

Testing for polymer leaching from thermoplastic sheets used for clear aligners

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Abstract

Objective: Owing to the escalated recognition of clear aligners to correct crooked teeth lately, novel materials have been presented in form of thermoplastic sheets. Long-term studies challenging the biocompatibility of those sheets are yet to be approached. The purpose of this study is to provide a naive, yet operative method to assess their leaching potential.

Materials and Methods: A redox reaction takes place in the presence of potassium permanganate, when combined with polymers from clear aligner sheet samples. Four different samples were tested. The sequence of colour change from purple to red to brown to yellow to clear was used to determine the amount of leaching; which is a

result of the stoichiometric relation between the oxidizing agent and the reducing sample. Colour changes were observed through naked eyes over a period of 24 h. Photographs were taken at 15 min, 8 h and 24 housing a camera.

Result: Diluted solution showed faster change in colour, due to the lesser amount of reagent. Scheu (Germany) was the first to leach, followed by Invisalign (USA), Flash Aligners (India) and Clear Correct (Switzerland).

Conclusion: This “Do-it-yourself” testis a repeatable and reproducible method that can be modified and used in clinical practice as a chair side method.

Keywords: Polymer leaching, Thermoplastic sheet, Do it yourself test.

Introduction

In 1980s, vacuum formed clear thermoplastic sheets fitting tightly over the teeth were introduced into orthodontics as “retainers”. They quickly became apparent that if the teeth were slightly reset before forming, a tooth moving device would result; hence the name “aligner” was used.¹ Adolescent and adult patients who are aware of their malocclusion traits and dissatisfied with their dental appearance tend to have psychosocial concerns.^{2,3}

On the other hand, the use of an orthodontic appliance to treat a malocclusion may lead to an impairment of quality of life, which is less severe when clear aligner therapy is performed.⁴

Despite the fact that orthodontic treatment with clear aligners is a quickly growing sector, there is still insufficient evidence with regard to the effectiveness and stability of the treatment compared with conventional brackets.⁵ Aligner therapy might treat mild non-extraction cases faster and more efficiently, but it requires more time than fixed appliance treatment for more complex cases. Furthermore, there is still limited evidence of aligner efficacy in arch expansion through bodily tooth movement, extraction space closure, and larger antero-posterior and vertical discrepancies.⁶ Anyhow, it was apparent that it could be used for far more than just minor movements. Today it is on the verge of bringing about a paradigm shift from un-aesthetic brackets and arch wires to invisible orthodontic treatment. Along with the increase in its usage, the duration of oral tissue contact of these plastic sheets have increased, thus there is a proportionately increasing concern on its biocompatible properties, since thermoplastic overlay appliances such as aligners, retainers, night guard, TMJ splints etc contact mucosae for months. Release of monomers such as

Bisphenol A can cause skin allergies, adverse effects on reproductive system, necrosis, endocrine disruption with weak estrogenic effect.⁷

There is a wide variety of thermoplastic sheets available in the market to choose from, with newer brands and materials emerging everyday. And the companies' confidentiality policies make the exact content unknown to the users, thus raising questions. There is an emerging need to find the most biocompatible product from the options available. The methods used otherwise include gas chromatography, mass spectrometry and high-performance liquid chromatography, which are very elaborate, expensive, require specific machinery and trained personnel. Thus, impractical in clinical practice.^{8,9} Thus, a need for a simpler and inexpensive chairside method to check for the content of harmful polymer leaching from those thermoplastic sheets yet remained. Hence this study was planned, as an attempt to provide for a viable screening option available for practical usage.

Material and Method

For this study, a ‘do it yourself test’ was contemplated, which could be performed by the clinician or an assistant in the clinic itself using easily available materials. The test is performed by preparing a solution of the reagent used. The solution is made by adding 1.6 potassium [i.e., KMnO_4 American Chemical Society reagent grade, 99% (0.001M solution)] to 1 litre of distilled water; and then diluting it 1:3 with distilled water. After stirring, the solution is left for at least an hour before use.¹⁰ For sample collection; multiple dental clinics & laboratories using thermoplastic sheets were consulted. Four most commonly used brands were shortlisted for the study, including Invisalign, USA, Clear correct, Switzerland; Flash Aligners, India and Scheu, Germany.

Of which Invisalign, Clear correct, & Flash aligners were taken from dental clinics as they are, for samples; while Scheu Duran samples were crafted out from the excess material left after manufacturing the aligners at a dental laboratory, hence they had undergone the usual heating and cooling cycle each sheet undergoes before delivery. All the samples are minced into smaller particle size using a straight handpiece with stainless steel round bur (Dentsply, United States) about 1 mm in diameter. 1 g of each powdered sheet is added to 5 ml of reagent in corked and marked test tubes.

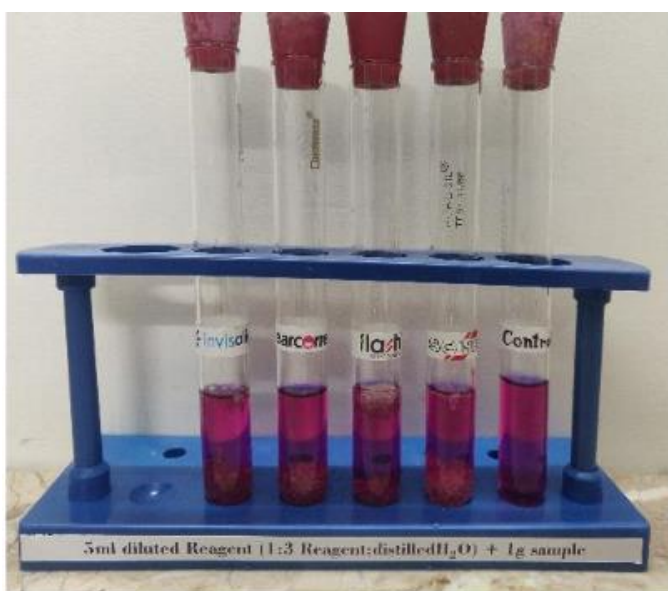


Figure 1: Powdered sheet + Reagent in corked & marked test tubes.

Colour changes are observed through naked eyes over a period of 24 hours; at 15 min, 8 h and 24 h interval. The test was repeated 15 times over a period of 15 days. Photographs were taken at intervals of 15 min, 8 h and 24 h respectively. The colour changes were graded by multiple investigators, in order to preclude any spectator or co-incidental bias.

Result

All the products tested leached, but the amount varied from one product to another [Figures 2-4]. The results

were fairly consistent on repeated testing. Within 15 minutes, Scheu Duran was the first to start changing colour to a lighter shade in the permanganate solution, followed by Invisalign which presented yellow discoloration, then came Clear correct and lastly Flash. After a longer period of 8 hours, reagent solutions showed yellowest discoloration with Invisalign particles, followed by flash and then Clear correct, whose colour were still more towards purple. By the end of 24 hours, Scheu Duran had already completed the reaction and turned colorless, followed by Invisalign which appeared lightest, then Flash and Clear correct being the yellowest then.

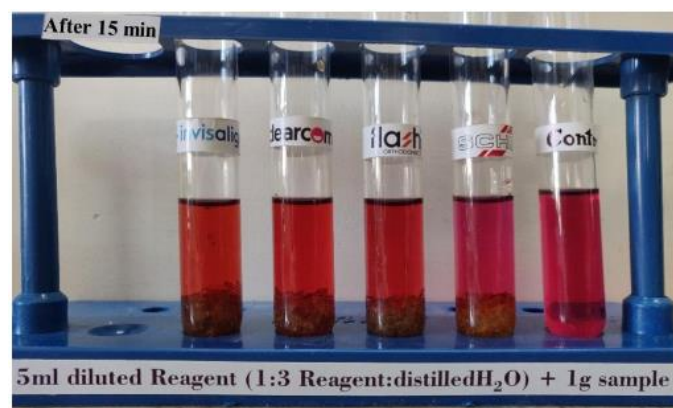


Figure 2: Sample in diluted reagent after 15 min

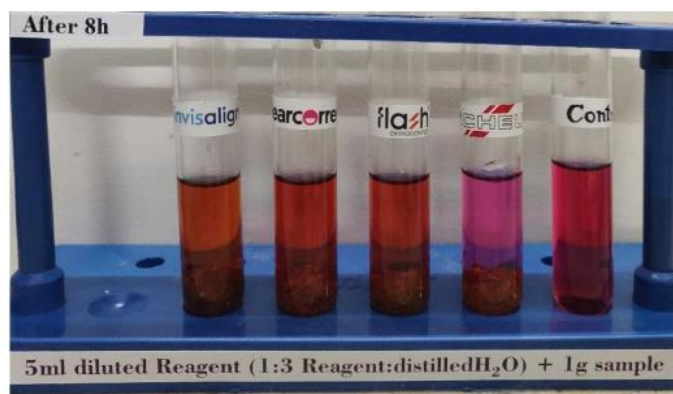


Figure 3: Sample in diluted reagent after 8 h

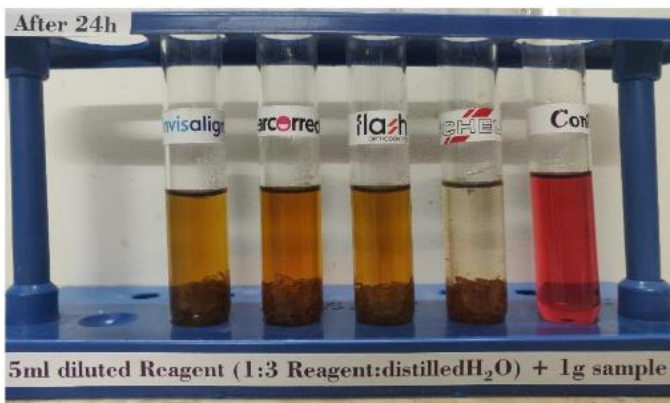


Figure 4: Sample in diluted reagent after 24 h



Figure 5: Follow up after 48 h

Discussion

These changes in the colour of solution(s) denotes the amount of polymer released from the thermoplastic sheets, as the permanganate in presence of polymers is reduced to manganese (IV) oxide (MnO_2) and manganese (III) oxide (Mn_2O_3) which precipitate and give the liquid a yellow brown colour, manganese is further transformed into a nearly colorless salt (Mn^{2+}). The amount of polymer in the solution determines the degree of progress of reaction; the sequence of colour is from purple to red to brown to yellow to clear. This is the result of a stoichiometric relation between the oxidizing agent and the reducing sample.¹⁰

Thus, suggesting Scheu to be leaching maximum amount of polymer, followed by Invisalign, Flash and then Clear correct, being the least polymer leaching thermoplastic aligner sheets. A simple do it yourself test was used in which an oxidation reduction reaction using $KMnO_4$ takes

place.¹¹ The permanganate is reduced to manganese(IV) oxide (MnO_2) and manganese(III) oxide (Mn_2O_3) in the presence of polymers in a neutral environment, which precipitates and gives the liquid a yellow brown colour. Manganese is then changed into a practically colorless salt (Mn^{2+}). The rate of reaction progression depends on the amount of polymer present in the solution; reaction colour shift from purple to red to brown to yellow to clear, owing to a stoichiometric relationship between the oxidising agent and the reducing sample.

In this study, a diluted solution of reducing agent with lesser concentration of $KMnO_4$ is used, hence it requires lesser amount of leaching product to complete the reaction and hence show faster changes in colour.

Based on the aforementioned information, a chairside DIY test can be created using potassium $KMnO_4$, a basic disinfectant that is readily available. Instead of weighing, a solution of permanganate of appropriate concentration can be made by adding water to the potassium $KMnO_4$ crystals until a newspaper could be read through an inch of solution held in a glass tube. A tablespoon of this solution can be used with a pinch of powder for general clinical use.¹⁰

In this study, we discovered that polymer leaching occurred in all products, though at varying rates. The study only provided an approximation of the degree to which a polymer leached oxidizable, organic matter.

Although the latter may not always be harmful, as a general rule the less leaching, the safer the product is considered. The method enables the manufacturer to improve his product, the clinician and the researcher to choose the least damaging, and the researcher to track the leaching's development over time by displaying the relative degree of leaching. There could be a number of causes for the varying levels of leaching observed.

According to Matasa¹², as the molecular weight of the polymer is increased and the crosslinked network gets denser the larger molecules become entangled and are kept within the polymer's structure thus reduces amount of leaching. It is typically advised to employ thermoplastic overlay orthodontic appliances for two weeks during each phase. Temperature changes in the oral cavity can alter the characteristics of these materials throughout this time.⁸ It was reported by Waked et al.¹³ that aging induced various dimensional changes in mouthguard materials, which have similar compositions to those of thermoplastic overlay orthodontic materials, depending on the materials and processing techniques. In contrast to our study, in a study by Schuster et al.⁸, in vitro aged and retrieved Invisalign appliances were found to leach no traceable amount of substance in an ethanol aging solution, this was basically attributed to composition of Invisalign appliances, which was found to be composed of polyurethane with added methylene diphenyl diisocyanate and ^{1, 6} hexanediol. The diphenyl structure provides stability and sufficient reactivity to form a polymer free of by-products. However, it was also added that it did not reflect its in vivo performance, due to various factors like potential abrasion from chewing action, along with attrition induced by the consumption of acidic beverages and the action of enzymes. In dentistry, bisphenol A (BPA) is a basic material for dental resins that is a precursor for BPA glycidyl Di methacrylate and BPA Di methacrylate. The reverse process of degradation is accelerated with heat, mechanical wear and bacterial or salivary enzymatic action.¹⁴ Leaching from thermoplastic sheets generally results in the release of monomers such as BPA. The implications of BPA released from dental biomaterials were first reported in a study that assessed dental sealants. BPA is known to cause skin allergies,

adverse effects on the reproductive systems of animals, cell death via necrosis and high haemolytic activity.¹⁵ In their study Terhune et al. have suggested that clinicians should extend caution in preventing extended contact of any of these materials with a patient's skin, mucosa and gingiva. BPA is also a well-known potent endocrine disruptor with a weak estrogenic effect.¹⁶ In a study done by Schuster et al., no cytotoxic or estrogenic activity of Invisalign appliances was documented in in-vitro assay, which used a standard model for the assessment of estrogenicity of materials.⁸ Other thermoplastic overlay appliances including retainers, nightguards, temporomandibular joint splints and bleaching trays are used for months in the oral cavity, which makes their biocompatibility of utmost importance. Won et al.¹⁷ reported that there is change in force and energy delivery properties of thermoplastic material after thermocycling or load cycling after three-point bending-recovery test was performed, which shows that by increasing the duration of use, the degradation of polymer could occur at different, possibly faster rate. This method has the drawback of only providing comparable data based solely on visual estimations; the precise amount of polymer leaching cannot be assessed. In light of the growing need for transparent aligner sheets, a far more precise yet straightforward method for evaluating polymer leaching from those sheets is required, especially considering its increasing demands.

Conclusion

The colour fading of permanganate solution is a time proven method to measure the purity of many chemical substances and allows discriminating dental plastics using simple means. This do-it-yourself test is a simple and effective method that could be used routinely to screen and select most biocompatible clear aligner and other

thermoplastic sheets. Based on the given stoichiometric relation between oxidizing agent and the reducing samples, we can conclude Scheu to be leaching maximum amount of polymer, followed by Invisalign, Flash and then Clear correct, being the least polymer leaching thermoplastic aligner sheets. Those being just comparative results based only on visual estimates; the exact amount of polymer leaching cannot be evaluated. A need for a much more accurate but simple method for evaluation of polymer leaching from clear aligner sheets, yet remains.

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