European Journal of Orthodontics 30 (2008) 89–93
doi:10.1093/ejo/cjm058
Advance Access publication 14 September 2007

Discolouration of orthodontic adhesives caused by food dyes and ultraviolet light

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SUMMARY Enamel discolouration after debonding of orthodontic attachments could occur because of irreversible penetration of resin tags into the enamel structure. Adhesives could discolour because of food dyes or ultraviolet irradiation. The aim of this study was to investigate the colour stability of adhesives during ultraviolet irradiation and exposure to food colourants.

Four different adhesives were exposed in a Suntest CPS+ ageing device to a xenon lamp to simulate natural daylight (Transbond XT, Enlight, RelyX Unicem, and Meron Plus AC). Tomato ketchup, Coca Cola©, and tea were chosen as the food colourants. After 72 hours of exposure, colour measurements were performed by means of a spectrophotometer according to the Commission Internationale de l'Eclairage L*a*b* system and colour changes (ΔE^*) were computed. Statistical differences were investigated using two-way analysis of variance (ANOVA) and Friedman test.

Unsatisfactory colour stability after *in vitro* exposure to food colourants and ultraviolet light was observed for the conventional adhesive systems, Transbond XT and Enlight. RelyX Unicem showed the least colour change and the resin-reinforced glass-ionomer cement (GIC), Meron Plus AC, the greatest colour change.

The investigated adhesives seem to be susceptible to both internal and external discolouration. These *in vitro* findings indicate that the tested conventional adhesive systems reveal unsatisfactory colour stability which should be improved to avoid enamel discolouration.

Introduction

Adhesive resin composites are multipart materials composed of synthetic polymers, particulate ceramic reinforcing fillers, and silane coupling agents which bond the reinforcing fillers to the polymer matrix (Ferracane, 1995). In addition, molecules which promote or modify the polymerization reaction are required (Ferracane, 1995). Over the years, the evolution of orthodontic adhesives has encompassed several areas, including modifications of filler levels and filler components and inclusion of the polymeric part of the resins (Brauer *et al.*, 1979; Taira *et al.*, 1988; Chung, 1990; Peutzfeld, 1997; Asmussen and Peutzfeld, 1998).

In orthodontics, direct bonding of orthodontic brackets to enamel is 'state of the art'. Since the basic investigations of Buonocore (1986) in etching tooth surfaces with phosphoric acid, satisfactory bonding between enamel and adhesive is achievable (Buonocore, 1986; Miyasaki and Hirohata, 1999; Dorminey *et al.*, 2003). There are a number of reports in the orthodontic literature on bond strength testing of brackets using various parameters (Forsberg and Hagberg, 1992; Sharma-Sayal *et al.*, 2003; Özcan *et al.*, 2004; Bulut *et al.*, 2006; Soderquist *et al.*, 2006), while colour stability of orthodontic adhesives has only been investigated in a few studies (Eliades *et al.*, 2001, 2004). Two reasons for enamel discolouration after debonding of orthodontic attachments are evident: the formation of white spots due to decalcification and the irreversible penetration of resin tags into the enamel structure (Eliades *et al.*, 2001). It is a common belief that the adhesive resin tags in the enamel structure reach a depth of 50 μm (Silverstone *et al.*, 1975; Eliades *et al.*, 2001). Debonding and cleaning procedures are not able to reverse resin impregnation into the enamel (Sandisson, 1981; Eliades *et al.*, 2001).

There are internal and external causes for the discolouration of orthodontic adhesives. External discolouration can be caused by food dyes and coloured mouth rinses (Khokhar *et al.*, 1991; Seher and Viohl, 1992; Dietschi *et al.*, 1994; Leibrock *et al.*, 1997). The material, e.g. the polymeric structure or filler content, and surface roughness play a decisive role in the extent of discolouration caused by diverse substances (Dietschi *et al.*, 1994; Leibrock *et al.*, 1997). The amount of colour change can be influenced by a number of factors including oral hygiene, water absorption, and incomplete polymerization (Arthur *et al.*, 2004). The reason for internal discolouration can be found in ultraviolet irradiation and thermal energy. Ultraviolet light can induce physico-chemical reactions in the polymer, which cause irreversible colour changes. Eliades *et al.* (2001, 2004) investigated the influence of ultraviolet light exposure on colour stability of orthodontic adhesives and the effect on tooth discolouration.

The aim of the present study was to determine the influence of the food colourants, tea, Coca Cola©, and tomato ketchup, and ultraviolet light exposure on discolouration of different orthodontic adhesives. Another concern of this investigation was to assess colour stability of a self-etching, self-priming (one-component) adhesive system, and a resin-reinforced chemically-cured glass-ionomer cement (GIC) in comparison with conventional three-component orthodontic adhesives.

Material and methods

A total of 200 round disks (50 for each adhesive group) of 10 mm diameter and 1 mm thickness were manufactured. For colour stability testing, the conventional adhesives Transbond XT (3M Unitek, Monrovia, California, USA) and Enlight (Ormco, Glendora, California, USA) were evaluated. In addition, the self-etching, self-priming (one component) adhesive system RelyX Unicem (3M Espe, Seefeld, Germany) and Meron Plus AC (Voco, Cuxhaven, Germany), a resin-reinforced chemically cured GIC, were used. With the exception of Meron Plus AC, all samples were light-cured with a light-emitting diode (LED) curing device (Ortholux LED, 3M Unitek) for 20 seconds.

For the food dyes, tomato ketchup (Heinz, Pittsburgh, Pennsylvania, USA), coke (Coca Cola©, Atlanta, Georgia, USA), and tea (Darjeeling, Lord Nelson, Lidl, Neckersulm, Germany) were chosen and placed in three small receptacles. In each receptacle 10 samples per adhesive group were stored for 72 hours. Ten disks per adhesive group, which served as the controls, were stored in distilled water under light exclusion for the same period. After 72 hours, colour measurements were performed.

To investigate the influence of ultraviolet irradiation on the adhesives, 10 samples of each group were subjected to artificial ageing following DIN EN 27491 (International Organization for Standardization, 1985) in a Suntest CPS+ ageing device (Heraeus Instruments, Hanau, Germany). The adhesives were exposed to a filtered xenon lamp with an irradiation value of 765 W/m^2 for 72 hours. This method can simulate a light strength of approximately 160 klux and corresponds to intensive natural sunlight in equivalent exposure time. To simulate alternating moisture by saliva, each 20 minute cycle consisted of a 3 minute rinse with deionized water at 37°C followed by a 17 minute dry phase. After 72 hours the colour values of the adhesives were measured and compared with a control group which had been stored under light exclusion in distilled water at room temperature.

The colour measurements were carried out using the Minolta spectrophotometer CM-C3500 (Minolta Co. Ltd, Tokyo, Japan) with a pinhole diaphragm of 3 mm diameter according to the L*a*b* system (Commission Internationale de l'Eclairage, 1976). A colour graph consists of L*, a*, and b* co-ordinates. The L* parameter corresponds to the degree of lightness and darkness and the a* and b* values to the chroma, where +a* is red, −a* is green, +b* is yellow, and −b* is blue. The calculation of the colour variation ΔE* between two colour positions in the three-dimensional L*a*b* colour space was as follows:

$$\Delta E^* = \left[\left(L^*_1 - L^*_2\right)^2 + \left(a^*_1 - a^*_2\right)^2 + \left(b^*_1 - b^*_2\right)^2\right]^{1/2}.$$

The medians and standard deviations were calculated. Statistical analysis was performed using two-way ANOVA and Friedman test. The level of significance was set at $\alpha = 0.05$.

Results

With the exception of RelyX Unicem, all adhesives showed clinically unacceptable ΔE values (median > 3.7) after exposure to tomato ketchup for 72 hours (Figure 1A), while Meron Plus AC showed the greatest colour changes after Coca Cola© and tea treatment for 72 hours (ΔE > 9.4; Table 1). Lower discolouration was observed for all tested adhesives after storage in Coca Cola© (Figure 1B,C).

Enlight and Meron Plus AC revealed a significant (P = 0.005) clinically detectable discolouration after ultraviolet light exposure, while for Transbond XT and RelyX Unicem, ΔE values lower than 3.3 were determined (Figure 1D).

After exposure to the tested food dyes or ultraviolet light, RelyX Unicem showed the least and the resin-reinforced GIC, Meron Plus AC, the greatest colour change (Table 1).

Discussion

Numerous tests have been used for artificial ageing of dental materials to investigate colour stability *in vivo* and *in vitro* (Rosentritt *et al.*, 1998; Stober *et al.*, 2001; Arthur *et al.*, 2004). In this investigation the exposure time to tomato ketchup, Coca Cola©, tea, and ultraviolet light was set to 72 hours because Stober *et al.* (2001) reported that a period of 24 hours of artificial treatment was too short to investigate discolouration of dental composites.

Discolouration can be differentiated by colourimeter or visually. Nevertheless, the sensitivity of the human eye in detecting small colour differences is limited and the interpretation of visual colour comparisons is subjective. For that reason colourimetric measurements are essential to obtain reproducible results of colour determination (Johnston and Kao, 1989; Buyukyilmaz and Ruyter, 1994; Rinke *et al.*, 1996). According to Eliades *et al.* (2001, 2004), ΔE values in the range of one unit are considered as a colour match because they cannot be identified by independent observers. In the present investigation the colour difference was set at 3.7 units since most studies fix the proposed acceptance limit for colour matching at this level (Johnston and Kao, 1989; Seghi *et al.*, 1989; Eliades *et al.*, 2001, 2004).

Arthur *et al.* (2004) stated that changes in optical properties within the polymer could be responsible for colour changes. Chemical discolouration has been attributed

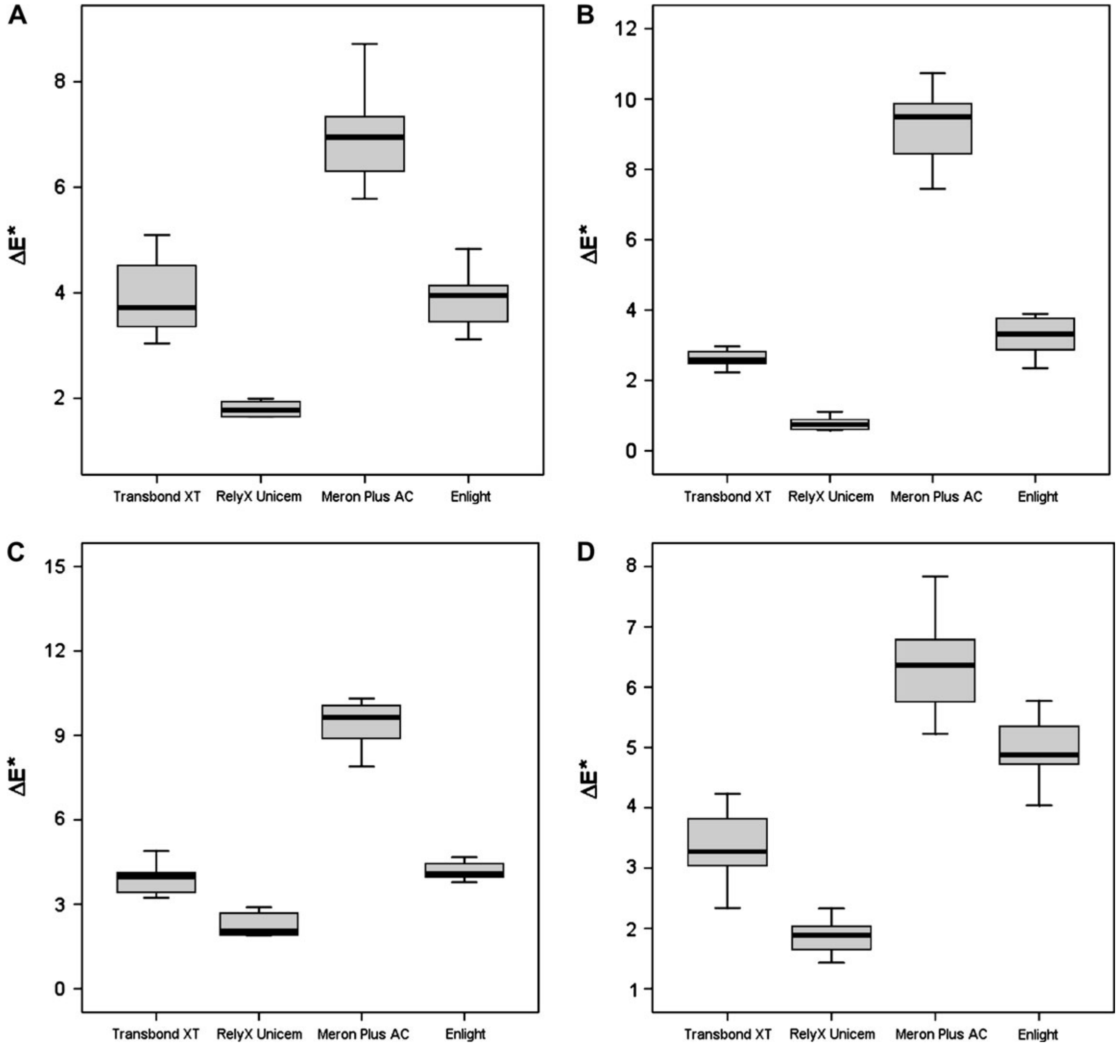

Figure 1 Discolouration ΔE* after 72 hours of exposure to (A) tomato ketchup, (B) Coca Cola©, (C) tea, and (D) ultraviolet light.

Table 1 Median values and standard deviations of discolouration ΔE* after exposure to food dyes or ultraviolet light.

	Ketchup	Coca Cola©	Tea	Ultraviolet light
Transbond XT	3.73±0.68	2.58±0.36	3.97±0.48	3.28±0.58
RelyX Unicem	1.77±0.32	0.75±0.17	2.05±0.38	1.89±0.28
Meron Plus AC	6.96±0.87	9.49±1.03	9.65±0.8	6.37±0.81
Enlight	3.95±0.56	3.33±0.51	4.09±0.28	4.88±0.78

to the oxidation of unreacted double bonds in the matrix of the resin and the subsequent formation of degradation products from water diffusion or the oxidation of the polymer (Arthur *et al.*, 2004). *In vitro* colour stability of veneer composites after exposure to ultraviolet light for 72 hours and storage in red wine or coffee for 10 days was investigated by Rosentritt *et al.* (1999). They described discernible but acceptable colour changes (ΔE* < 3.3) after ultraviolet irradiation (72 hours), though no synergetic effects on colour behaviour after ultraviolet ageing and storage in food dyes were reported.

In the present study, tea showed the greatest colour change for almost all adhesives. Unsatisfactory colour stability after *in vitro* exposure to food colourants and ultraviolet light was observed for the conventional adhesive systems, Transbond XT and Enlight. The dual-curing, self-adhesive resin RelyX Unicem showed less discolouration than all other tested adhesives. A possible reason for its colour stability could be the elevated inorganic filler content of approximately 72 per cent by weight (grain size: 9.5 µm). Setz and Engel (1994) were able to establish a correlation between discolouration and the filler component in resin composites. Eldiwany *et al.* (1995) found that not only the type but also the amount of filler affects colour stability of composites. According to Wilson *et al.* (1983) and Ruyter *et al.* (1987), higher contents of inorganic filler in dental composites resulted in lesser discolouration than lower filled polymers.

The greatest discolouration values were observed for the resin-reinforced chemically cured GIC, Meron Plus AC, where especially Coca Cola© and tea exposure caused undesirable colour changes ($\Delta E > 9.4$). However, it should be borne in mind that the bonding procedure for GICs differs from that for composite resins. The initial low pH of the GIC induces a local dissolution of apatite on the enamel surface which is followed by a reversible hydrolytic molecular bond mechanism between ionized glass-ionomer carboxyl groups and enamel calcium (Wilson *et al.*, 1983; Eliades *et al.*, 2001). Therefore, no resin-infiltrated zone stays on the enamel after debonding and cleaning. Eliades *et al.* (2001) investigated the influence of enamel colour changes after bonding with resin and GIC. They stated that the main surface features following debonding and cleaning are those of polished enamel.

Most of the adhesives became ‘yellower’ after ultraviolet light treatment. Ferracane *et al.* (1985) reported that yellowing of the polymer is accompanied by a reduction in the quantity of residual unreacted double bonds in the resins. They stated that a possible explanation for the yellowing could be oxidation of the unreacted C=C to produce coloured peroxide compounds. The polymeric structure and filler content, as well as the polymerization conversion, seem to be the most important factors that influence the colour stability of dental polymers.

Many variables could affect colour stability of orthodontic adhesives. Chemical differences among the resin components, such as residual monomers, polymeric structure, and the concentration of amines and diketones may influence colour stability (Eldiwany *et al.*, 1995). In addition, differences in both filler content and composition may explain the fact that composites with a higher content of inorganic filler show greater colour stability than polymers with low filler content (Eldiwany *et al.*, 1995; Ruyter and Svedsen, 1981).

Eliades *et al.* (2001) stated that some alterations in enamel colour are unavoidable during bracket bonding because of microstructural modifications associated with enamel bonding and debonding procedures. Consequently, it is necessary to reduce the tendency of orthodontic adhesives to internal and external discolouration to a minimum to reduce the amount of enamel colour change.

Conclusions

These *in vitro* findings indicate that the tested conventional adhesive systems reveal an improvement in colour stability. The investigated highly filled one-component adhesive showed greater colour stability than resin-reinforced GIC which showed the greatest discolouration. Within the limitations of this *in vitro* study, it could be concluded that the tested orthodontic adhesives seem to be susceptible to both internal and external discolouration.

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