer components
Z100 (3M) <sup>a</sup>	Silanized zirconia/silica	77–87	BisGMA (5–9%) TEGDMA (5–9%)
Z250 (3M) <sup>b</sup>	Silane treated ceramic	75–85	BisGMA (5–10%) UDMA (5–10%) BisEMA (5–10%) TEGDMA (1–5%)
TPH (L.D. Caulk) <sup>c</sup>	Barium glass/Silica	77.5	uBisGMA, BisGMA, TEGDMA, modified TEGDMA

Cholesterol esterases and pseudocholinesterase, Both enzymes are capable of hydrolyzing esters. Cholesterol esterases preferentially degraded BisGMA and PCE showed higher specificity toward TEGDMA. Rate of degradation was also found to depend on concentration of enzymes



## Hydrogen bonding in dental composites polymer

### References

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