

## Fracture Toughness Evaluation of Hybrid and Nano-hybrid Resin Composites after Ageing under Acidic Environment

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### Abstract

**Statement of Problem:** Tooth-coloured restorative materials are brittle with the major shortcomings of sensitivity to flaws and defects. Although various mechanical properties of resin composites have been studied, no fracture toughness test data for nano-hybrid composites under acidic condition for a long period of time has been published.

**Objectives:** To compare the fracture toughness ( $K_{Ic}$ ) of two types of resin composites under tensile loading and to assess the effect of distilled water and lactic acid on the resistance of the restoratives to fracture after three months of immersion.

**Materials and Methods:** Four resin composites were used: three nano-hybrids [EsteliteSigma Quick (Kuraray), Luna (SDI), Paradigm (3M/ESPE)] and one hybrid, Rok (SDI). The specimens were prepared using a custom-made polytetrafluorethylene split mould, stored in distilled water (pH 6.8) or 0.01mol/L lactic acid (pH 4) and conditioned at 37°C for 24 hours, 1 or 3 months. They were loaded under tensile stress using a universal testing machine; the maximum load (N) to the specimen failure was recorded and the fracture toughness ( $K_{Ic}$ ) was calculated. Data were analysed by ANOVA and Tukey's test using SPSS, version 18.

**Results:** The results of two-way ANOVA did not show a significant combined effect of material, time, and storage medium on fracture toughness ( $p=0.056$ ). However, there was a strong interaction between materials and time ( $p=0.001$ ) when the storage medium were ignored. After 24 h of immersion in distilled water, Paradigm revealed the highest  $K_{Ic}$  values followed by Rok, Luna and Estelite. Immersion in either distilled water or lactic acid significantly decreased the fracture toughness of almost all materials as time interval increased.

**Conclusions:** Paradigm showed the highest fracture toughness followed by Rok, Luna and Estelite respectively. As time increased,  $K_{Ic}$  significantly decreased for almost all resin composites except for Luna which showed a slight decrease after one month of immersion in distilled water.

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### Introduction

Dental composites are multipurpose materials that

have grown fast since 50 years ago when they were introduced to the market. Patients frequently request resin composites restorations due to their excellent

aesthetic. These materials are brittle and their major shortcomings are sensitivity to flaws and defects, low tensile strength, and susceptibility to catastrophic failure [1]. Each composite contains a unique combination of resin and filler particle types and sizes. Reducing filler particle sizes and increasing filler volume percentages tend to improve the physical and mechanical properties of new resin composites [2,3].

The first introduced dental composites (macrofill) had average particle sizes of more than 50  $\mu\text{m}$ , which made them very strong, but difficult to polish. To overcome this drawback, manufacturers began to formulate "microfill" composites [4]. The average size of the amorphous spherical silica reinforcing particles was approximately 40 nm, hence it is believed that "microfill" would have more accurately been called "nanofill" [5]. Due to low filler level of this material, they have a low strength. Therefore, further development of resin composites resulted in introducing new materials with combination of strength and polishability to be used for anterior and posterior application called "micro-hybrids" with average particle sizes of 0.4–1.0 $\mu\text{m}$ . In order to achieve a better performance and more aesthetic, microhybrid composite was improved with the addition of proprietary nanoparticles and nanoclusters which are bound in the resin matrix. The result is an optimized nanohybrid composite including more nanoparticles, and possibly pre-polymerized resin fillers that are similar to micro-hybrids and it is difficult to differentiate between those [6]. The mechanical properties, such as flexure strength and modulus of elasticity of those two, have been revealed to be similar, with slightly higher for micro-hybrids than nano-hybrids, and both being greater than microfills [7]. The most recent improvement has been the development of the "nano composites", containing only nano-scale particles [4].

In the harsh environment of the oral cavity, materials are exposed to acidic food and beverages that may result in surface damage [8]. Strong acids could disorganize the surface and dissolve filler particles on the surface of the composites [9,10]. While this process increases, it leads to micro porosities on the surface due to filler loss and increases the penetration of the beverages to the pores [9,10]. This degradation is due to the uptake of beverages by the polymer matrix, causing the cross-linked polymer network to swell, reducing the frictional forces between the polymer chains and concurrently, leaching of alkali ions and dissolving the glass network, causing an irreversible loss of strength [11]. It has been demonstrated that aging of resin composites in liquids that represent the oral cavity, accelerates the degradation process and leads to loss of mechanical properties of these materials [10,12]. However, other studies have demonstrated that aging in water has an initial desirable effect on resin composites, causing an increase in flexibility [13] and the fracture toughness of the materials [14].

Restorative materials are repeatedly exposed to environmental stresses, such as acid from acid-

producing bacteria and acidic food and beverages. Fracture toughness is one of standard and most recommended tests to be used for assessing the strength of brittle restorative materials. Fracture toughness ( $K_{Ic}$ ) is an inherent characteristic of a material that describes its ability to resist crack propagation [15], as it indicates the largest amount of force that a material can withstand prior to failure.

Our previous study showed that the effect of lactic acid on the fracture toughness of resin based cements varies depending on the materials tested, while increased  $K_{Ic}$  of some materials decreases that of the others [16]. No data have been published comparing fracture toughness of nano-hybrid composites using short rod design in acidic media for a long-term immersion. Due to the wide growth of various types of resin composites, to ensure secure fracture toughness, it is necessary for new tooth-coloured materials to resist crack propagation and catastrophic failure under tensile loading.

The objective of the present study was to place four resin composites used for direct restorations into either distilled water or lactic acid at 37°C up to 3 months and determine: 1) the effect of storage media and immersion time on the material strength, using tensile loading; 2) whether a relationship exists between the fracture toughness and the material composition. The null hypothesis is that the storage media, time and type of the material do not affect the mechanical properties.

## Materials & Methods

Four resin composites were studied in this experiment (Table 1). A polytetrafluoroethylene (PTFE) split mould was utilised to prepare a total of 144 specimens ( $n=6$ ). A schematic of the specimen and details of the dimensions were described in our previous studies [16,17] in accordance with ASTM Designation: E399-83 [18]. The mould was assembled using bolts, and resin composite was packed into the form. As described by Kovarik *et al.* [19], a razor blade was inserted into the notch to introduce a sharp pre-crack in the specimen during preparation. The top of the mould was covered with plastic mylar-strips, which were pushed down with a glass slab to extrude any excess resin-composite. The material was cured using LED curing light with a wavelength range of 440-480 nm at an output of 1500mW/cm<sup>2</sup> (Radii plus LED; SDI, Bayswater, Vic, Australia), in accordance with the exposure times recommended by the manufacturer for polymerization (40 seconds at a distance of lower or equal to 1mm from the mould). After curing, the upper plate of the mould was detached and the razor blade was removed. The specimen was then light-cured on the opposite side for the same amount of time, separated from the mould and gently polished with wet silicon carbide paper 600-1200 grit to remove any irregularities and to obtain a smooth surface. The specimen was rinsed briefly between each

**Table 1:** Description of all the resin composites used in the study

Resin composite	Type	Manufacturer	Resin Matrix	Filler content (Vol%), Type, Sizes	Lot Number
Paradigm	Nano-hybrid	3M/ESPE, St Paul, MN	Bis-GMA, UDMA, BIS-EMA, PEGDMA, TEGDMA	(68%), zirconia/silica (3µm), Na Silica (20nm)	N557215
Rok	Hybrid	SDI, Vic, Australia	UDMA, Bis-EMA	(67.7%), SAS, AS. 0.02-2.5 µm	131112
Luna	Nano-hybrid	SDI, Vic, Australia	UDMA/Bis-EMA/TEGDMA	(61%) SAS, AS0.02-2 µm, 200-400 nm	131016T
Estelite Sigma Quick	Nano-hybrid	Tokuyama, Dental Co. Tokyo	Bis-GMA, TEGDMA	(63 %), SiO <sub>2</sub> , ZrO <sub>2</sub> , PFSC, 200nm and 0.2 µm	114E71

SAS= Strontium aluminosilicate, AS= amorphous silica, PFSC= prepolymerized filler of silicacomposite, Na=Non-agglomerated, PEGDMA=poly(ethylene glycol) dimethacrylate, Bis-EMA= bisphenol a Ethylmethacrylate, Bis-GMA=bisphenol a glycidylmethacrylate; TEGDMA=triethyleneglycoldimethacrylate; UDMA = urethane dimethacrylate

grade of the paper. For each material, 36 specimens were prepared. Half of the specimens were placed in distilled water (pH= 6.8) and the other half into 0.01 mol/L lactic acid (pH= 4) and conditioned at 37°C for 24 hours, 1 month and, 3 months.

After storage, the specimens were removed from the media, washed entirely, dried and measured the dimensions mentioned below. Then the fracture toughness of the specimens was tested using a universal testing machine ((Zwick/Roll Z020; Zwick GmbH & Co, Germany) at a crosshead speed of 0.05mm/min applying tensile load [11,12]. The maximum load prior to catastrophic failure was recorded (N). Fracture toughness ( $K_{Ic}$ ) was calculated using the following formula:  $K_{Ic} = P_c \times f(a/w) / BW^{0.5}$ . Where  $P_c$  is the maximum load at specimen fracture,  $f(a/w)$ = function of  $a$  and  $w$ ,  $B$ =specimen thickness,  $W$ = dimension from the un-notched edge of the specimen to the plane centre line of the loading holes.

**Statistical Analyses**

A factorial analysis of variance (2-way ANOVA) was performed to assess the effects of multiple independent variables on the dependent variable of fracture toughness. One way ANOVA and Tukey’s test were conducted to compare the mean fracture toughness of each material in individual storage condition for all time intervals.

**Results**

Univariate analysis of variance showed no interaction

between the three factors (materials, environment and time,  $p=0.056$ ), between the environment and time ( $p=0.276$ ) or materials and environment ( $p=0.68$ ). It means lactic acid did not significantly affect the fracture toughness. However, there was a strong interaction between materials and time ( $p<.001$ ) and differences were material dependent.

Table 2 shows the mean fracture toughness and standard deviation for each material stored in distilled water or lactic acid for 24 hours, 1 or 3 months. After 24 h of immersion in distilled water, Paradigm had the highest fracture toughness value followed by Rok, Luna and Estelite. Immersion in either distilled water or lactic acid significantly decreased the fracture toughness values of Paradigm, Rok and Estelite as the time interval increased (Figure1 and 2). Luna showed a significant increase in fracture toughness after 1 month of immersion in distilled water.

**Discussion**

Results of the present study indicated that the null hypothesis was rejected. There were significant differences in fracture toughness between resin composites, after storage in either medium for 24 hours, 1 or 3 months. Aging in water demonstrated to have an initial undesirable effect on resin composites, causing a decrease in fracture toughness of almost all materials. All resin composites showed a significant reduction of  $K_{Ic}$  after 1 month of immersion and even more after 3 months, except for Luna that increased after 1 month and decreased again after 3 months.

**Table 2:** Mean fracture toughness (MPam<sup>0.5</sup>) and standard deviations (± SD) of the materials following the time interval in distilled water and lactic acid (n = 6)

Materials	Distilled Water			Lactic Acid		
	24h	1month	3month	24h	1month	3month
Paradigm	0.81±(0.21) <sup>aA</sup>	0.56±(0.2) <sup>bA</sup>	0.50±(0.17) <sup>bcA</sup>	0.77±(0.25) <sup>aA</sup>	0.57±(0.19) <sup>bA</sup>	0.47±(0.15) <sup>cB</sup>
Rok	0.69±(0.22) <sup>aB</sup>	0.58±(0.12) <sup>bcA</sup>	0.53±(0.14) <sup>bA</sup>	0.66±(0.22) <sup>acB</sup>	0.61±(0.18) <sup>cA</sup>	0.54±(0.15) <sup>bA</sup>
Luna	0.55±(0.18) <sup>bc</sup>	0.63±(0.21) <sup>aB</sup>	0.57±(0.2) <sup>bA</sup>	0.57±(0.19) <sup>bc</sup>	0.57±(0.19) <sup>bA</sup>	0.53±(0.18) <sup>bA</sup>
Estelite	0.53±(0.22) <sup>ac</sup>	0.44±(0.19) <sup>bc</sup>	0.46±(0.18) <sup>bb</sup>	0.66±(0.15) <sup>cB</sup>	0.37±(0.22) <sup>db</sup>	0.42±(0.18) <sup>bdB</sup>

Means with the same upper-case letter in each column were not significantly different ( $p> 0.05$ ). Means with the same lower-case letter in each row were not significantly different ( $p> 0.05$ ).

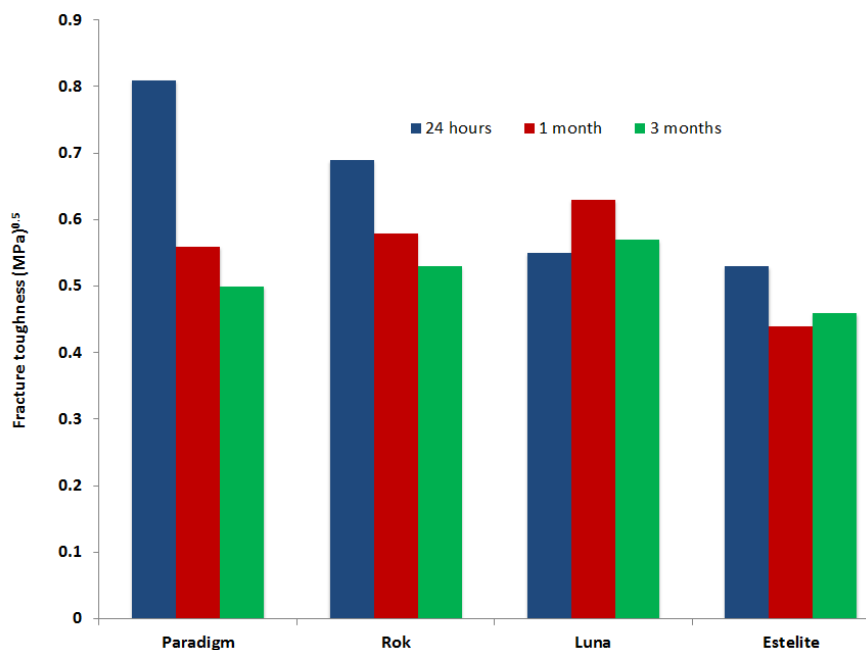


Figure 1: Fracture toughness versus time interval for all materials in distilled water

The differences among the tested resin composites could be multifactorial dependent such as filler volume percentages, filler type and sizes, pre-polymerized resin fillers, type of resin matrix, and the ratio of high molecular monomer (Bis-GMA) to the low molecular ones (UDMA, TEGDMA, Bis-EMA [17,20,21].

A significant progression of resin composites is primarily related to the filler volume and sizes and today they are mostly classified as hybrid, micro-hybrid, nano-hybrid, and nano-filled. Hybrid and micro-filled are the most traditional composites for restorative purposes. More recently, nano-filled and

nano-hybrid composites were introduced in an attempt to provide universal restorative materials [22].

Nano-hybrid composites were recently introduced to provide better physical and mechanical properties than traditional hybrid and micro-hybrid composites [22-24].

Some studies reported similar physical and mechanical properties for nano-hybrids and micro-hybrids and speculated that nano-hybrids may be defined and perform similarly to micro-hybrids due to the use of nanosized particles in nano-hybrids and loss of large particles, as in micro-hybrids [25,26].

Results from the current study found Paradigm as

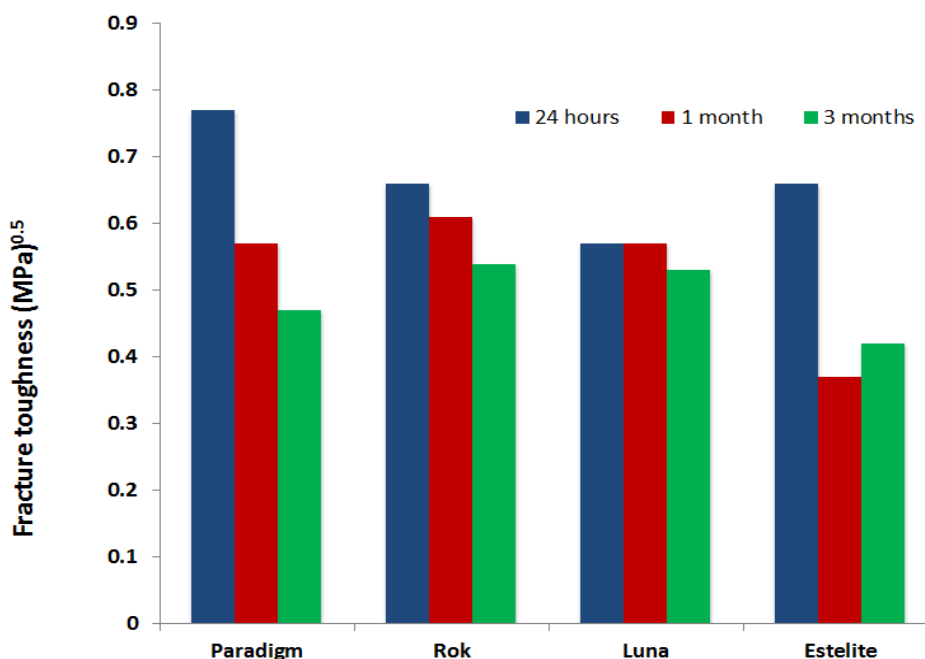


Figure 2: Fracture toughness versus time interval for all materials in lactic acid.

a nano-hybrid composite to have significantly higher fracture toughness than other two nano-hybrid composites (Luna and Estelite) when stored in distilled water for 24 h. Rok as a hybrid composite showed a lower fracture toughness than Paradigm but significantly higher than Luna and Estelite. The result could be related not only to the filler loading, filler composition, and filler sizes but also to the combined effect of grinding and mixing different sizes of filler particles in to nano-hybrid composites. Moraes *et al.* [27] in their study investigated the properties of nano-hybrid in comparison with a nano-filled and a micro-hybrid composite and detected inferior properties for the nano-hybrids compared with the nano-filled and similar or slightly better results compared with the micro-hybrid materials. The authors [27] also used SEM/EDS analysis to characterize inorganic fillers, reporting that their filler compositions (Ba-Al-Si glass fillers) are the same as almost all of the traditional hybrids and their filler sizes are a mixture of nanosized particles with large fillers as in micro-hybrids. Therefore, it is speculated that nano-hybrids are not new materials similar to nano filled composites; instead they are very similar to traditional micro-hybrids in terms of composition and properties [27]. However, the manufacturer (3M/ESPE) claims that the filler technology of Paradigm™ nano-hybrid universal restorative is a unique hybridization of particles, including engineered nanoparticles and replacing some of the TEGDMA with PEGDMA make the composite with a lower shrinkage and higher mechanical properties compared to the other composites in this class of materials.

Aging conditions may result in water uptake of resin composites that may affect physical and mechanical properties of resin composites such as hardness, colour stability, fracture toughness, and shear bond strength [8,20,21]. Different materials allow uptake of media to varying degrees due to the polarity of the polymethyl methacrylate molecules and diffusion mechanisms of the composite material. Shin *et al.* [12] showed that with increased temperature there is increased leaching of inorganic ions with strontium leaching at a faster rate than silicon glass [12]. Depending on the ratio and individual properties of these fillers, and thus the relative amounts of leaching and hydrolysis of the filler-matrix interface that occurs, could be partially responsible for loss of strength after 3 months of immersion of most of the materials used in this study.

Immersion in lactic acid did not change the results significantly when compared to the aging method of water storage; yet it decreased the fracture toughness of all materials slightly. On the other hand, comparing the  $K_{Ic}$  values of all tested materials after 24 h of immersion in distilled water did not show a significant difference with that of lactic acid. Therefore, the authors speculated that reduction of the  $K_{Ic}$  values can be due to hydrolysis of the filler particles or filler-matrix interface, by up-taking water through resin matrix

rather than chelation effect of the lactic acid. Although the clinical relevance of exposure duration to lactic acid (PH=4, 3m) could be questioned, exposure of the specimens to this medium may act as the accelerator effect of acidic beverages over time on composite restorations in the oral cavity. Örtengren *et al.* [28] found that for all composite materials tested and all pH ranges, there was a steady increase in solubility from 1 to 7 days. After 7 days, all materials decreased in solubility for 60-180 days, reaching equilibrium at 180 days [28].

## Conclusions

Under the conditions of this in vitro study, the following conclusions were drawn: fracture toughness values of the resin composites were significantly decreased, either immersed in distilled water or immersed in lactic acid after the 3-month evaluation period. Paradigm as a nano-hybrid composite showed significantly higher  $K_{Ic}$  than its other 2 competitive composites in this class of material. Rok as a hybrid composite showed significantly higher  $K_{Ic}$  than Luna and Estelite but lower than Paradigm. Duration of exposure time and the composition of the resin composites had a significant effect on the fracture toughness of all restorative materials.

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