Use of Reparative Agents Topical Fluoride Activated by CO₂ Laser and Curodont™ Repair and NR-5™ on Vickers Hardness and Micro-Shear Bond Strength of Eroded Enamel to Composite Restoration

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Abstract: Aim: This study aims to assess the impact of various reparative remineralizing agents, specifically topical fluoride (TF) and a combination of a carbon dioxide laser (CO₂ laser) with TF, as well as regenerative agents such as Curodont™ Repair and NR-5™, on two key factors—the micro-Vickers hardness (VH) of eroded enamel and the micro-shear bond strength (µSBS) of composite restoration. Materials and Methods: A total of 50 single-rooted premolars with intact enamel were sectioned mesiodistally into two halves, making a sample size of 100 specimens. All of the samples were then exposed to Coca-Cola™ for 2 min each day over 1 month to induce erosion on the enamel surface. The specimens were then embedded in acrylic cold-cure resin facing a flat surface upward. The samples were then arbitrarily divided into five groups based on the remineralizing and regenerative agents used, as follows (n = 20): Group 1: No remineralizing agent, Group 2: Curodont™ Repair, Group 3: NR-5™, Group 4: TF, and Group 5: CO₂ laser + TF. The VH of the pretreated enamel surfaces was analyzed and µSBS testing and failure mode of composite restoration were performed using a universal testing machine (UTM) and stereomicroscope. ANOVA and Tukey’s post hoc were performed for data analysis. Results: In Group 3, the (NR-5™)-treated teeth exhibited the highest VH values and µSBS. In Group 1, the (No remineralizing agent)-treated specimens displayed the lowest VH and the lowest µSBS. An intergroup comparison analysis unveiled that Group 3, Group 4 (TF), and Group 5 (CO₂ laser + TF) presented comparable outcomes of microhardness and bond strength. The Group 2 (Curodont™ Repair) samples exhibited no significant difference in VH and µSBS, as compared to Group 1. Conclusions: The use of a combination of NR-5™ technology and a CO₂ laser in conjunction with TF has been shown to significantly augment the natural mineralization process. This enhancement results in increased microhardness and an improved bond strength in the treated enamel.

Keywords: micro-shear bond strength; Vickers hardness; CO₂ laser; topical fluoride

1. Introduction

Human enamel is the hardest layer of the tooth and is highly structured [1]. Teeth are naturally protected by a layer of salivary pellicle, which possesses the ability to neutralize the demineralization effect caused by a low pH [2]. Erosion of the tooth surface can be caused by both intrinsic and extrinsic factors, i.e., the consumption of acidic food and acidic beverages and acid reflux in patients with gastroesophageal reflux disease (GERD) [3]. A prolonged exposure to erosive substances exacerbates the demineralization of tooth surfaces, resulting in decreased levels of essential inorganic mineral ions, such as fluoride, calcium, and phosphate [4]. Therefore, a carefully performed restorative treatment becomes necessary when erosive wear worsens the tooth’s structural integrity [5].
The existing research has emphasized the prevention of demineralization and the promotion of remineralization before restoring the tooth [6,7]. There are two main types of remineralization technology used in dentistry techniques, including those that improve fluoride effectiveness and those that mimic the natural healing mechanisms [8,9]. Fluoride facilitates tooth remineralization by fostering the creation of fluorapatite crystals on partially demineralized sub-surface crystals [10]. Likewise, the utilization of lasers in contemporary dentistry has seen substantial expansion [11]. Previous experimental studies have shown that CO₂ laser irradiation can cause melting and subsequent recrystallization in dental hard tissues, leading to an enhanced resistance to acidic substances [7,12]. Laser irradiation has been proposed as a method to improve the effectiveness of topical fluoride treatment by increasing fluoride absorption into the enamel and promoting the conversion of hydroxyapatite into fluorapatite crystals [13,14]. Nonetheless, it is important to note that both of these techniques are limited to the remineralization of the tooth and cannot fully regenerate the lost tooth structure. Consequently, there is an ongoing endeavor to shift from reparative approaches to regenerative biomineralization therapies, which have the potential to promote the growth of structured apatite crystals.

Curodont™ Repair, which is formulated using proprietary CUROLOX technology, was developed to promote enamel regeneration. The active ingredients in Curodont™ Repair include fluoride, sodium chloride, calcium phosphate, and oligopeptides [15]. It also contains a self-assembled peptide matrix PI1-4 that promotes the creation and the deposition of hydroxyapatite crystals on enamel [16,17]. These peptides can mimic the natural process of enamel formation by attracting calcium and phosphate ions to facilitate the growth of hydroxyapatite crystals on the tooth’s surface [18]. By promoting the deposition of hydroxyapatite, such peptides help to repair and strengthen the enamel, which can be eroded or damaged by factors such as acidic foods, bacteria, and mechanical wear [19,20]. Furthermore, pioneering research has unveiled a novel two-component NR-5™ technology that combines calcium silicate and sodium phosphate [18]. This groundbreaking technology is purported to create a crystal structure closely resembling hydroxyapatite, the predominant mineral found in tooth enamel [17]. However, it is worth noting that there is a significant gap in the existing research when it comes to understanding the impact of NR-5™ technology and Curodont™ Repair on µSBS and VH. Further research is essential in order to conduct a comprehensive and in-depth examination of how these innovations affect these specific properties.

The existing scientific literature exhibits a notable dearth of data about the influence of Curodont™ Repair and NR-5™ technology on micro-shear bond strength (µSBS) and Vickers hardness (VH). Given the aforementioned deficiency, a hypothesis was developed, positing that there would be no statistically significant disparity in the Vickers hardness (VH) of eroded enamel when subjected to different reparative techniques (TF alone and TF activated by a CO₂ laser) and regenerative substances (Curodont™ Repair and NR-5™) in comparison to untreated enamel (the control group). Similarly, it was also expected that there would be no substantial variation in the µSBS of composite restorations when bonded to repaired and regenerated enamel in comparison to degraded enamel. Thus, the main objective of this research was to evaluate the effects of the most recent enamel repair and regeneration substances on the Vickers hardness (VH) of degraded enamel and the µSBS of composite restorations.

2. Materials and Methods

2.1. Sample Preparation

A total of fifty single-rooted premolars with intact enamel surfaces were obtained immediately after extraction due to orthodontic and periodontal reasons. Following the extraction procedure, the teeth underwent a cleaning process utilizing pumice powder. Subsequently, they were preserved in a solution of physiologic saline supplemented with a small quantity of thymol crystals, at a temperature of 4 °C, for less than 2 months. The
exclusion criteria encompassed teeth that had visible or detectable caries, restorations, hyperplastic lesions, stains, cracks, and bleaching. The premolars underwent decoronation utilizing a diamond disk (Horico, Berlin, Germany). The included specimens were sectioned into two halves with intact buccal and palatal coronal surfaces along the mesiodistal plane, resulting in a total sample size of 100 samples. The flat surface of the buccal and lingual surfaces was attained by using a sequence of silicon carbide abrasive sheets, ranging from 600 to 3000 grit. This was followed by fine polishing using a water-based diamond paste with a particle size of 1–0.25.

All of the samples were then exposed to an aerated beverage by immersing them in Coca-Cola™ (Hindustan Coca-Cola™ Beverages Private Limited, Bengaluru, India), pH 2.3, for 2 min each day over 1 month to induce erosion on the enamel surface. The beverage was replaced daily. Following the induced erosion, the specimens were embedded in acrylic cold-cure resin (DPI-RR Cold Cure, DPI, Mumbai, Bengaluru, India) and filled in a custom-made metal mold in such a way that the enamel surface of all of the samples faced upward. Subsequently, all of the study samples were arbitrarily divided into 5 groups based on the reparative and regenerative agents used (n = 20), as follows:

Group 1: In this group, the samples were not treated with any remineralizing agent.

Group 2: Curodont (Curodont Repair, Credentis AG, Windisch, Switzerland) (P11-4 oligopeptide solution) was diluted with 0.05 mL of deionized water. A single drop of this solution was then applied to the demineralized enamel surfaces and left undisturbed for 5 min. This was then followed by washing the surface with distilled water [21].

Group 3: The study samples involved in this group were treated with the regenerative Enamel Science™ Advanced Toothpaste (a CSSP-based product) for 5 min. This was followed by the application of Advanced Enamel Serum for 3 min. This was then followed by washing the surface with distilled water [18].

Group 4: The specimens in this group were applied with topical fluoride (TF) solution, specifically Nupro Neutral™ (Johnson and Johnson, Inc., New Brunswick, NJ, USA), containing 2.0% NaF (9047 ppm). The fluoride gel was then washed from the surface with distilled water after 4 min using tissue paper [22].

Group 5: In this group, TF was applied in the same manner as that used for Group 4. This was followed by irradiation of the TF-treated surface with a CO₂ laser (PC 015-D CO₂ Laser System, Shanghai JueHua Laser Tech. Development Co., Ltd., Shanghai, China) with an adjusted power of 0.5 W and an energy density of 0.44 J/cm² and pulse duration of 100 s, with a 0.001-sec interval between pulses. The surfaces were then washed with distilled water [22,23].

2.2. Microhardness Assessment

A total of 50 samples, with 10 specimens from each group, underwent VH testing. The standard load applied was 500 g of force for 20 s, with a total of 3 indentations obtained from each specimen to assess the mean microhardness.

2.3. Bonding Procedure

For µSBS testing, 10 samples from each group were applied with 35% phosphoric acid gel (Ultradent Ultra-Etch, Gunz Dental York, UK) for etching, followed by a bonding agent (3M ESPE, Saint Paul, MN, USA) by a single operator, according to the instructions provided by the manufacturer. On the pretreated eroded enamel, a plastic tube with an internal diameter of 3 mm and a height of 2 mm was placed. The surface was then restored with composite restoration (Filtek Z350; 3 M ESPE) within the confines of the plastic tube. The composite was then cured using an LED light for polymerization. All of the testers were then incubated for 24 h at 37 °C in a humid atmosphere. This was followed by placing the specimens in an Automated ThermoCycler (Applied Biosystems, Foster City, CA, USA), exposing the samples to a total of 8000 cycles between 5 °C and 60 °C, with a dwelling length of 30 s.
2.4. µSBS Testing and Failure Analysis

A custom-made jig was utilized to secure the specimen within the universal testing machine (UTM) (Instron, Z020, Zwick Roell, Ulm, Germany) using cyanocrylate glue. The composite–enamel interface of all of the testers was subjected to a tensile load at a crosshead speed of 1 mm/min to induce fracture. The failure load of each sample was measured in megapascals (MPa). At 40× magnification, the stereomicroscope was employed to examine the failure pattern. The fracture modes were classified as adhesive, cohesive, and admixed.

2.5. Statistical Analysis

The collected data were analyzed using IBM SPSS. Data normality was assessed using the Shapiro–Wilk W-test (p-value > 0.05). One-way analysis of variance (ANOVA) and Tukey’s post hoc analysis were performed for µSBS composite and VH of the remineralized surface. (p < 0.05)

3. Results

Table 1 presents the VH values of the eroded enamel after applying remineralizing and regenerative agents. The outcomes have shown that, in Group 3, the (NR-5™)-treated teeth exhibited the highest VH values (333.0 ± 82.3). However, in Group 1, the (No remineralizing agent)-treated specimens displayed the lowest VH (235.4 ± 32.2) score. Through an intergroup comparison analysis, we discovered that the Group 3, Group 4 (TF), (293.0 ± 67.2), and Group 5 (CO₂ laser + TF) (310.8 ± 77.3) samples displayed comparable findings of VH. Furthermore, Group 2 (Curodont™ Repair) (250.5 ± 50.2) exhibited no significant difference in their hardness number when compared with the Group 1 samples.

Table 1. VH scores after treatment with different remineralization protocols.

<table>
<thead>
<tr>
<th>Remineralizing Pretreatment</th>
<th>Mean</th>
<th>Standard Deviation (SD)</th>
<th>p-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group 1: No remineralizing agent</td>
<td>235.4</td>
<td>32.2</td>
<td></td>
</tr>
<tr>
<td>Group 2: Curodont™ Repair</td>
<td>250.5</td>
<td>50.2</td>
<td></td>
</tr>
<tr>
<td>Group 3: NR-5™</td>
<td>333.0</td>
<td>82.3</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Group 4: TF</td>
<td>293.0</td>
<td>67.2</td>
<td></td>
</tr>
<tr>
<td>Group 5: CO₂ laser + TF</td>
<td>310.8</td>
<td>77.3</td>
<td></td>
</tr>
</tbody>
</table>

Table 2 shows the mean and SD of the µSBS scores in MPa for each trial group. The results of the existing study have revealed that, in Group 3, the (NR-5™)-(9.99 1.45 MPa)-treated study samples presented the maximum bond integrity values of tooth color restoration to erosive enamel. However, it was found that the Group 1 (No remineralizing agent) samples demonstrated the lowest µSBS score (8.161.22 MPa). An intergroup comparison analysis has revealed that Group 3, Group 4 (TF) (9.171.44 MPa), and Group 5 (CO₂ laser + TF) (9.551.26 MPa) presented comparable outcomes of bond strength. Similarly, the Group 2 (Curodont™ Repair) (8.66 1.15 MPa) samples exhibited no significant difference in their µSBS when compared with the Group 1 testers.
Table 2. µSBS of composite restoration after treatment with different remineralization protocols.

<table>
<thead>
<tr>
<th>Remineralizing Pretreatment</th>
<th>Mean</th>
<th>Standard Deviation (SD)</th>
<th>p-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group 1: No remineralizing agent</td>
<td>8.16</td>
<td>a</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Group 2: Curodont™ Repair</td>
<td>8.66</td>
<td>a</td>
<td></td>
</tr>
<tr>
<td>Group 3: NR-5™</td>
<td>9.99</td>
<td>b</td>
<td></td>
</tr>
<tr>
<td>Group 4: TF</td>
<td>9.17</td>
<td>b</td>
<td></td>
</tr>
<tr>
<td>Group 5: CO2 laser + TF</td>
<td>9.55</td>
<td>b</td>
<td></td>
</tr>
</tbody>
</table>

Topical fluoride (TF), CO2 laser irradiation + topical fluoride (CO2 laser + TF). The different small letters denote a statistically significant difference, showing significant differences among the study groups (ANOVA and Tukey multiple comparison test).

Figure 1 displays the failure mode observed within the experimental groups. The predominant form of failure found was cohesive, specifically in the case of the NR-5™, CO2 laser + TF, and TF-treated groups. In contrast, the control group and the Curodont™ Repair-treated group exhibited adhesive and admixed failure the most.

![Figure 1](image)

**Figure 1.** Modes of failure among the different investigated groups are cohesive, adhesive, and admixed.

4. Discussion

This contemporary research was based on the hypothesis that there will be no significant difference in the VH of eroded enamel when treated with the latest reparative and regenerative remineralizing agents (TF, CO2 laser + TF, Curodont™ Repair, and NR-5™) compared to the control. Secondly, it was also predicted that there would be no significant difference in the µSBS of the composite restoration bonded to the remineralized and regenerated enamel compared to the eroded enamel. The results have indicated that both of the stated hypotheses can be completely rejected, as both the VH and the bond strength are better in the experimental groups than those found in the control. The Vickers method for testing hardness is extensively employed in the field of dentistry, due to its ability to assess the degree of mineralization in dental substrates. This method provides a reliable means of measuring the hardness of dental materials and tissues, including enamel and dentin, which is crucial for evaluating their health, strength, and resistance to wear and damage [24,25]. In the present study, Coca-Cola™ was used for enamel demineralization, as the drink is abundantly consumed and is a common cause of enamel demineralization [26].
The available literature has supported the concept that an increase in the microhardness of enamel and dentin leads to a better adhesive strength of the restorative material bonded to the substrate. The findings of the existing work have suggested that the NR-5™ technology-treated samples displayed the highest bond integrity and VH among all of the tested groups. The observed results can be attributed to the capability of NR-5™ technology to enhance the natural mineralization process facilitated by human saliva [7]. This enhancement occurs by releasing additional calcium through the breakdown of calcium silicate and phosphate from sodium phosphate salts. This process, in turn, encourages the formation of hydroxyapatite (HAP) crystals, ultimately leading to the remineralization of the tooth enamel [27]. The outcome of this remineralization is improved bond strength and an increase in microhardness, which are positive indicators of the treatment’s effectiveness in strengthening and repairing the enamel [28,29]. Moreover, the outcomes from the current in vitro study have also backed the idea that applying fluoride chemicals in a gel or solution form improves the VH of degraded enamel and the μSBS of composite restoration. This is in agreement with the findings of the studies conducted by Irmaleny et al. and Itota et al. [24,30]. This may be facilitated by the development of calcium fluoride deposits on the enamel surface. A decrease in the local pH levels can trigger the release of fluoride ions (F⁻) from calcium fluoride deposits. Simultaneously, the demineralization process causes the release of calcium ions (Ca²⁺) from the tooth surface. As this occurs, hydroxide ions (OH⁻) are substituted with fluoride ions (F⁻), resulting in the formation of either fluorapatite or fluoridated hydroxyapatite [10]. This process represents the important role of fluoride in protecting tooth enamel by promoting the formation of more resistant and caries-resistant mineral compounds on the tooth’s surface [28,29].

Similarly, these findings have also shown that the utilization of CO₂: laser irradiation in conjunction with TF leads to a notable increase in the VH and a significant enhancement in bond integrity. The previous research by Mahmoudzade et al. and Farhadian and coworkers has substantiated the result of the current inquiry and has elucidated the collaborative impact of laser irradiation and fluoride application in impeding enamel demineralization and facilitating the transformation of hydroxyapatite into fluorapatite [31,32]. This results in the improved bond integrity and microhardness of the eroded surfaces.

Furthermore, these outcomes have indicated that Curodont™ Repair showed a significantly lower VH and bond strength among the groups tested with remineralizing agents. The literature has demonstrated the dubious and contradictory impact of Curodont™ Repair on the bond strength and microhardness of decalcified enamel surfaces [17]. However, the reported outcome of the existing study can be attributed to the development of a hydrophobic surface after the application of Curodont™ Repair, potentially impeding the bonding of the resin to dentin [33,34]. Regarding the failure mode, it was observed that the bond failures that were seen were primarily cohesive or mixed, regardless of the specific dentin pretreatment method employed. Cohesive failure refers to a situation where a material fractures or breaks within itself, rather than at the interface with another material [35,36]. The failure occurs due to the weaknesses or limitations present within the material’s structure. This type of failure indicates that the material’s internal cohesion is insufficient to withstand the applied forces or stresses, leading to its fracture or separation [37,38], whereas mixed failure occurs when both adhesive and cohesive failures are present, due to a combination of factors related to the material properties, bonding strength, stress distribution, and environmental conditions.

This study has several acknowledged limitations. Firstly, it lacks a positive control (sound enamel) for assessing the efficacy of remineralization treatment. Secondly, there is a deficiency in long-term assessments regarding how remineralizing agents affect the microhardness (VH) and bond strength of composite restorations. This absence impedes a comprehensive understanding of the enduring effects of these agents. Additionally, the chosen experimental model inadequately replicates the impact of dentinal fluid on the degradation of the resin composites, potentially limiting the study’s ability to fully simulate real-world conditions. The inclusion of supplementary analyses, particularly an
evaluation of the mineral content and permeability, could have provided valuable insights into the effects of the remineralizing agents. Furthermore, the study could have benefited from employing advanced imaging techniques, such as scanning electron microscopy (SEM) and atomic force microscopy (AFM), to assess the changes in the surface topography following the application of the latest remineralizing agents.

5. Conclusions

In brief, the integration of NR-5™ technology, CO2 laser irradiation with TF, and TF itself yields a potent and mutually reinforcing methodology that not only enhances the enamel durability, but also enhances the adhesion between the restorative substances and the tooth’s surface, thereby ultimately promoting comprehensive dental wellbeing and extending the lifespan of dental restorations. The possibility for the increased longevity of dental restorations exists through the enhancement of enamel resilience and an enhanced adherence to restorative materials. These therapeutic interventions have the potential to exert a substantial influence on the field of preventative dentistry by reducing the probability of dental issues and augmenting the efficacy of therapy.

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Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author. The data are not publicly available due to privacy.

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Conflicts of Interest: The authors declare no conflict of interest.

References


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