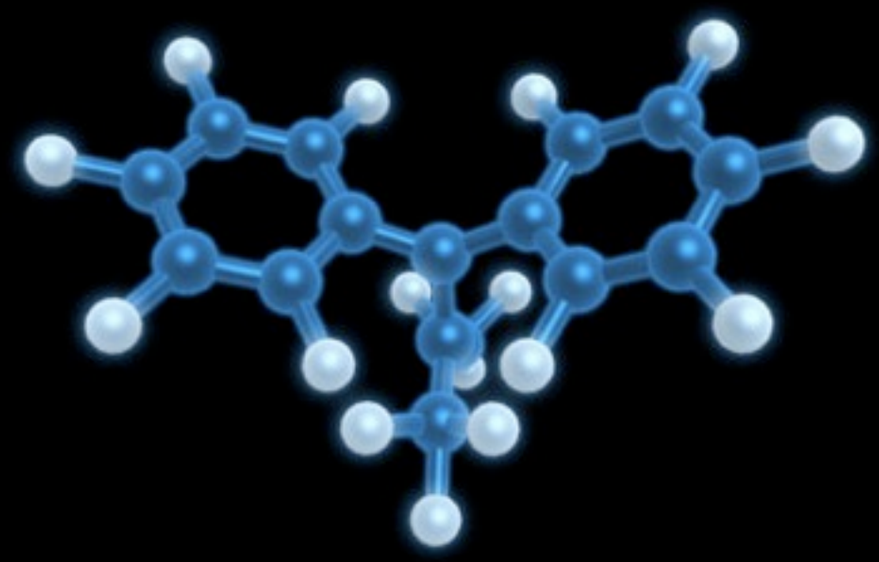
Università Degli Studi Di Torino
Facoltà di Medicina E Chirurgia
DIPARTIMENTO DI SCIENZE BIOMEDICHE ED ONCOLOGIA UMANA

CORSO DI LAUREA SPECIALISTICA IN ODONTOIATRIA E PROTESI DENTARIA
INSEGNAMENTO DI CONSERVATIVA ED ENDODONZIA
Titolari: Prof. Elio BERUTTI, Dr. Damiano PASQUALINI, Dr. Nicola SCOTTI

LE RESINE COMPOSITE

Becoming the most widely accepted material of choice by dentists and patients because of their esthetic qualities and new advances in their strength

Composito Dentale: miscuglio di particelle di vetro silicatico inglobate in un monomero acrilico che viene polimerizzato durante l'applicazione



COMPOSITE CHEMISTRY

Dental composite is composed of a resin matrix and filler materials.
Coupling agents are used to improve adherence of resin to filler surfaces.
Activation systems including heat, chemical and photochemical initiate polymerization.
Plasticizers are solvents that contain catalysts for mixture into resin.
Monomer, a single molecule, is joined together to form a polymer, a long chain of monomers.
Physical characteristics improve by combining more than one type of monomer and are referred to as a copolymer.
Cross linking monomers join long chain polymers together along the chain and improve strength.

FASE ORGANICA
(matrice)

FASE INTERMEDIA
(agente legante)

FASE DISPERSA
(filler o riempitivo)

FASE ORGANICA
(matrice)

FASE INTERMEDIA
(agente legante)

FASE DISPERSA
(filler o riempitivo)

Bis-GMA bisfenolo A glicidilmetacrilato

Bis-GMA modificato

TEG-DMA (trietilen-glicoldimetacrilato)

Uretano-dimetacrilato

Bis-GMA

ESTREMAMENTE VISCOSO

ridotta dall'aggiunta di TEGDMA

maggior scorrimento
aumentata conversione
aumentati legami crociati
aumentata contrazione

Tab. I Classification of composites according to matrix components

Matrix	Chemical system	Group	Example of material
Conventional matrix	Pure methacrylate	Hybrid composite	Tetric EvoCeram®
		Nano composite	Filtek supreme XT®
Inorganic matrix	Inorganic polycondensate	Ormocers	Admira® Definite®
Acid modified methacrylate	Polar groups	Compomers	Dyract eXtra®
Ring opening epoxide	Cationic polymerisation	Silorans	Filtek Silorane®

FASE ORGANICA
(matrice)

FASE INTERMEDIA
(agente legante)

FASE DISPERSA
(filler o riempitivo)

molecole bipolari che fungono da anello di congiunzione, in grado di legarsi a gruppi ossidrilici (silice) e di copolimerizzare con i doppi legami dei monomeri

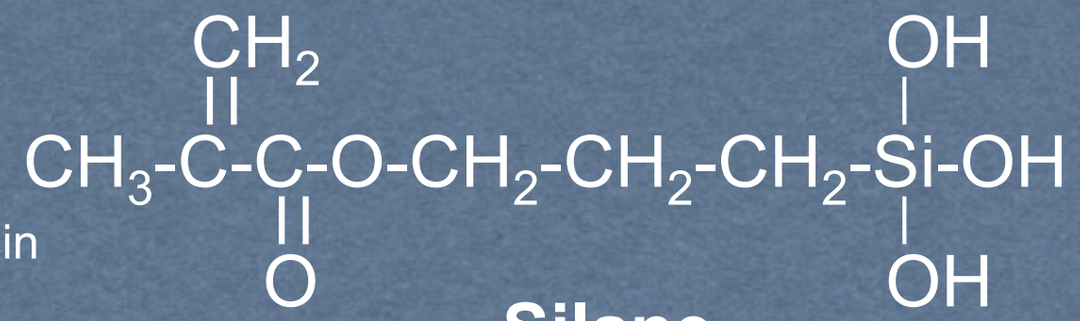
FASE ORGANICA
(matrice)

FASE INTERMEDIA
(agente legante)

FASE DISPERSA
(filler o riempitivo)

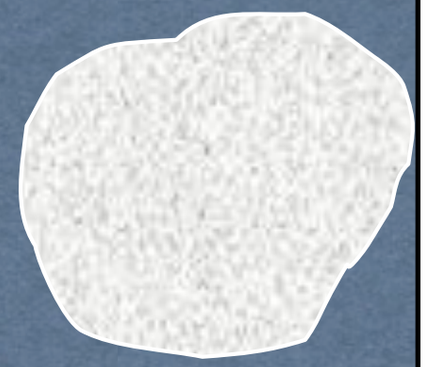
Bis-GMA

Bonds with resin



Silane

Bonds with filler



1

The stable bond between the filler and matrix further influences the material properties. The quality of the bond affects the abrasion resistance of the restorative material (Manhart et al. 2000)

2

Silanisation of the filler is important for material strength (Ikejima et al. 2003)

FASE ORGANICA
(matrice)

FASE INTERMEDIA
(agente legante)

FASE DISPERSA
(filler o riempitivo)

inibisce la deformazione della matrice

riduce il coefficiente di dilatazione termica

TIPO DI RIEMPITIVO

PHYSICAL PROPERTIES OF COMPOSITE ARE IMPROVED BY FILLERS, HOWEVER, COMPOSITE CHARACTERISTICS CHANGE BASED ON FILLER MATERIAL, SURFACE, SIZE, LOAD, SHAPE, SURFACE MODIFIERS, OPTICAL INDEX, FILLER LOAD AND SIZE DISTRIBUTION.

ioni di Litio e di Alluminio

Bario, Zinco, Boro, Zirconio,

Ittrio

cristalli di quarzo

vetro borosilicato

vetro di bario

parti colloidali

silicato di bario, di stronzio e alluminio

fluoruro di calcio

TIPO DI RIEMPITIVO

classificazione

- FILLERS ARE CLASSIFIED BY MATERIAL, SHAPE AND SIZE.
- FILLERS ARE IRREGULAR OR SPHERICAL IN SHAPE DEPENDING ON THE MODE OF MANUFACTURE.
- SPHERICAL PARTICLES ARE EASIER TO INCORPORATE INTO A RESIN MIX AND TO FILL MORE SPACE LEAVING LESS RESIN.
- ONE SIZE SPHERICAL PARTICLE OCCUPIES A CERTAIN SPACE.
- ADDING SMALLER PARTICLES FILLS THE SPACE BETWEEN THE LARGER PARTICLES TO TAKE UP MORE SPACE.
- THERE IS LESS RESIN REMAINING AND THEREFORE, LESS SHRINKAGE ON CURING THE MORE SIZE PARTICLES USED IN PROPER DISTRIBUTION.

TIPO DI RIEMPITIVO

Fracture Toughness of Experimental Dental Composites Aged in Ethanol

J.L. Ferracane and H.X. Berge

Department of Biomaterials and Biomechanics, Oregon Health Sciences University, 611 SW Campus Drive, Portland, Oregon 97201

Table 2. Composition and degree of conversion of composites with variable filler volumes

Composite	Filler Volume	Degree of Conversion (%)
C62VOL	62	63.2 ± 0.8[d]
C53VOL	53	66.8 ± 1.5[c]
C48VOL	48	68.9 ± 2.2[b]
C37VOL	37	71.7 ± 1.1[a]
C28VOL	28	68.9 ± 1.6[b]
RESIN	0	70.3 ± 1.1[a,b]

Mean values (± 1 s.d.) for degree of conversion (n = 6) with the same superscript were not significantly different.

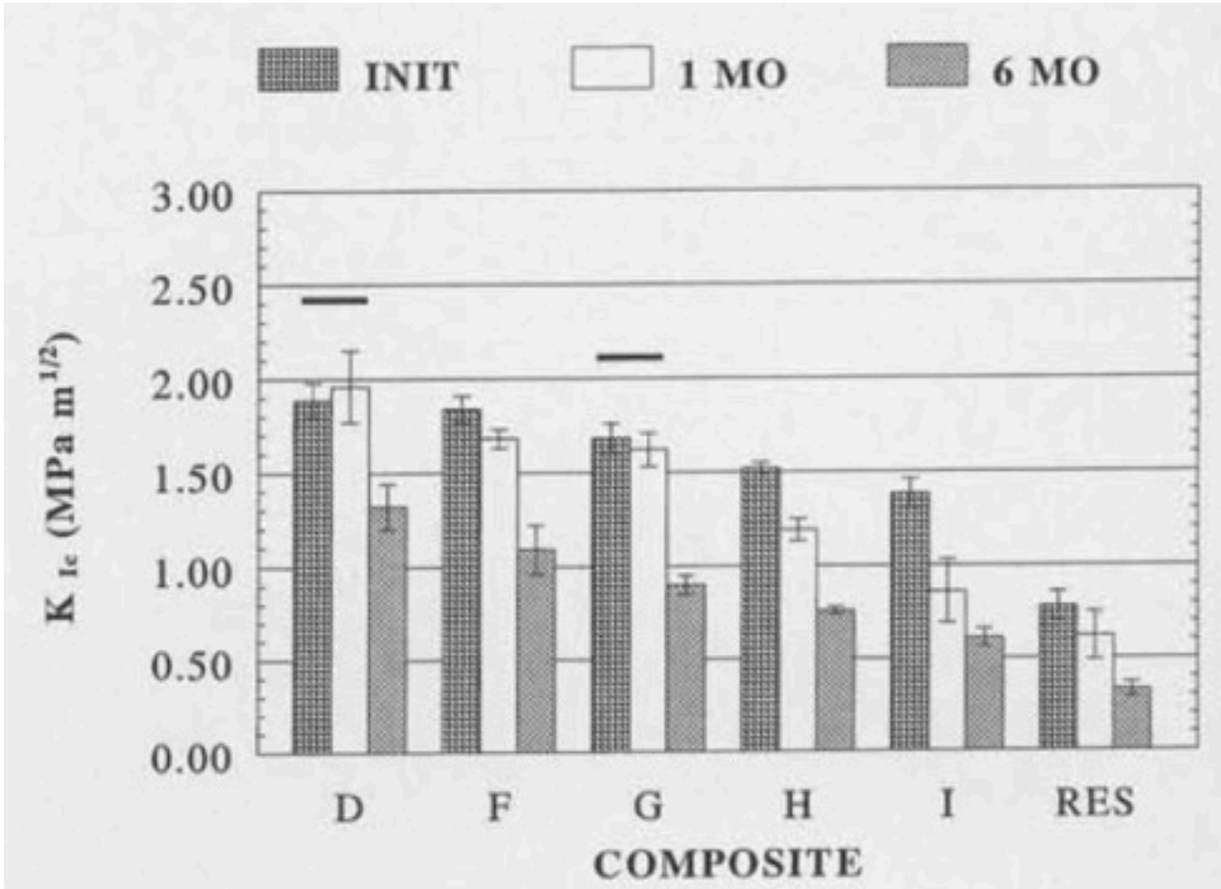
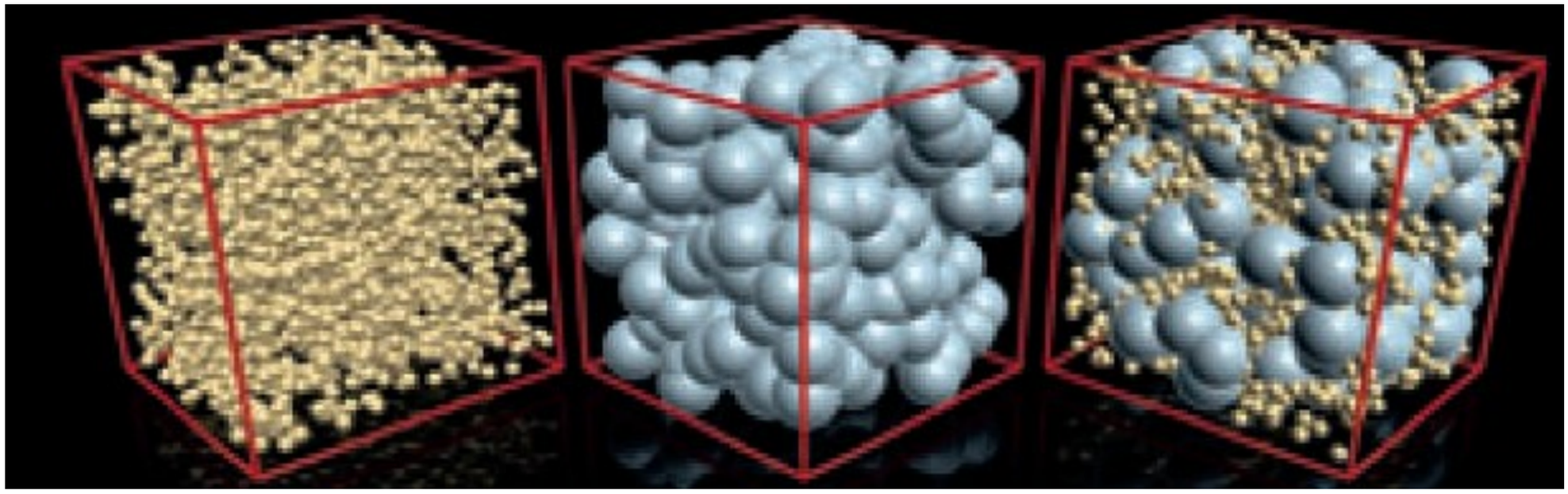


Figure 2. Histogram showing the change in K_{Ic} for the composites with varied filler volumes as a result of being aged in the ethanol solvent. Means connected by bars were not significantly different ($p \leq 0.05$). D = C62VOL; F = C53VOL; G = C48VOL; H = C37VOL; I = C28VOL.

PERCENTUALE DI RIEMPITIVO

% IN PESO

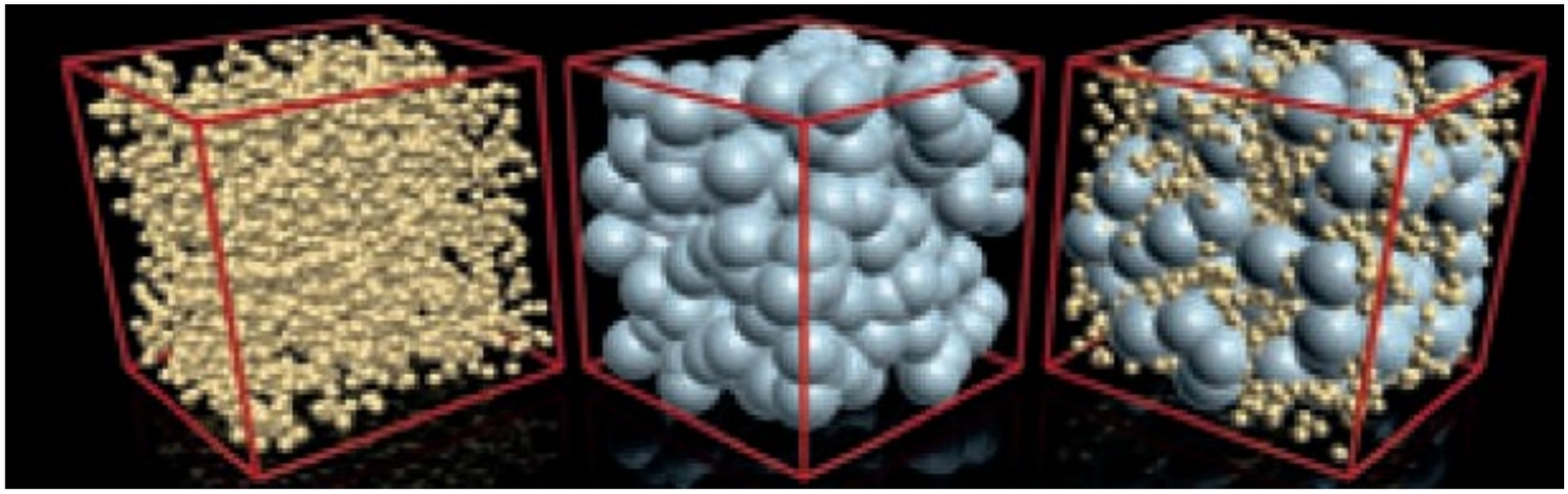


% IN VOLUME

con l'aumentare dell'area superficiale del riempitivo diminuisce la fluidità del materiale

PERCENTUALE DI RIEMPITIVO

% IN PESO

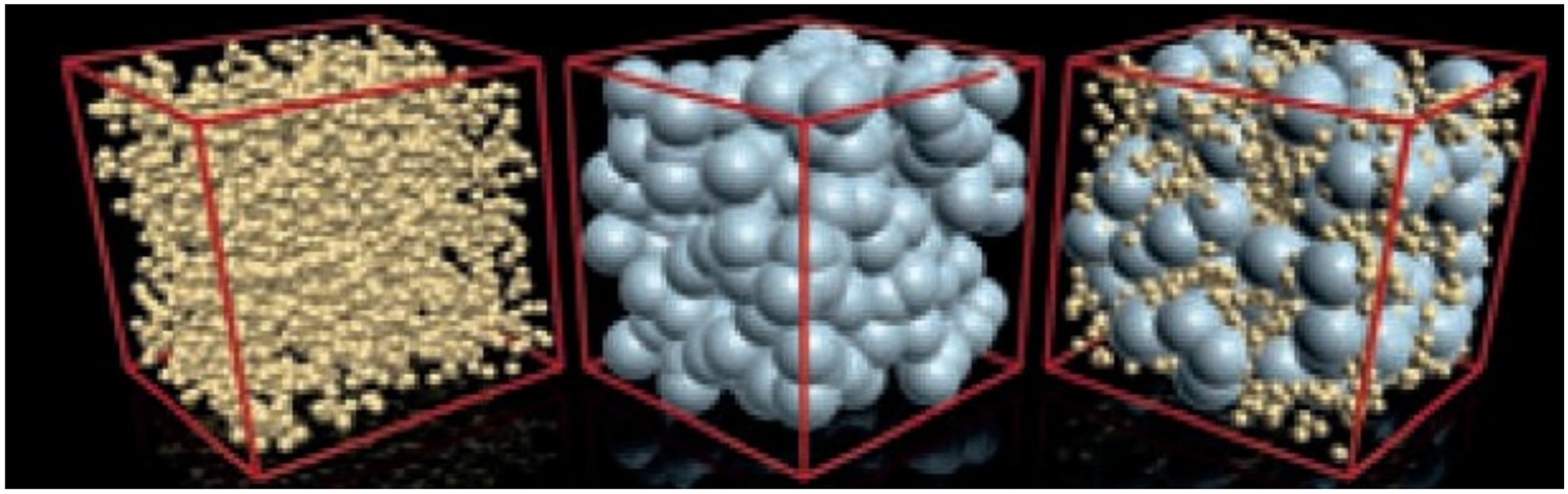


% IN VOLUME

Il riempitivo a base di silice ha una densità pari a circa 3 volte quella del monomero

PERCENTUALE DI RIEMPITIVO

% IN PESO



% IN VOLUME

Il riempitivo a base di silice ha una densità pari a circa 3 volte quella del monomero

DIMENSIONI DELLE PARTICELLE

Nanofillers and nanoclusters enhance the long-term stability and the polishing properties of micro-filler composites are made possible by the use of nanoparticles and nanoclusters.

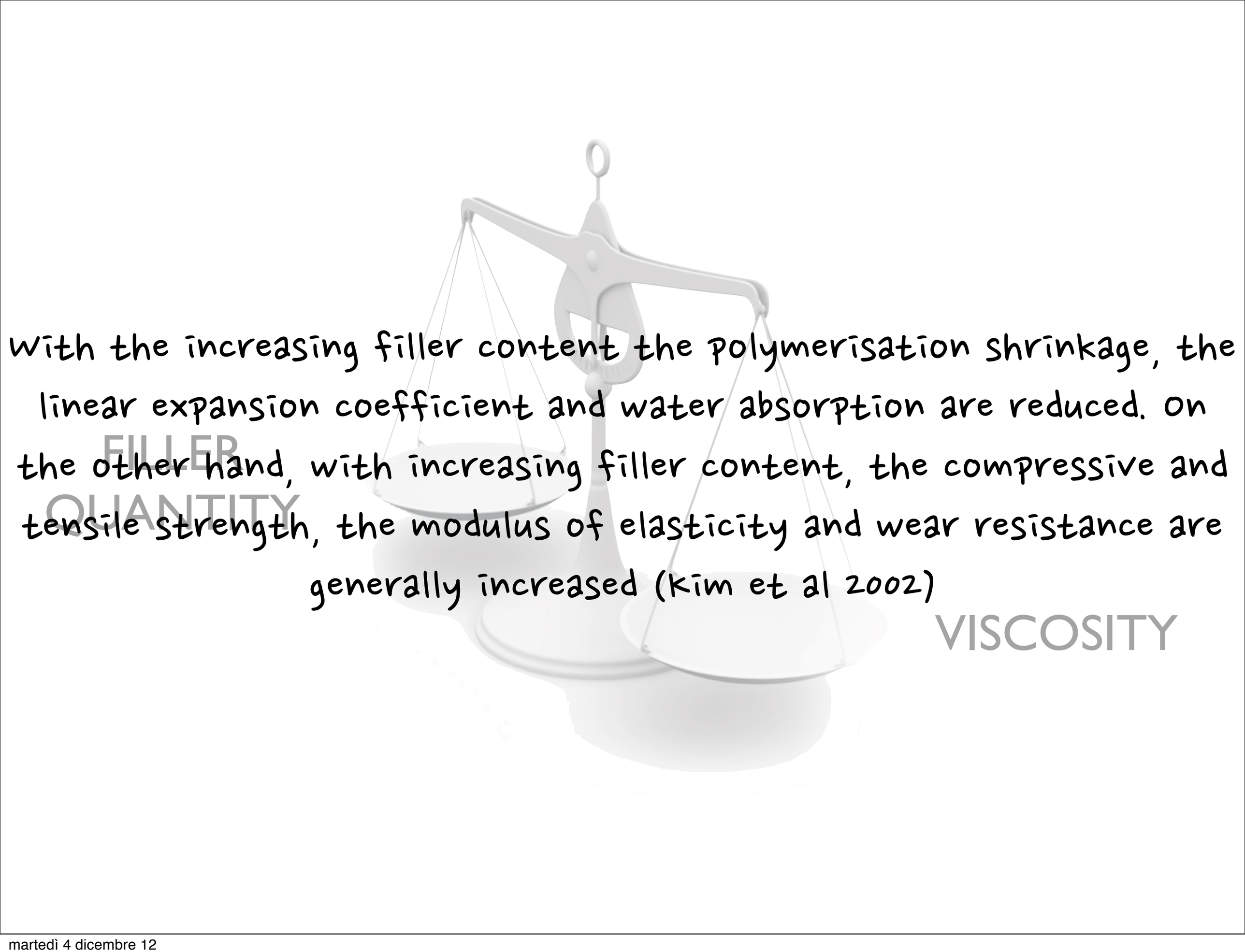
DIMENSIONI DELLE PARTICELLE

The mechanical stability achieved in hybrid composites is due to larger filler particles or "nanoclusters". Superficial filler particles are lost due to abrasion. The nanoclusters of the nano- composites are hereby broken down into nanoparticles. These particles are smaller than the wavelengths of visible light. It has been shown that surface polish is preserved longer after wear tests in composites with filler particles <0.4 μm (Mitra et al. 2003). Nanoparticles can be incorporated into cells but their toxic potential is still largely unknown (Koeneman et al. 2009).

FILLER

QUANTITY

VISCOSITY



With the increasing filler content the polymerisation shrinkage, the linear expansion coefficient and water absorption are reduced. On the other hand, with increasing filler content, the compressive and tensile strength, the modulus of elasticity and wear resistance are generally increased (Kim et al 2002)

FILLER SHAPE

Pre-polymerised Fillers

COMPOSITES WITH LOWER FILLER CONTENT AND LOWEST FLEXURAL STRENGTH AND HARDNESS

Round Fillers

COMPOSITES WITH HIGHEST FILLER CONTENT AND HIGHER HARDNESS AND HIGH FLEXURAL STRENGTH

Mixed Filler Particles

NO LINEAR RELATIONSHIP BETWEEN FILLER CONTENT AND FLEXURAL STRENGTH

Clin Oral Invest (2009) 13:427–438
DOI 10.1007/s00784-009-0258-4

ORIGINAL ARTICLE

Investigations on mechanical behaviour of dental composites

Nicoleta Ilie · Reinhard Hickel

FILLER SHAPE

Less difference were found between hybrid, packable, ormocer- based, nano-composites and compomers, attesting higher mechanical properties than the flowables composites, flowable compomers and micro-filled composites

Table 3 Influence of fillers—volume and weight—and material categories on the mechanical properties

Variables	Vol.%	Wt.%	Material type
Flexural Modulus of Elasticity (FM)	.439	.253	.037
Flexural Strength (FS)	.345	.172	.016
Compressive Strength (CS)	.229	.074	.065
Diametral Tensile Strength (DTS)	.129	.067	.023

The higher the partial η^2 values, the higher is the influence of the selected variables on the mechanical properties

The filler volume was shown to have the highest influence on the measured properties, attending a maximum FS and FM at a level of ca. 60%

CLASSIFICAZIONE

METODO DI POLIMERIZZAZIONE

- Heat Catalyst
- Photochemical Catalyst
  - Light-curing
  - Chemical Catalyst

CLASSIFICAZIONE

METODO DI POLIMERIZZAZIONE

H e a t C a t a l y s t

La polimerizzazione della resina richiede iniziazione da parte di un radicale libero.
L'iniziazione induce propagazione o continua unione di molecole a doppi legami fino alla conclusione della reazione.
Il calore applicato all'iniziatore induce una rottura della struttura chimica per produrre radicali liberi; tuttavia, i monomeri possono polimerizzare quando si applica calore anche senza iniziatori.
Resine richiedono stabilizzatori per evitare polimerizzazione spontanea. Stabilizzatori sono usati anche per controllare la reazione di attivatori e miscele di resina.
Idrochinone è più comunemente utilizzato come stabilizzatore.
Iniziatori di calore comuni sono a base di perossidi, per esempio:
benzoilperossido
t-butilperossido
t-cumythydroxyperoxide

CLASSIFICAZIONE

METODO DI POLIMERIZZAZIONE

Photochemical Catalyst

Primi sistemi fotochimici utilizzati erano l'estere di metil-benzoile, che è sensibile a lunghezze d'onda UV a 365 nm. I sistemi UV hanno avuto un uso limitato perchè ridotta profondità di polimerizzazione. Attivazione da parte di luce visibile dei dichetoni sono i sistemi fotochimici più utilizzati. I dichetoni attivati da luce visibile per produrre reazioni lente. Le ammine sono aggiunte per accelerare il tempo di polimerizzazione.

Attualmente, compositi diversi utilizzano diversi sistemi fotochimici. Questi sistemi sono attivati da differenti lunghezze d'onda. Inoltre, le lampade da polimerizzazione diverse producono diverse gamme di lunghezze d'onda che non potrebbero corrispondere lunghezze d'onda di attivazione dei compositi. Questo può portare a nessuna o parziale polimerizzazione. I materiali compositi devono corrispondere alle luci polimerizzazione.

Comuni iniziatori fotochimici sono:

canforochinone

Acenaphthene

Benzyl

Leucerina TPO

Fenilpropadenione

CLASSIFICAZIONE

METODO DI POLIMERIZZAZIONE

L i g h t - c u r i n g

Light curing can be accomplished with:-

1) Quartz-Tungsten-Halogen
2) Plasma Arc Curing
3) Light Emitting Diode

CLASSIFICAZIONE

METODO DI POLIMERIZZAZIONE

Chemical Catalyst

Attivazione chimica di perossidi produce radicali liberi. Acceleratori chimici spesso non sono stabili nel colore e sono stati migliorati per questo motivo.

Il termine self-cure o polimerizzazione duale (in combinazione con la iniziazione fotochimica) definisce questi materiali.

Compositi chimici derivano dal mix di una pasta base e una pasta catalizzatrice per la self-cure.

Collanti mescolano i due liquidi.

Miscelazione di due paste incorpora aria nel composito.

Ossigeno inibisce polimerizzazione, risultando in un restauro più debole.

Acceleratori chimici sono:

Dimetil-p toludine

N, N-bis (idrossi-inferiore-alchile) -3,5-xilidina

CLASSIFICAZIONE

DIMENSIONE DEL RIEMPITIVO

Macrofillers (10-100)

Midifillers (1-10)

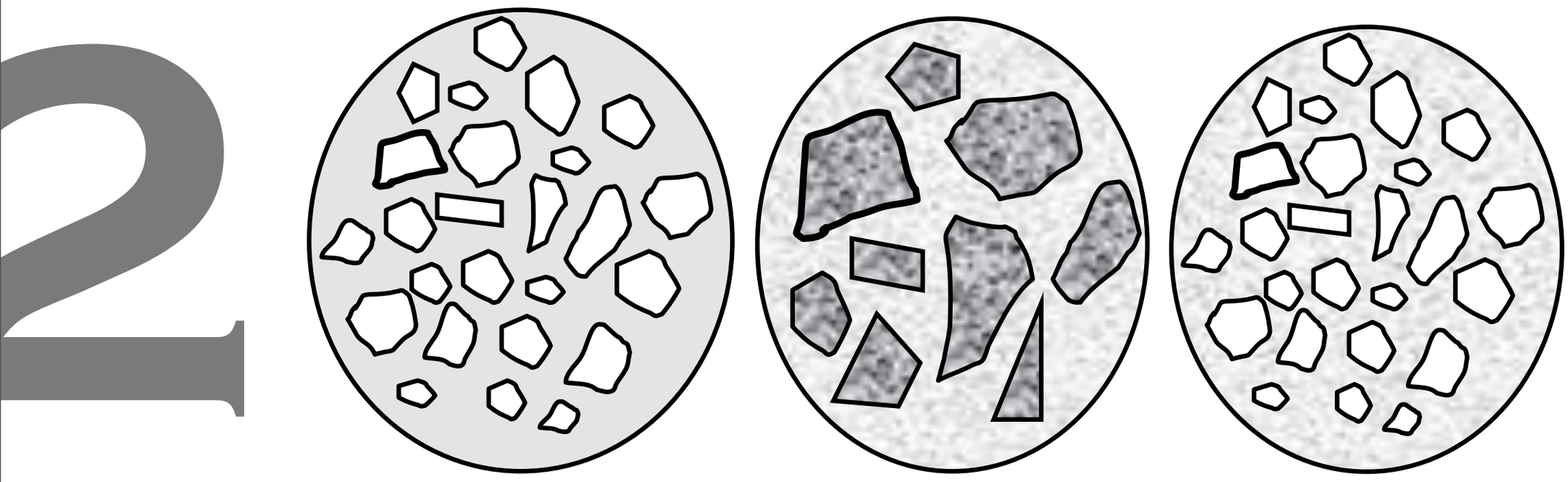
Minifillers (0.1-1)

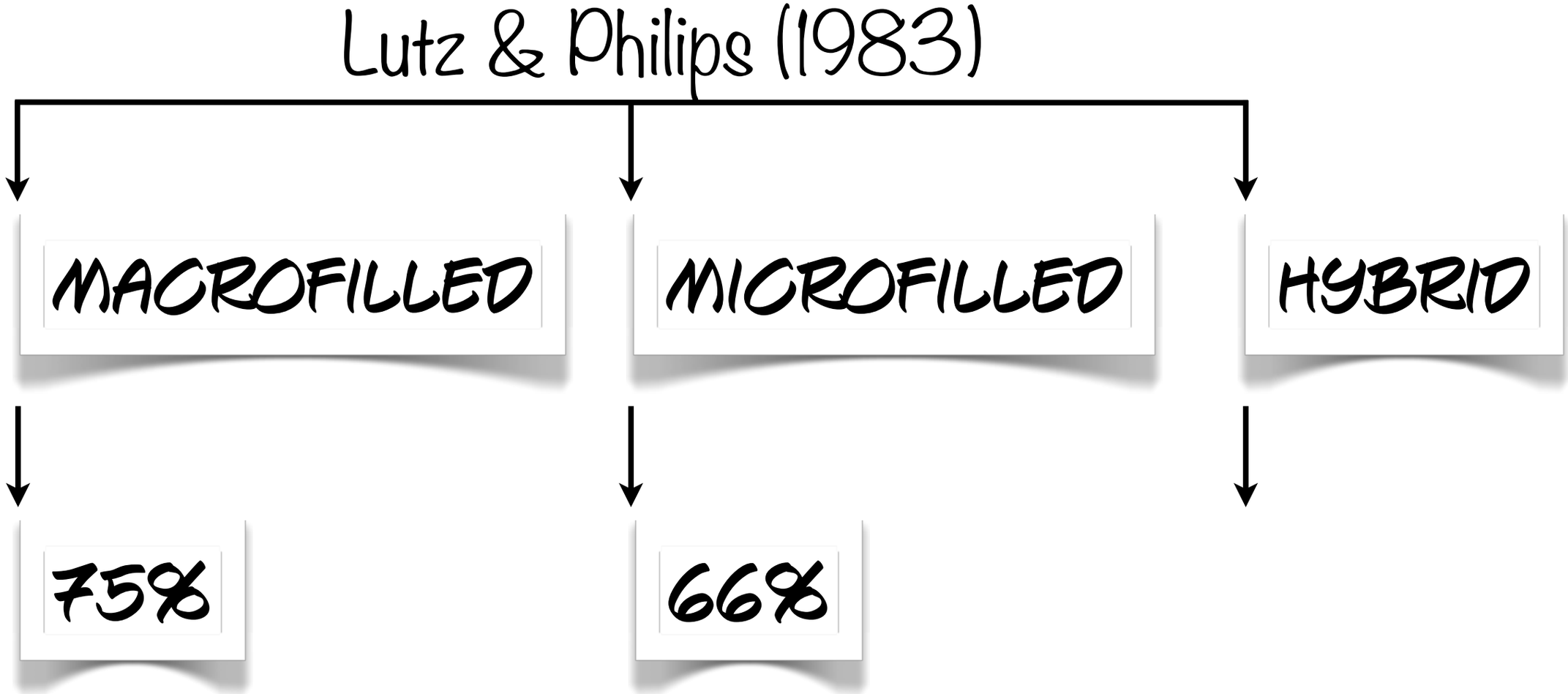
Microfillers (0.01-0.1)

Nanofillers (0.005 - 0.01)

CLASSIFICAZIONE

DIMENSIONE DEL RIEMPITIVO





Lutz F, Phillips RW. A classification and evaluation of composite resin systems. J Prosthet Dent. 1983 Oct;50(4):480-8.

Lutz & Philips (1983)

MACROFILLED

MICROFILLED

HYBRID

contengono particelle di riempitivo piu' grandi; possiedono durezza elevata, ma superficie ruvida ed irregolare.

Bassa resistenza all'usura.

Lutz F, Phillips RW. A classification and evaluation of composite resin systems. J Prosthet Dent. 1983 Oct;50(4):480-8.

Lutz & Philips (1983)

MACROFILLED

MICROFILLED

HYBRID

Miglior estetica e lucidabilita'

Aumentato potenziale di frattura

Ridotta radiopacita'

usura clinica lineare

Lutz F, Phillips RW. A classification and evaluation of composite resin systems. J Prosthet Dent. 1983 Oct;50(4):480-8.

Lutz & Philips (1983)

MACROFILLED

MICROFILLED

HYBRID

Particelle di dimensione diversa consentono di massimizzare il "filler loading". Le microparticelle inoltre migliorano la maneggevolezza e riducono l'appiccicosita'

Lutz F, Phillips RW. A classification and evaluation of composite resin systems. J Prosthet Dent. 1983 Oct;50(4):480-8.

Lutz & Philips (1983)

Tab. II Classification of composites according to filler particles (LUTZ & PHILIPS 1983)

Filler	**Macro-filler (>10 µm)**	**Micro-filler (0.01–0.1 µm)**	**Micro-filler complexes**	
Composite type	Macro-filler composite	Hybrid composite	Homogenic Micro-filler composite	Inhomogenic Micro-filler composite
Properties	+ physical properties + radiopacity – polishability – wear resistance	+ radiopacity + polishability + physical properties – polymerisation shrinkage	+ polishability – wear resistance – water absorption – radiopacity – polymerisation shrinkage	+ polishability + aesthetics – physical properties
Purpose	Core build-up material under indirect restoration? No longer indicated	All classes of restoration	Small anterior restorations Class V	Small anterior restorations Class V
Example	Prisma-Fil®	Tetric Ceram®	Palfique®	Filtek A110®

+: positive property, performance acceptable –: negative property, performance unacceptable

Lutz F, Phillips RW. A classification and evaluation of composite resin systems. J Prosthet Dent. 1983 Oct;50(4):480-8.

Property	Traditional	Microfilled	Small Particle	Hybrid
Compressive strength (MPa)	250-300	250-300	350-400	300-350
Tensile strength (MPa)	50-65	30-50	75-90	70-90
Elastic Modulus (GPa)	8-15	3-6	15-20	7-12
Coefficient of Thermal Expansion (10^{-6}/ºC)	25-35	50-60	19-26	30-40
Knoop Hardness	55	5-30	50-60	50-60

1871 **SILICATI** molto solubili, proprietà meccaniche scarse

1948 **RESINE ACRILICHE** alta contrazione da polimerizzazione

1962 **BIS-GMA** resine più resistenti

migliorate proprietà meccaniche

1969 **RESINE COMPOSITE RIEMPITE**

minor contrazione

sistemi pasta/pasta

1970's **MORDENZATURA & MICRORIEMPITI**

1980's **FOTOPOLIMERIZZAZIONE & IBRIDI**

1990's **COMPOSITI FLUIDI E MICROIBRIDI**

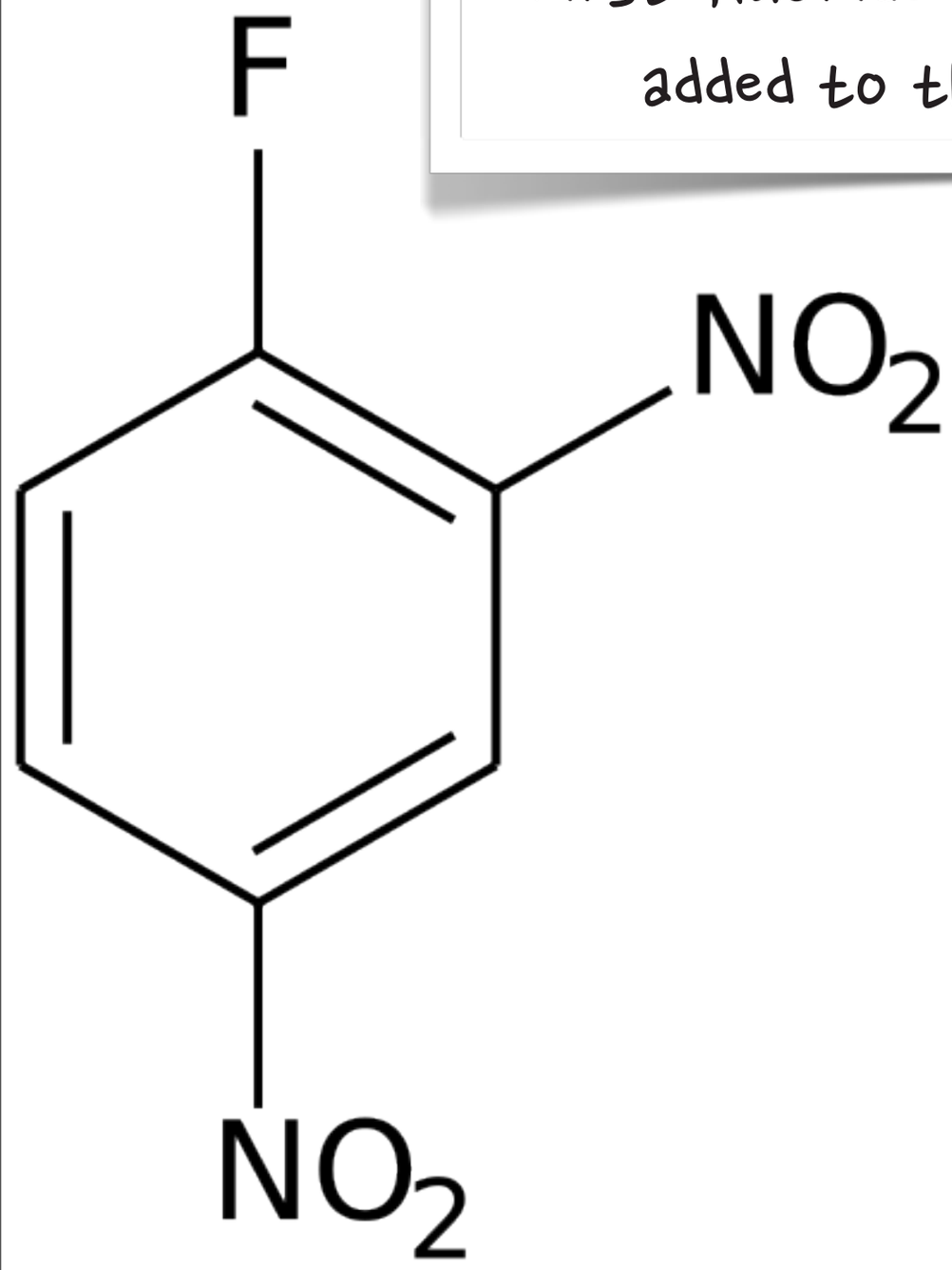
2000's **NANORIEMPITI**

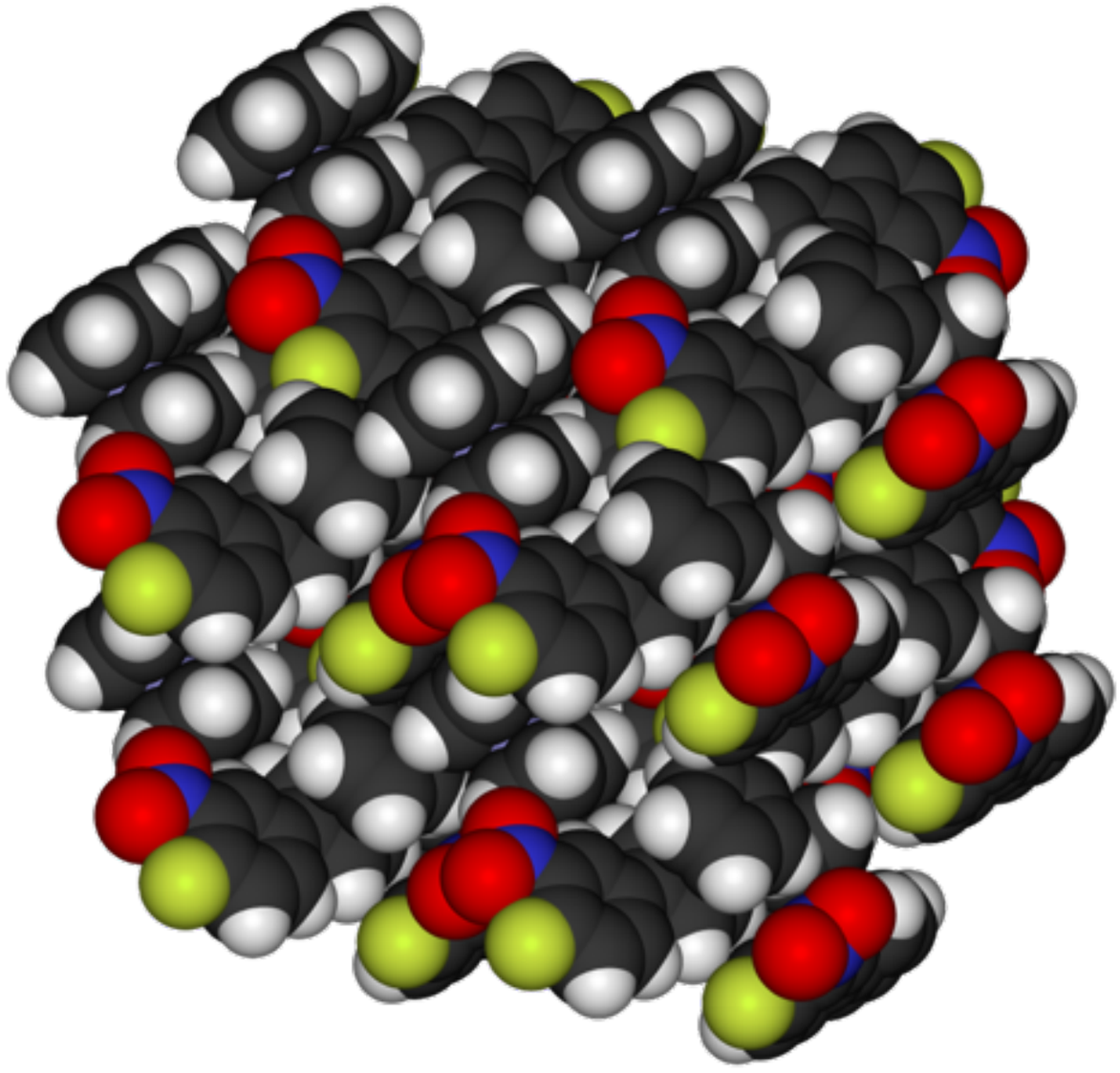
2010's **LOW-SHRINKAGE**

Rueggeberg F, J Prosthet Dent 2002

Fluoride-Release Composites

First fluoride salts (NaF, KF, SrF_2 , SnF_2) were added to the matrix (Swartz et al. 1976)





Fluoride-Release Composites

While these salts release fluoride at first, this effect decreases quickly. Furthermore, the fluoride salts adversely affect the mechanical properties of the restorative material.

Later filler materials containing fluoride were used (fluoroaluminiumsilicate-glass, YbF3) (Xu & Burgess 2003).

Fluoride-Release Composites

Available online at www.sciencedirect.com
SCIENCE DIRECT®
Biomaterials 24 (2003) 2451–2461
Biomaterials
www.elsevier.com/locate/biomaterials

Compressive strength, fluoride release and recharge of fluoride-releasing materials

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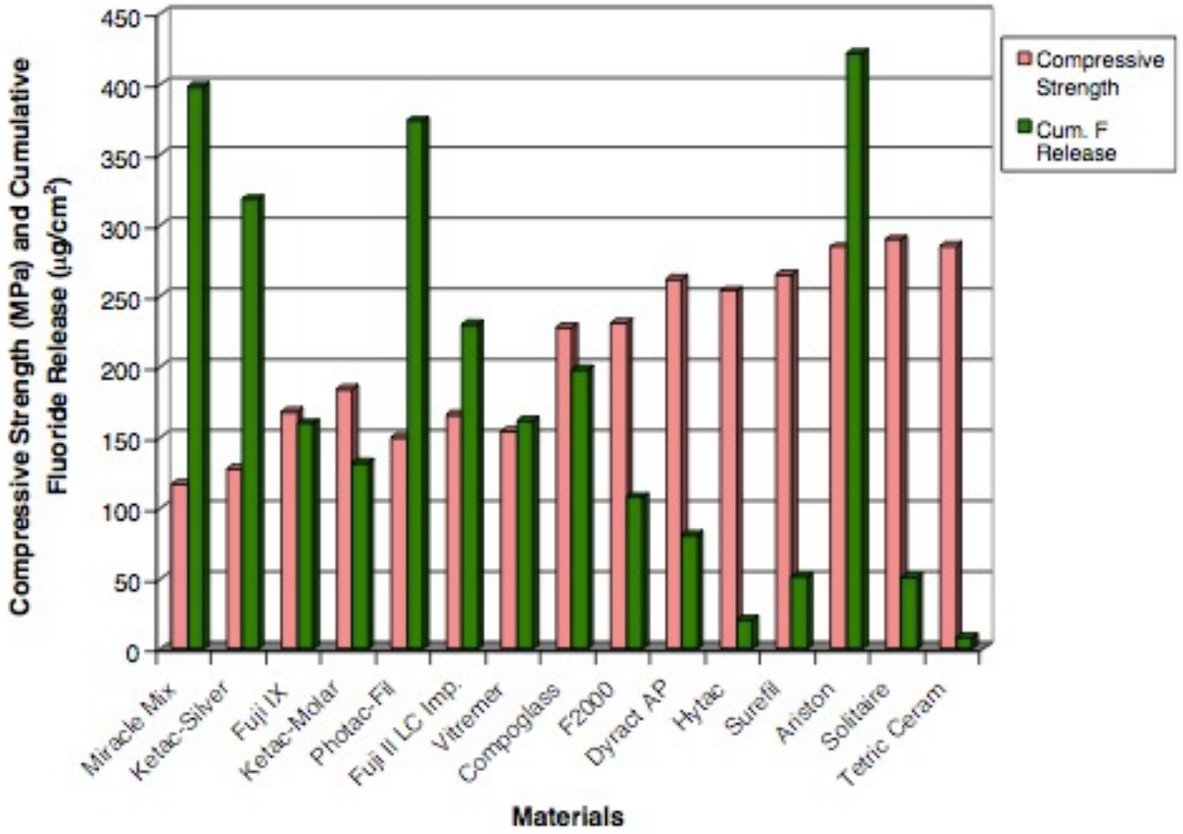
Table 1
Fluoride releasing restorative materials used in this study

Materials	Manufacturer	Resin or liquid composition	Filler composition	Filler (wt%)	Filler (vol%)	Mean filler size (μm)	Classification
Fuji IX	GC America	PAA, H_2O	Ca–Al–F–silicate glass	74		4.4	Glass ionomer
Miracle Mix	GC America	PAA, H_2O	Ca–Al–F–silicate glass, AgSnCu alloy	83		4.4, 23 (metal)	Glass ionomer
Ketac-Molar Aplicap	3M ESPE	Poly(co-acrylic acid/ maleic acid), tartaric acid, H_2O	Ca–Al–F–silicate glass	73–74	23–24	2–3	Glass ionomer
Ketac-Silver Aplicap	3M ESPE	Poly(co-acrylic acid/ maleic acid), tartaric acid, H_2O	Ca–Al–F–silicate glass, sintered Ag	78–79	17–19	4–5	Cermet glass ionomer
Vitremer	3M ESPE	poly(acrylic-itaconic acid) with pendent methacrylate, H_2O HEMA, tartaric acid,	Fluoroaluminosilicate glass, microencapsulated redox catalysts	71	51	3	Resin-modified glass ionomer
Photac-Fil Quick Aplicap	3M ESPE	Poly(co-acrylic acid/ maleic acid), HEMA, H_2O, GI compatible monomers	Fluoroaluminosilicate glass	76–77	25–26	5–7	Resin-modified glass ionomer
Fuji II LC Improved	GC America	PAA, HEMA, H_2O TEGDMA	Ca–Al–F–silicate glass	76		1.8	Resin-modified glass ionomer
Compoglass	Vivadent	DCDMA, P-BisGMA, UDMA, TEGDMA	Ba–Al–F–silicate glass, YbF_3, mixed oxides	79	56	0.2–1.6	Compomer
F2000	3M ESPE	CDMA oligomer GDMA	Al–F–silicate glass	84		3	Compomer
Dyract AP	Densply/ Caulk	TCB, UDMA	Sr–F–silicate glass, SrF_2	73	47	0.8	Compomer
Hytac	3M ESPE	MPAE, UDMA	Zn–Ca–Al–F–silicate glass, YbF_3	81		5	Compomer
Ariston pHc	Vivadent	BisGMA, UDMA, TEGDMA	Alkaline glass, Ba–Al–F–silicate glass, YbF_3, SiO_2	79	59	1.3	Composite
Surefil	Caulk/ Densply	Urethane-modified BisGMA	Ba–B–Al–F–silicate, glass, TiO_2, fumed SiO_2	82	66	0.8	Composite
Solitaire	Kulzer	Bis-GA, TEGDMA	Porous SiO_2, Ba–B–Al–F–silicate glass, Al–F–silicate glass, SrF_2	90	65	2–20	Composite
Tetric Ceram	Vivadent	P-BisGMA, UDMA, TEGDMA	Ba–Al–F–silicate glass, Ba–glass, SiO_2, YbF_3	78	60	0.6	Composite

BisGMA, bisphenol A glycidyl dimethacrylate; BisGA, bisphenol A glycidyl diacrylate; CDMA, dimethacrylate functional oligomer of citric acid; DCDMA, cycloaliphatic dicarboxylic acid dimethacrylate; GDMA, glyceryl dimethacrylate; HEMA, hydroxyl ethyl methacrylate; MPAE, methacrylated phosphoric acid esters; PAA, polyacrylic acid; P-BisGMA, propoxylated BisGMA; TCB, a reaction product of butane tetracarboxylic acid and hydroxyl methyl methacrylate; TEGDMA, triethylene glycol dimethacrylate; UDMA, urethane dimethacrylate.

Fluoride-Release Composites



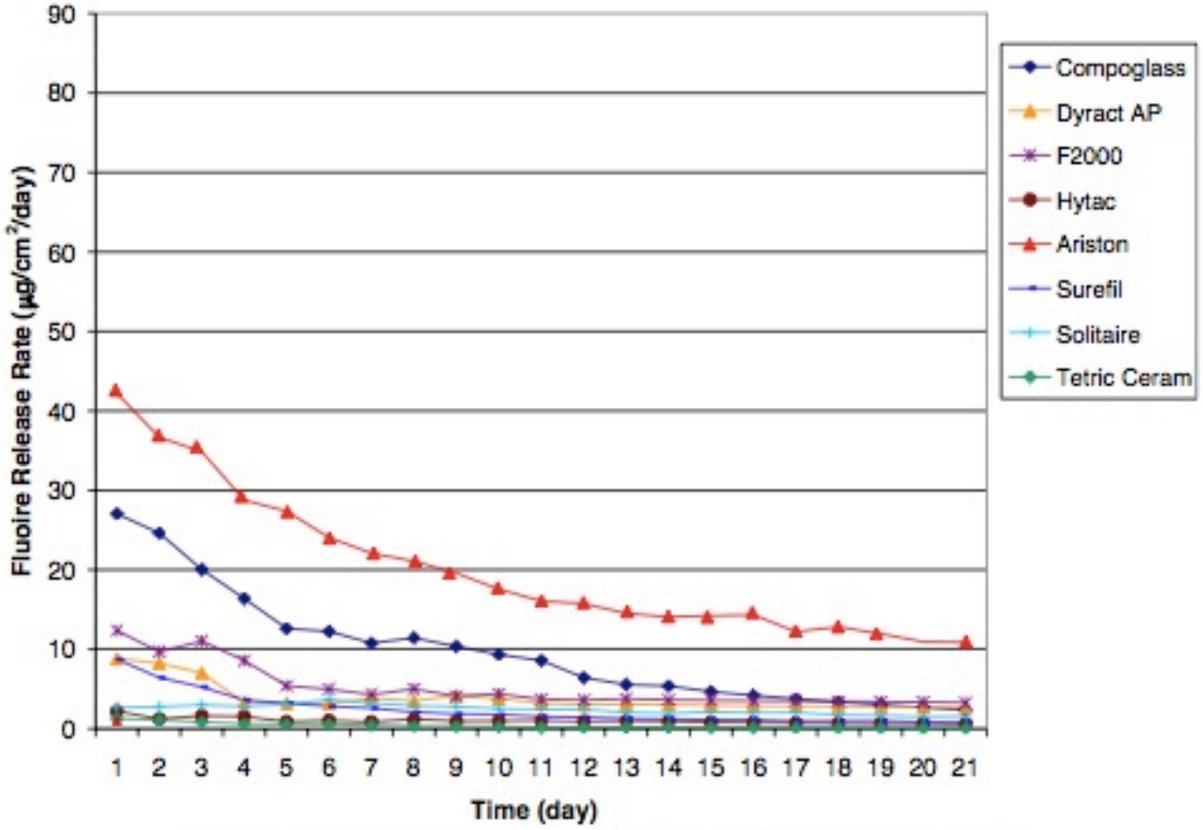


Fig. 4. Fluoride release profile of compomers and composite resins.

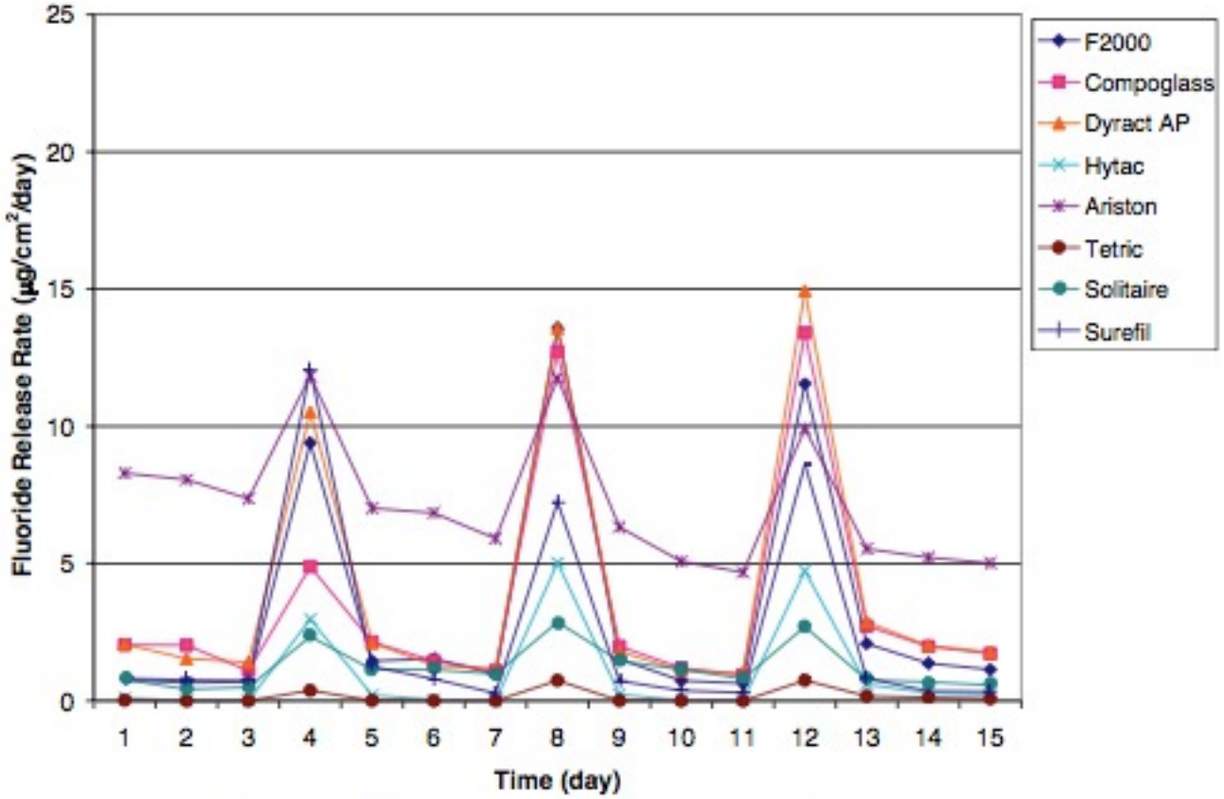


Fig. 9. Fluoride recharge profile of compomers and composite resins.

Fluoride-Release Composites

The use of fluoride containing fillers in addition to tetrabutylammonium fluoride (TBAF) in the monomer matrix has lead to an improved release and storage of fluoride in the filling material in in-vitro tests (Xu et al. 2006). In addition, the mechanical and physical properties of the restorative material are acceptable, whereas the solely addition of TBAF to the matrix results in deterioration of these properties (Glasspole et al. 2001, Xu et al. 2006).

Anti-Microbial Composites

Clorexidina

negative effect on the mechanical properties of the material

Ioni d'Argento

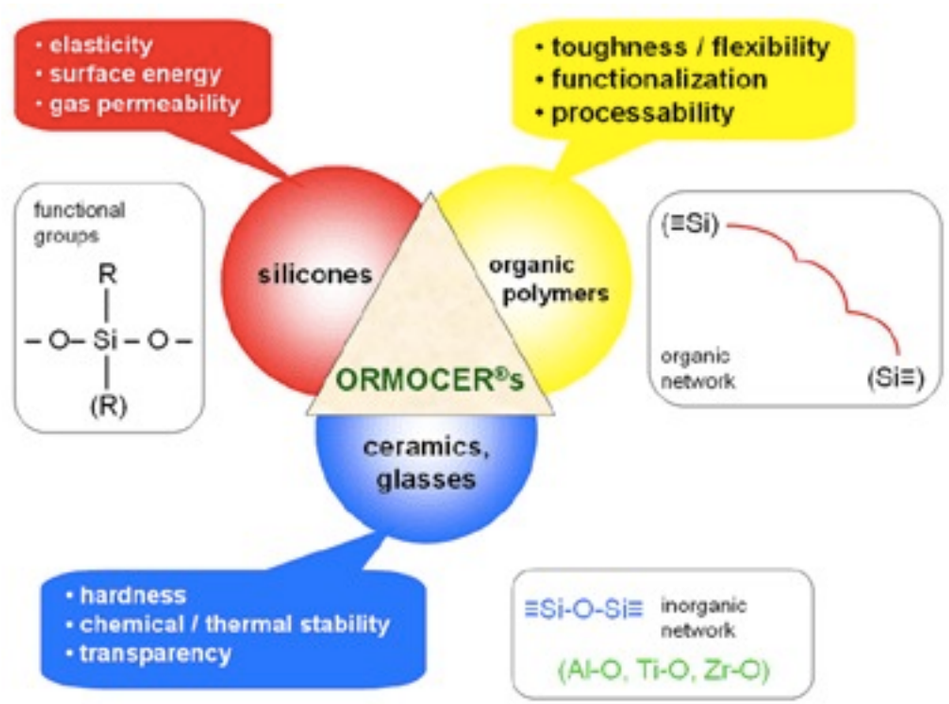
very good protective effect against S. mutans (Yoshida et al. 1999)

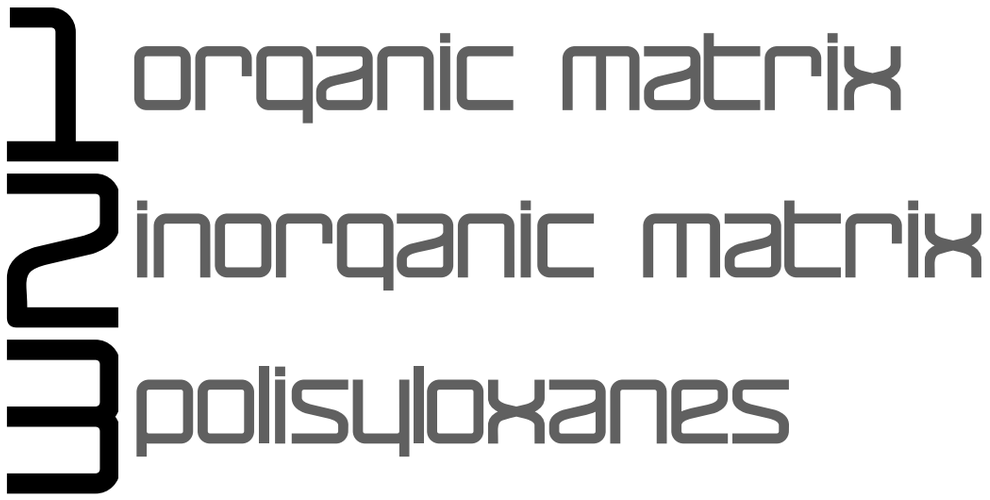
However silver has an unfavourable influence on the colour of the restorative material, which in turn must be masked by other substances.

ORMOCERS

In contrast to conventional composites, the ormocer matrix is not only organic but also inorganic. Therefore monomers are better embedded in the matrix what reduces the release of monomers.

ORMOCERS





ORMOCERS

1. The organic polymers influence the polarity, the ability to cross link, hardness and optical behaviour.
2. The glass and ceramic components (inorganic constituents) are responsible for thermal expansion and chemical stability.
3. The polysiloxanes influence the elasticity, interface properties and processing.

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ORIGINAL ARTICLE

N. Kournetas · M. Chakmakchi · A. Kakaboura ·
C. Rahiotis · J. Geis-Gerstorfer

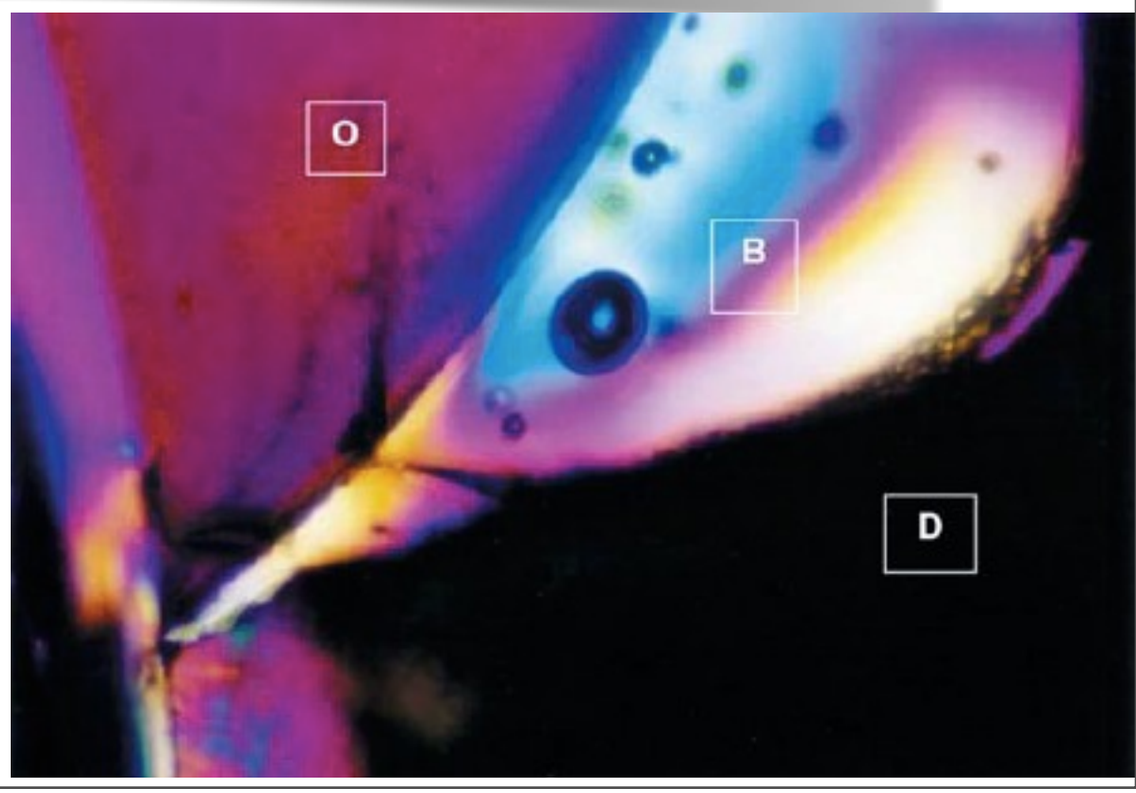
Marginal and internal adaptation of Class II ormocer and hybrid resin composite restorations before and after load cycling

their performance (cervical and occlusal marginal adaptation) was significantly worse when compared to today's hybrid composites, after cyclical loading in a laboratory test (Kournetas et al. 2004)

Table 2 Results from the marginal adaptation evaluation (n =8)

Subgroups	Occlusal margins	Cervical margins
	Excellent	Excellent
ADa[a]	4 (50%) [b]	2 (25%)
ADb[a]	2 (25%)	0 (0%)
DFa	4 (50%)	2 (25%)
DFb	2 (25%)	2 (25%)
SPa	8 (100%)	8 (100%)
SPb	8 (100%)	7 (87.5%)

[a] *a* unloaded, *b* loaded
[b] Numbers in parenthesis show the percentage of restorations



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ORIGINAL ARTICLE

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Marginal and internal adap[illegible] Class II ormocer

However, no significant differences were found in a five-year clinical comparison of Admira® (ormocer) and Tetric Ceram® (hybrid composite) (Bottenberg et al. 2009).

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Table 2 R[illegible]

Subgroups		
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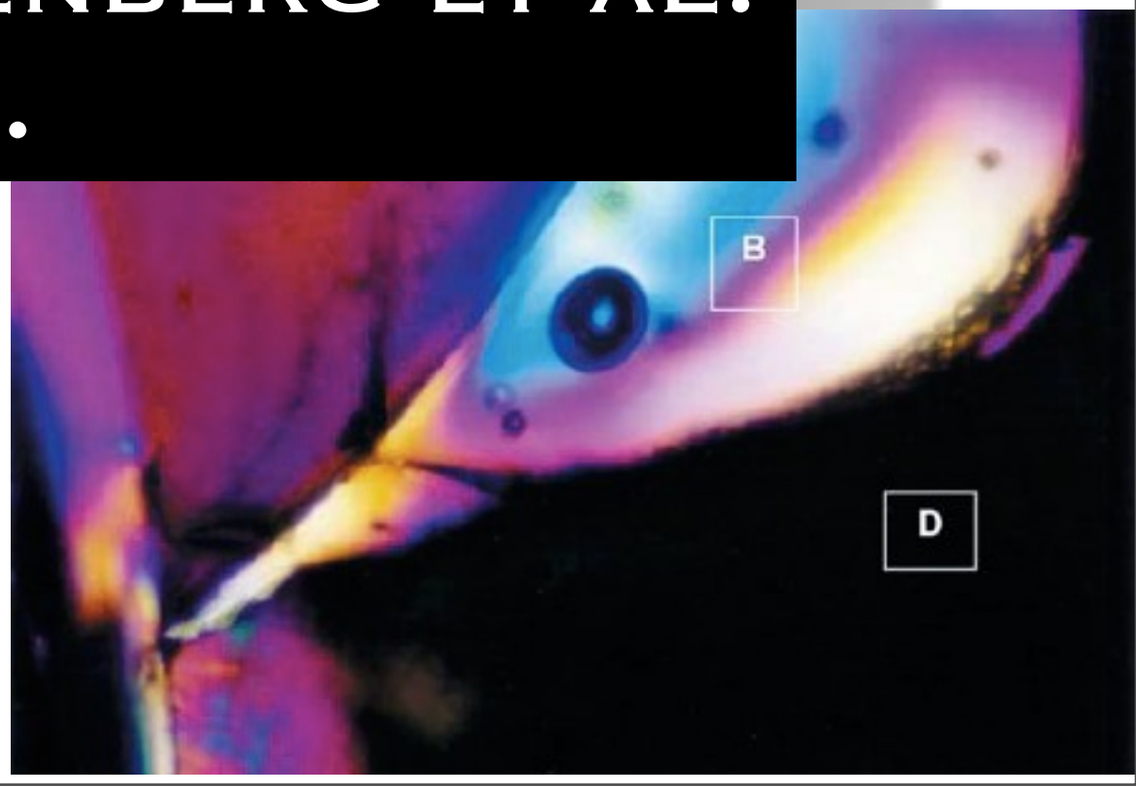

At the same filler content, ormocers have a reduced polymerisation shrinkage compared to hybrid composites (Yap & Soh 2004) or at a lower filler content of the ormocer the polymerisation shrinkage is equal to that of a conventional composite (cattani-Lorente et al. 2001).

ORMOCERS

Rosin et al. (2003, 2007) investigated the "in-vivo" quality of ormocer restorations in a clinical trial over one and two years. The clinical application was acceptable, but there were concerns about the marginal adaptation and the indication for class v restorations due to poor adhesion.