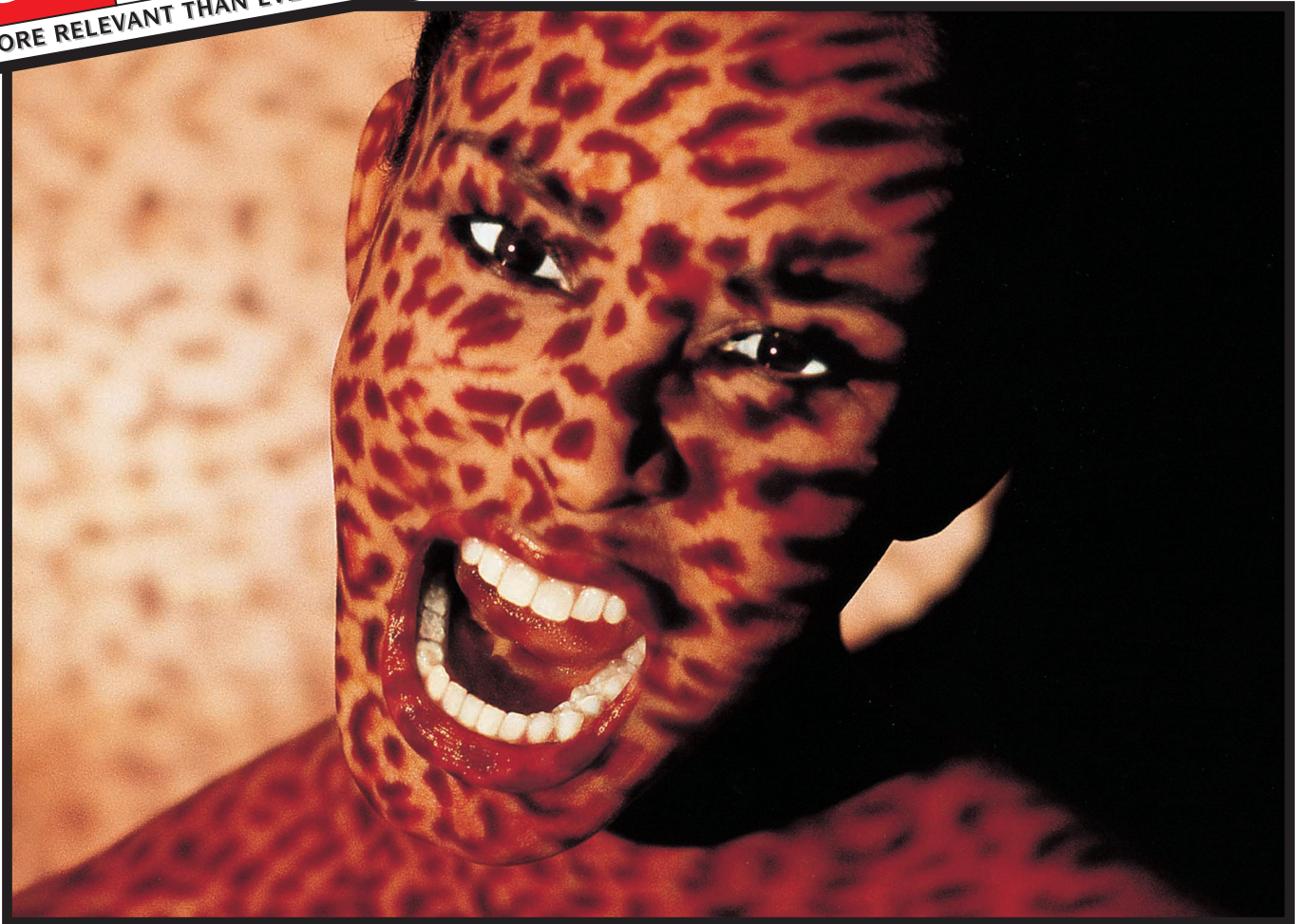


GLASS IONOMERS  
**30 years**  
MORE RELEVANT THAN EVER TODAY



## Product Dossier

**KETAC<sup>®</sup>-MOLAR**

*Remarkable Plasticity!*

## Table of Contents

<b>1. Introduction</b>	<b>3</b>
1.1 History	3
1.2 Indications	4
<b>2. Chemical Background</b>	<b>5</b>
<b>3. Physico-technical Data</b>	<b>7</b>
<b>4. Material-related Aspects</b>	<b>8</b>
4.1 Biocompatibility	8
4.2 Fluoride Release	8
4.3 Chemical Adhesion	9
<b>5. Competitors in Today's Market</b>	<b>10</b>
<b>6. Bibliography</b>	<b>13</b>

# 1. Introduction

## 1.1 History

Cements are material compounds in powdered form which are premixed with water or aqueous solutions.

Breakdown of cements according to their main components:

Powder	Liquid	
	<b>Phosphoric acid</b>	<b>Polyacrylic acid</b>
<b>ZnO</b>	Phosphate cement	Carboxylate cement
<b>Glass</b>	Silicate cement	Glass ionomer cement

When the two components are mixed, an acid-base reaction takes place which produces a salt gel that later sets as a more or less amorphous mass. Since some of the cement components are not affected by this reaction, a matrix will generally form which cements or cross-links the remaining metal oxide grains (e.g. in zinc phosphate cement).

Cements have a variety of applications in the field of dental science. For example, they can be employed as definitive or temporary filling cements, as cavity lining material, as root fillers, or to attach metal restorations and orthodontic brackets.

The dental cements available today are the result of an ongoing development since the middle of the 19th century. As early as 1856, Sorel produced a formulation for a magnesium chloride cement. The search for improved filling materials led to the development of numerous new types of cement, so that by the end of the 1920s the three basic cement types: zinc phosphate, zinc oxide eugenol and silicate, were firmly established in dental practice. Although the scientific material properties of these substances improved dramatically over the following 50 years, the basic composition of these cements has remained the same.

It was not until 1966 that D.C. Smith introduced a new cement type whose powder composition was essentially the same as that of zinc phosphate cements, but whose liquid component consisted of an aqueous polyacrylic acid. With this so-called carboxylate cement, Smith opened up a whole new field of adhesive fillers.

In 1969, Wilson et al. successfully developed a novel glass ionomer cement from modified finely-ground silicate glass and polyacrylic acid. The first preparation was introduced three years later under the name of ASPA = Alumino-Silicate-Poly-Acrylate.

The development of glass ionomers in the past 20 years has led to many variations in powder components and polycarbonic acid. These differences in composition and the resulting variety of characteristics demonstrated by today's glass ionomer cements make them particularly well-suited for the wide range of indications specific to this type of cement.

KETAC-MOLAR represents the logical development of ESPE proven glass-ionomer filling material KETAC-FIL. It combines the advantages of glass ionomers with packing characteristics and flow properties that are novel for glass ionomer cements.

## 1.2 Indications

KETAC-MOLAR is a conventional, metal-free glass ionomer cement that has been specially designed as filling material for the lateral tooth area. Its improved mechanical properties, its packable consistency and greater radiopacity make it well-suited for linings under composite fillings of cavity classes I and II, for core build up under crowns, for primary-tooth fillings and for cavity class I restorations in non-occluded regions. Additional areas of indication include cavity class V fillings when aesthetic aspects do not play a major role, and temporary fillings for cavity classes I and II.

Due to its wide range of indications, its quality criteria and its packable consistency KETAC-MOLAR can also be used as a temporary amalgam substitute.

## 2. Chemical Background

KETAC-MOLAR is, like all conventional glass ionomer cements, a powder/liquid system and is supplied both in hand-mixed and automatically mixed capsule systems (APLICAP).

Unlike the capsule products KETAC-MOLAR APLICAP no polycarbonate acid is added to the powder in the hand-mixed version. The liquid in the hand-mixed version contains a correspondingly higher concentration of acid, however. For all versions in the KETAC-MOLAR range of products the same overall concentration of acid is obtained in the mixed state.

In Table 1 the powder and liquid relationship and the percentage proportion of the acid components in powder and liquid are listed.

Product	Powder/liquid ratio	Acid in powder	Acid in liquid
Ketac-Molar Aplicap	3,4 : 1	25 %	75 %
Ketac-Molar Hand-mixed version	3,0 : 1	0 %	100 %

The powder/liquid ratio (by weight) for the hand-mixed version lies between 3.0 and 1. This corresponds to a dosage of one spoonful of powder and to one drop of liquid.

The powder used for the capsule preparations contains, alongside the ultrafine radiopaque aluminium-calcium-lanthanum-fluorid-silicate glass, 5% spray dried ESPE polycarbonate acid (a copolymer from acrylic and maleic acid).

This acidic to the powder leads to a greater overall acid concentration in the cement, resulting in increased cross-linkage and improved mechanical values without a dramatic increase in the initial viscosity. The cement's liquid component, contained in capsule pillows, is an aqueous solution of polycarbonic acid and tartaric acid. The powder/liquid ratio is 3.5.1.

KETAC-MOLAR is supplied in the well-known APLICAP capsule. However, because of the higher viscosity the application nozzle has been shortened, the cross section of the channel has been enlarged and the bending radius improved so that the cement can be pressed out more easily.

When the powder and aqueous acidic solution are premixed in universal mixing unit, e.g. ESPE ROTOMIX unit, carbonic acid  $\text{COOH}$  dissociates to  $\text{COO}^-$  (carboxylate ion) and  $\text{H}^+$  (hydrogen ion). The positive  $\text{H}^+$  ion attacks the surface of the glass, where primarily  $\text{Ca}^{2+}$  ions are released along with a small number of  $\text{Na}^+$  ions in the form of fluoride complexes.

The liberated ions react with the acid and cross-link with the polyacrylic acid as calcium bridges to form a calcium polycarboxylate gel (Fig. 1) in which the non-reacted glass is embedded.

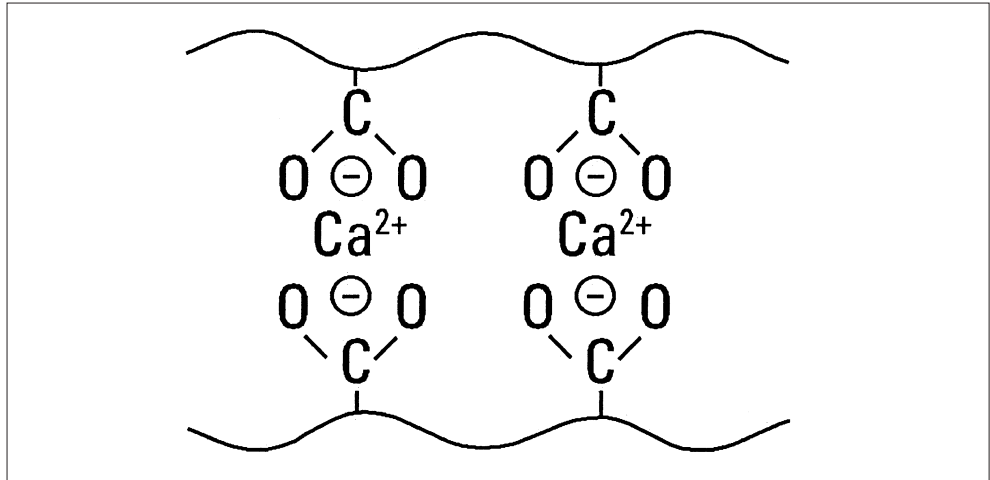


Fig. 1: Polycarboxylate gel

The continued attack of hydrogen ions cause a delayed release of  $Al^{3+}$  ions from silicate glass in the form of  $AlF_2^+$  ions which are deposited in the already preformed matrix to form a water-insoluble Ca-Al-Carboxylate gel.

Storing in water an extended period of time further stabilizes the cement's microstructure (Fig. 2).

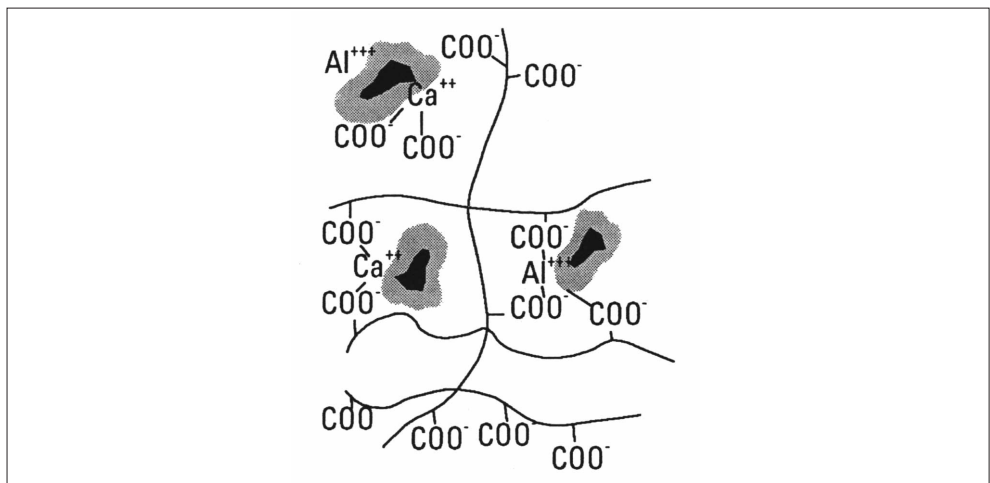


Fig 2: The structure of a glass ionomer cement. The black areas represent non-reacted glass bodies which are encased in the gel matrix. This is formed as a result of the acidic attack and the subsequent release of  $Al^{3+}$  and  $Ca^{2+}$  ions from the glass.

To achieve high strength properties and a packable consistency while maintaining good bonding characteristics, the grain distribution and the pretreatment of the glass have been specially optimized for KETAC-MOLAR.

This means that 50% of the glass particles in KETAC-MOLAR are no greater than approx. 2,8  $\mu m$  in size, with 90% of the particles having a diameter of less than 9,6  $\mu m$ .

### 3. Physico-technical Data

Because of the optimised glass particle size, KETAC-MOLAR has excellent mechanical properties. In Table 2 the material properties for the three KETAC-MOLAR products are compared, as measured using standardised methods:

	<b>KETAC-MOLAR APLICAP (average values)</b>	<b>KETAC-MOLAR HAND-MIXED version</b>
Curing time (min) ISO 9917	2:30	3:30
Compressive strength (MPa) ISO 9917	230	210±13
Surface hardness (MPa) DIN 53456	460	420±82
Radiopacity (%) ISO 4049	260	250
Flexural strength (MPa) ISO 4049	33	37±6

## 4. Material-related aspects

### 4.1 Biocompatibility

Dental materials should not be used intra-orally until the anticipated biological reaction processes have been clearly documented by histological studies conducted under application conditions and the materials have been classified as being safe to use. A large number of publications have certified that the pulpa compability of glass ionomer cements is satisfactory to good, yet just as many doubts have also been expressed, particularly after cell culture tests.

The polyacrylic acids present in glass ionomer cements are relatively weak acids. However, the degree of acidity and the duration of acid release are highly dependent on the powder/liquid ratio. The high viscosity of KETAC-MOLAR is achieved by its high powder factor and thus only a low level of acid release can be expected. In addition, the administered form in capsule preparations allows for exact dosing and thus a constant acid ratio.

### 4.2 Fluoride release

The powder component of glass ionomer cements contains crystalized ingredients rich in calcium fluoride. After the powder and liquid have been premixed and the acid/base reaction initiated, the negative fluoride ions are released from the powder along with the positive  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Na}^{+}$  ions and build up in the cement matrix as ions, salt compounds or complex compounds. Most of the fluoride released from the set cement is delivered by these compounds.

Glass ionomer cements exhibit a high degree of initial fluoride discharge, since most of the fluoride released is stored in the surface of the filling. The rate of fluoride release continues to decline over several month and then stabilizes at a constant level. The liberated fluoride proceeds from the interior of the filling to its surface, where it then goes into solution. The use of tooth-paste, gels or solutions containing fluoride can enhance the refluoridization of glass ionomer cements fillings.

KETAC-MOLAR releases on the whole less fluoride than other glass ionomer cements because its solubility is less than that of comparable cements. Test samples of KETAC-MOLAR, which were placed in water 1 hour later exhibit a total solubility of 0.05% after 24 hours (KETAC-FIL 0,2%). When the samples were placed in water after only 10 minutes ("10-minute solubility"), solubility values of 0.18 – 0.26% (GIZ "H" 1.7%) were measured for KETAC-MOLAR.

Since glass ionomer cements release considerably greater amounts of fluoride than silicate cements, compomers or even composites, their use is particularly suited for treating children, adults with caries or the elderly.

### 4.3 Chemical adhesion

The adhesive bonding behaviour of filling materials makes it possible to form preparations that are gentle on tooth substance. However, the borders of a glass ionomer cement filling must achieve a thickness of at least 0.5 mm in order to avoid any breaking off of the filling's borders. The chemical adhesion of a cement to the hard dentine substance was already shown by the carboxylate cements, whose polyacrylic acids form a chelate bond with the calcium ions hard dentine substances (enamel and dentine).

The initial bonding process probably arises through the formation of hydrogen bridges between the carboxyl groups and the hydroxyl apatite of the hard dentine substances, although it is likely that the ionic bonds thus formed then predominate. Furthermore, an additional chemical bond is thought to exist with amino acids and the carbonic acids of dentine collagen. Due to the high percentage of hydroxyl apatite in the enamel, one must assume that the bonding forces to enamel are stronger than those to dentine.

Although glass ionomer cements can also bond directly to enamel and dentine in the presence of a smear layer, its removal can increase adhesive bonding forces. For this reason pretreatment with KETAC CONDITIONER (a 25% polyacrylic acid solution) is recommended before applying KETAC-MOLAR.

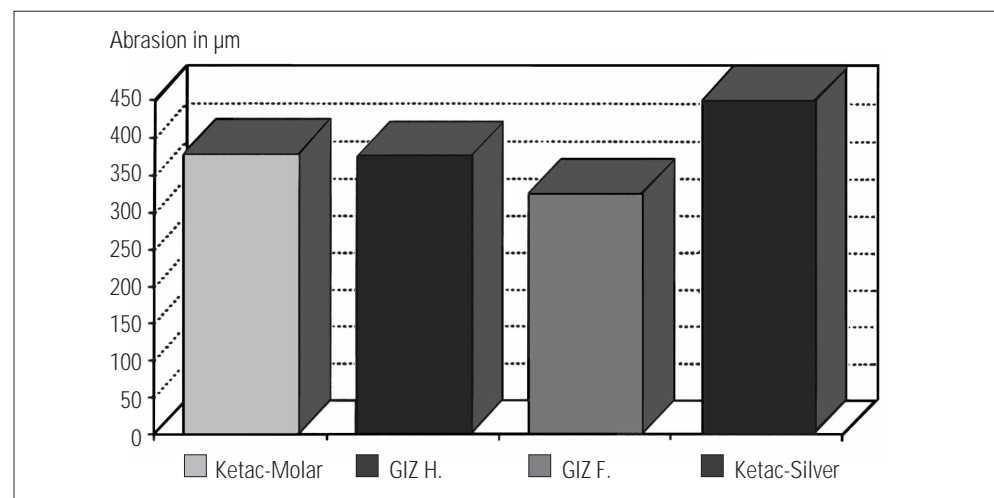
Conditioner	Dentin adhesion [MPa] median	25%/75% quantile [MPa]
without Polyacrylic acid	1.2	1.0/2.5
10 sec Polyacrylic acid	2.1	1.1/3.3
30 sec Polyacrylic acid	3.2	2.5/3.8
60 sec Polyacrylic acid	3.0	2.5/4.3

**Fig 3: Dentine adhesion using KETAC-MOLAR APLICAP on noncarious human molars (shear test according to ISO TR No. 11405); Universität Regensburg, Dr. Friedl**

## 5. Competitors in today's market

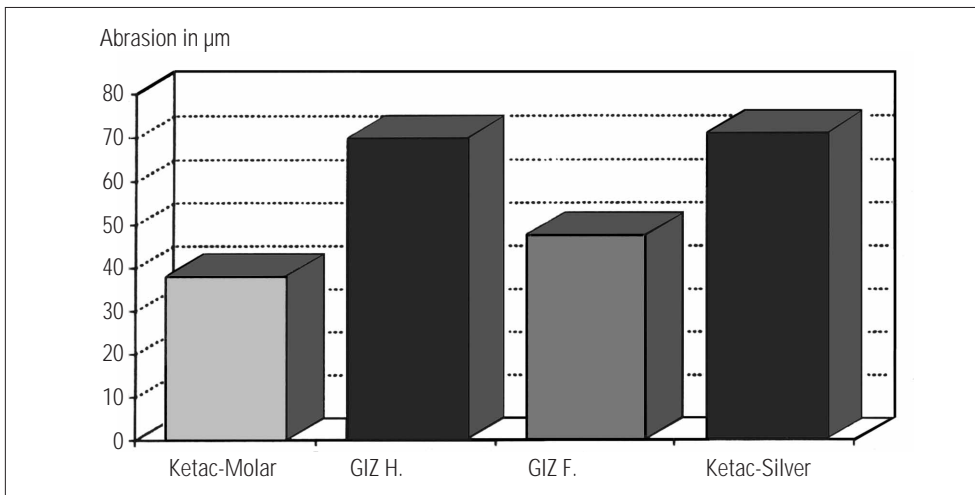
Since current glass ionomer cements fail to achieve sufficient hardness and resistance to fracture and have a low abrasion resistance, many dental manufacturers have tried to create glass ionomer cements with improved mechanical properties by modifying their composition. By varying the powder/liquid ratio of the grain distribution and the polycarbonic acid balance in liquid and powder, greater strength properties and a packable consistency can be achieved while maintaining good setting properties.

In a comparative study of abrasion resistance as measured by two-body abrasion tests under simulated intra-oral conditions, KETAC-MOLAR showed an abrasion resistance comparable to GIC "H" (Fig. 4).



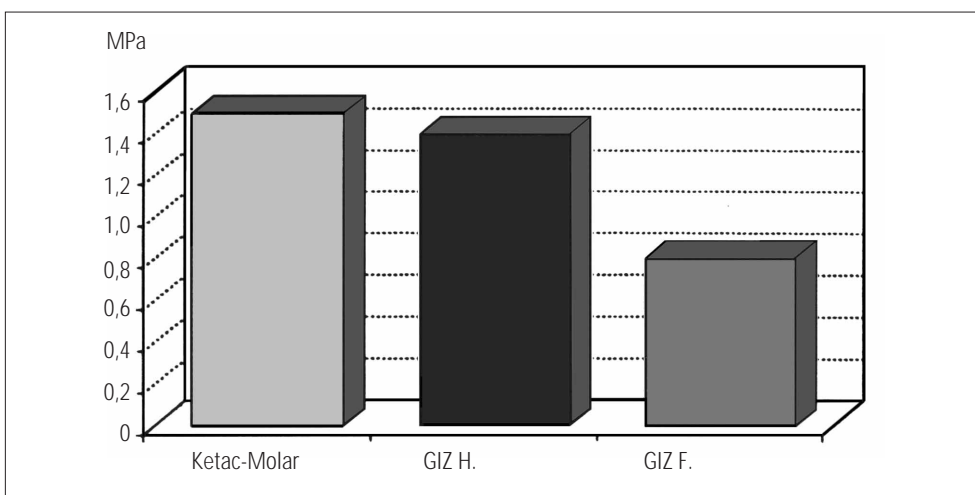
**Fig. 4:** Abrasion values of KETAC-MOLAR, GIC "H", GIC "F9" and KETAC SILVER after 2,000 load cycles with a vertical force of 50 N using the pin-on-block method. Tests were conducted with cylinder-shaped  $\text{Al}_2\text{O}_3$  antagonists at the Munich mastication simulator.

Three-body abrasions tests for simulating food abrasion on contactless surfaces show abrasion values for KETAC-MOLAR that are lower than the other tested materials (Fig. 5).



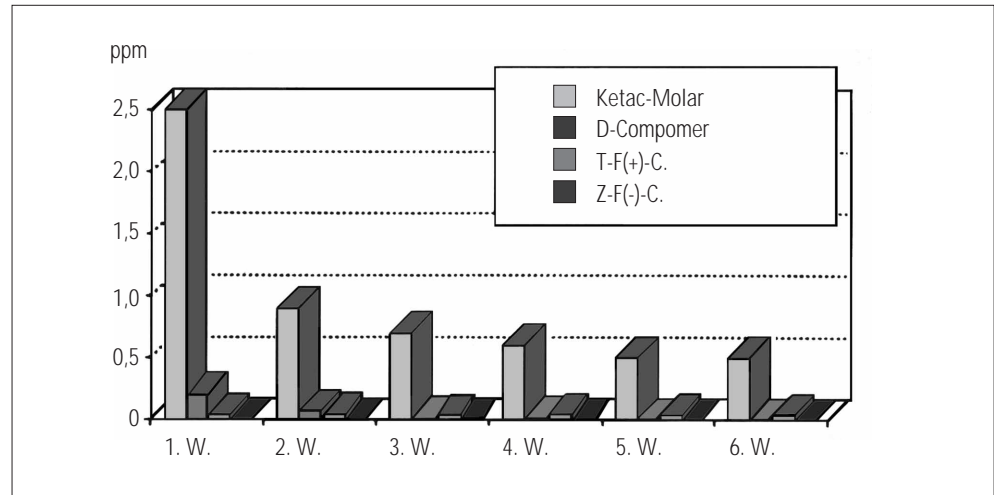
**Fig. 5:** Three-body abrasion values of KETAC-MOLAR, GIC "H", GIC "F9" and KETAC SILVER after 200,000 abrasion cycles in the ACTA-machine (Munich version). Tests were conducting using a millet suspension and 15 N application force.

In terms of dentine adhesion, the adhesive strength of KETAC-MOLAR is comparable to that of GIC "H", GIC "F9", with KETAC-MOLAR und GIC "H" showing slightly better values when compared to GIC "F9" (Fig. 6).



**Fig. 6:** Dentine adhesion using bovine dentine, in MPa (in-house data)

A comparison of fluoride ion release data shows that KETAC-MOLAR exhibits considerably lower values than the other materials tested. This can be explained by the low solubility of KETAC-MOLAR in comparison with other glass ionomer cements referred to previously. However, this property does ensure good surface quality and a tight seal along the cavity border over a comparably longer period of time.



**Fig. 7: Fluoride release of KETAC-MOLAR, compomer "D", the composite "T" containing fluoride, and the fluoride-free composite "Z". The test bodies were placed in water 1 hour after setting. The fluoride levels of the chart were determined after 1 week of water storage.**