

Chapter 5

NEW APPROACHES IN REPAIR OF AESTHETIC RESTORATIVE MATERIALS

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One of the aims of restorative dentistry is to provide it happen functional and aesthetic restorations. Developments in new restorative materials and the increasing interest in aesthetics composite resin restorations that can mimic natural teeth' appearance have become frequently preferred by dentists ¹.

Composite resin and porcelain are suitable materials for indirect restorations due to their aesthetic appearance, long clinical life, durability, less microleakage, and postoperative sensitivity. Nowadays, there is a wide variety of ceramic materials and systems for indirect restorations such as laminate veneers, inlays and onlays. Its advantages include superior aesthetic properties, adequate fracture resistance against occlusal forces, excellent connection resistance between the tooth and ceramic surfaces, and production techniques facilitated using CAD / CAM (computer-aided design manufacturing) to increase the use of full ceramic systems ².

Composite resins bonded to the dental tissue with adhesive systems fail due to their structural properties deteriorating over

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time and degradation of the adhesive layer. The secondary caries development, coloration, abrasion, restoration or tooth fracture formation can also be seen as a result of the microleakage that may occur on the adhesive surface ³. Although Academy of Operative Dentistry European Section (AODES) sees composite resins with appropriate content and properties as the “preferred material” for use in posterior teeth minimally invasive dentistry applications, AODES states that composite resins are still lacking some properties. The AODES highlights the importance of performing refurbishment and repair techniques to extend the longevity of restorations ⁴.

Restoration repair is a minimally invasive treatment performed by removing the part that failed in the old restoration and placing the new composite on the surface. The three factors that form a successful repair process are the surface preparation methods used in the repair process, the adhesive systems used, and the compatibility of the tooth surface with the repair composite ^{5,6}.

SURFACE PREPARATION METHODS USED IN THE REPAIR OF COMPOSITE RESINS

The repair process's success depends on the strength of the bonding between old and new composite resin materials ⁷. Due to the oxygen barrier layer, the bonding between the two composite layers does not polymerize ^{6,8}. The water absorbed by diffusion by the composite resin in the oral environment adversely affects the binding of the new composite to the old composite. The aging and water absorption causes the oxygen inhibition layer to disappear, and the unsaturated double carbon-carbon bonds to decrease. For this aim, various surface preparation protocols should be applied to the old composite resin surface. These chemomechanical surface treatments are abrasion with carbide or diamond burs, hydrofluoric or phosphoric acid roughening, adhesive resin applications, laser roughening, tribochemical silica coating and air abrasion ⁹.

Most studies reveal that increasing the surface roughness of the old composite resin is effective in repair strength⁵. Mechanical bonding is provided by increasing the surface roughness. This process increases unreacted methacrylate groups. As a result, the superficial layer of the old composite resin is removed to obtain a clean connection surface with high energy, and filler particles are exposed to¹⁰.

Surface Roughening by Bur Cutting

The method frequently used in the clinic for roughening composite surfaces is roughening with diamond burs. Then, adhesive systems used in composite resin repair can be used by roughening with phosphoric acid¹¹. Oskoe et al. reported that the bond strength values obtained on diamond bur roughened and laser-roughened surfaces were higher than other groups in their studies investigating the effect of various surface treatments on the repair bond strength of composites¹².

Surface Roughening by Acid Etching

The phosphoric or hydrofluoric acid is typically used for roughening surfaces. However, there are conflicting data about the effectiveness of acid roughening on the bond strength of repaired surfaces in the literature. Phosphoric acid is a weak acid. It cannot create sufficient surface roughness on the composite resin surface¹³. In many in vitro studies, it has been shown that etching with acid does not have a sufficient effect on the repair bond strength values. While the resin material must be partially or completely removed in the repair of composite restorations, tissue loss may also occur in enamel and dentin in some cases¹⁴. Phosphoric acid acts on enamel and dentin but does not directly affect the surface properties of composites, ceramics and metals. Loomans et al. concluded that phosphoric acid alone did not affect the roughness of the resin composite¹⁵.

Gupta et al. used 4 different acids for use in the repair mechanism: 30% citric acid, , 7% maleic acid, 10% hydrofluoric acid

and 37% phosphoric acid. According to the results, they observed that the best repair bond strength was in hydrofluoric acid ¹⁶. Hydrofluoric acid attacks and dissolves the glass filler particles that are exposed, unlike phosphoric acid. Thus, it reduces the irregularities available for silane bonding without affecting the resin matrix. It has been noted that hydrofluoric acid's effect largely depends on the composition of the filler particles in the material. Therefore, roughening with hydrofluoric acid is considered convenient for composite repair ¹⁷. It has been found that sufficient concentration is between 4%-10% to obtain suitable repair bond strength values ¹⁶. However, hydrofluoric acid has been limited concerning the dangers of oral hydrofluoric acid ¹⁸.

Surface Roughening by Air Abrasion and Tribochemical Silica Coating

Air abrasion is used to clean the substrate surface, change the surface topography, and increase the surface area of the linkage, surface energy, and wettability. Afterward, it is recommended to apply silane, followed by the adhesive used with it ¹⁹.

Sandblasting is a tribochemical silica coating system. Tribochemical method means creating a chemical bond using mechanical energy. The tribochemical silica coating process is the embedding of silica-coated alumina particles under pressure by spraying to achieve a more chemically reactive surface and is recommended as an effective method to increase the adhesion of the resins to the restoration. Generally, it is used for repairing ceramics and nanoceramics with composite resins. With this method, restoration is roughened in the laboratory (RocatecTM, 3M / ESPE, Germany) or the clinic (CoJetTM, 3M / ESPE, Germany). For intraoral procedures, such as direct repair of fractures of CoJet, metal-ceramic, and all-ceramic restorations with composite resin or adhesive cement, Rocatec is designed for laboratory use ²⁰.

Various reports have reported that sandblasting with 50 μm aluminum oxide said that the repair composite provides superior surface roughness and wetting potential compared to chemical

processes. It shows adequate bond strength values for composite repair ^{9,21,22,23}.

Chemical Bonding

While the surface roughness provides the micro-mechanical retention of the repair composite, intermediate materials such as adhesive resin, silane coating agents, or flowable resin composite are still required to provide wetting of the surface and subsequent permanent bonding between the old and repair resin composite ^{22,24}. Reactive monomers are exposed to surface preparation methods, and chemical connections are established with the monomers included in the repair material. The superficial composite resin layer that is contaminated with the mouth environment is removed ²⁵.

Silane has a bifunctional molecule structure and has an essential place in all composite resin structures as bonding agent. The silanol group of the silane agent forms a chemical bond with silica modified surfaces. The other end of the silane, the methacrylate group, reacts with the methacrylate groups of the adhesive and composite resin. It briefly initiates chemical reactions by providing physical adhesion ²⁶. The silane provides the wettability by reducing the adhesion and contact angle of the inorganic and organic matrix. Silanes increase repair bond strength by increasing the surface energy, which is the prerequisite of wetting optimized for close contact between resin composites. The adhesive use after silanization is recommended for ideal attachment without micro gap ²⁷. The most common silane used in contemporary dentistry applications is the 3-trimethoxysilylpropylmethacrylate (MPS). Many in vitro studies using silane in composite repairs have shown that this agent has positive effects on repair bond strength values ^{27,28}. In contrast, Nassoohi et al. They found that using silane in composite repair caused the weakest bonding strength⁹.

Surface Roughening by Laser

Due to the frequent use of lasers in dentistry recently, the technique of surface preparation with lasers has been on the same agenda ^{29,30}. The laser makes changes in surface topography to create sufficient bonding in the repair of composite resins. Although this situation is similar to other mechanical treatment methods, laser is considered to be more conservative than other mechanical treatment alternatives ^{21,31}.

The studies on the use of Erbium yttrium aluminum garnet (Er: YAG) and neodymium yttrium aluminum garnet (Nd: YAG) lasers for caries removal, cavity preparation, surface roughening applications and periodontal processes have been conducted. The Erbium laser family has two different wavelengths: Er: YAG laser (2940 nm) and (Er, Cr: YSGG) laser (2780 nm). The advances in laser technology have shown Er: YAG laser as a method of surface preparation in the repair process ¹². Oskoe et al. evaluated the effectiveness of different lasers on surface roughness in their studies. According to the results, Er, Cr: YSGG laser showed more successful repair binding strength values than Nd: YAG and CO₂ lasers without creating a smear layer ³⁰.

Alizadeh Oskoe et al. reported mechanical surface treatments, i.e. diamond burs, air abrasion, and Er, Cr: YSGG laser. They compared the effects of the siloran-based composites on the repair bond strength that repair bond strength values of laser and bur treatments were significantly higher ¹². Similar findings were obtained in another study using the same treatment protocols for repair a methacrylate-based resin composite and reporting that the laser-treated group had the highest bonding values ³¹.

Murray et al. suggested laser treatment as an appropriate treatment option for advanced repair bonding forces ³²; similarly, Rossato et al. found that laser and bur treatment in the repair process gave similar results ³³.

EVALUATION OF THE IMPACT OF DEVELOPMENTS IN THE CONTENT OF COMPOSITE RESINS ON REPAIR PROCESS

It has been reported that the effectiveness of repair treatment of composite resin restorations depends on the structure of the existing composite resin to be repaired, and it has been argued that it should be restored with composite resins of similar structure. However, most of the time, physicians do not know which type of composite resin the restoration they will perform before was done ¹⁷. According to the results of their study, Ribeiro et al. reported that high shear bond strength was obtained after the bonding of composite resins with similar organic and inorganic structure to each other ³⁴. Shahdad and Kennedy stated that shear bond strengths obtained by repair restoration with composite resins with the same organic matrix do not show significantly higher values compared to repair with composite resins with different types of organic matrix ³⁵.

Bis-GMA (Bisphenol A diglycidylmethacrylate) molecules in the structure of composite resins have a higher viscosity, and low conversion degree, smaller and flexible TEGDMA (Triethylene glycol dimethacrylate) is used as a diluent monomer and increases the degree of conversion. The modified monomer Bis-EMA (Ethoxylated bisphenol A dimethacrylate) has been shown to increase the degree of conversion and reduce water absorption. It has been claimed that resin composites' water saturation reduces existing free radicals, thereby reducing repair bonding forces ³⁶.

The most used composite resins in dentistry are methacrylate-based composite resins. The contraction of these composite resins during polymerization creates stress on the cavity walls. This stress causes leakage, secondary caries development, post-operative sensitivity, marginal coloration, and cracks in the enamel. To overcome these problems, siloran based composite resins containing monomers with low polymerization shrinkage have been developed in recent years ³⁷. The polymerization mech-

anism of the siloran resin composites is based on the photo cationic ring-opening, which is different from the radical reaction found in methacrylate materials. The photo-cationic ring-opening is significantly lower than methacrylate composites (4%), reducing polymerization shrinkage to almost 1% ³⁸.

It has its adhesive system consisting of two components for better bonding of siloran based composites to dental tissue. The first component is a self-etch primer. The hydrophilic structure of the first component is important for adhesion to the tooth tissue. To connect the siloran-based (hydrophobic) composite to the dental tissue, it is necessary to coat it on the hydrophilic primer layer with a hydrophobic adhesive layer. The second component serves this work. An adhesive system containing hydrophobic dimethacrylate monomer without hydrophilic 2-hydroxyethyl methacrylate (HEMA) monomer should be used for bonding siloran-based composite resins ³⁹. There are many types of research on the repair protocol of siloran based composite resins. Composite resin is hydrophobic due to its siloxane molecules. Therefore, it is recommended to be treated with a hydrophobic adhesive system during the repair process ⁴⁰.

The factors that determine the surface characteristic of the existing and defective composite resin restoration are the type, size, distribution, organic matrix structure, polymerization degree, and hardness of the material's filler particles. The parameter that most affects the repair bond strength is the property of the filler particles of the material. Composite resins containing particles with a large filler size are known to react more extensively with functional monomers of adhesive systems ²⁴. In the literature, it is recommended to repair composite resins with composite resins of the same structure ⁴¹.

Lühns et al. have stated that the repair protocols of methacrylate-based composite resins can be applied in repairing composite resins based on siloran ⁴². According to the study of Oskoe et al. on the use of laser in the surface preparation pro-

tocol of siloran based composites, Er, Cr: YSGG reported as the most effective laser ³⁰. Lima et al. showed that composite resins' surface preparation based on siloran has similar repair bond strength values after sandblasting with diamond burs and aluminum oxide ¹³.

In cases where defective restoration is not known to be a siloran-based composite resin, it has been reported that it can be repaired with methacrylate-based composite resins and shows adequate repair bond strength ⁴³. As a result of using silorane-based composite resins in the repair of methacrylate-based composite resins, lower repair bond strengths are obtained ⁴¹. According to the studies of Bacchi et al., siloran-based composite resins show lower repair bond strength compared to methacrylate-based composite resins, due to the less reactivity of the siloran groups after polymerization ⁴⁴. If the composition of the material is unknown, it is recommended to apply with phosphoric acid roughening, sandblasting (Al_2O_3 in sizes of 30 μm and 50 μm), silane, and adhesive systems ¹⁷. Previous studies have reported that silane application is mandatory for the adhesion of methacrylate-based adhesives to silorane surfaces ⁴⁵. Wiegand et al. suggest that silane application is not necessary when silorane composite and compatible silorane adhesive system is used in the repair mechanism ⁴⁰.

It is claimed that nanocomposites have promising physicomechanical properties due to their high content of filling particles. Due to its high filler content, nanocomposite resins, which have lower water absorption rate compared to other composites, are less sensitive to aging and more suitable for repair ⁷. Nassoohi et al. reported that the microhybrid resin composite may have a better repair bonding strength compared to nanocomposites, and nanofil and nanohybrid types are less different from each other ⁹. Moncada et al. reported that hybrid composites provide better repair strength than micro filled resins ⁴⁶.

EVALUATION OF THE IMPACT OF DEVELOPMENTS IN ADHESIVE SYSTEMS ON REPAIR PROCESS

Adhesive restorations provide better transmission and distribution of functional stresses to the tooth with their potential to strengthen weakened tooth tissue while reducing marginal discoloration and fractures, secondary caries, and even microleakage, which can lead to the development of pulpal pathology.

The adhesive systems can be classified as total-etch adhesives, self-etch adhesives, and glass ionomer-based adhesives. In recent years, new single-stage self-etch adhesive systems, also known as universal or multi-mode systems, have been released. They are single-stage self-etch adhesives produced with the 'all-in-one' concept. It gives physicians a chance to choose with adhesive strategy: etch & rinse can be applied with self-etch and selective etch technique. This approach combines the advantages of enamel etch & rinse technology and the additional chemical bonding of apatite crystals of dentin simplified self-etch procedure⁴⁷. Some researchers report that some functional monomers (Bis-GMA (bisphenol A glycidyl methacrylate), HEMA (hydroxyethyl methacrylate), GPDM (glycerol di methacrylate ester), MEP-P (methacryloxyethyl phenyl hydrogen phosphate), MMP (Methacryloyloxypropyl dihydrogen phosphate), MEP (methacryloxyethyl dihydrogen phosphate), PENTA-P (dipentaeritrolpentaakrilol dihydrogen phosphate), 4-META (4-methacryloxyethyl trimellitate anhydride), MAC-10 (metakriloloksialkil asit fosfat), 10-MDP (10 metakriloyloksidesil dihydrogen phosphate) in self-etch and universal adhesives increase the bond strength of adhesive systems⁴⁸. However, manufacturers of universal adhesives claim that those containing silane improves bonding to glass ceramics or composite resins without additional preparation procedures. The 10-MDP monomer has been reported to play an important role in achieving a chemical connection between the enamel and dentin and a stable and durable interface⁴⁹. Yoshida et al. reported that the 10-MDP functional mon-

omer included in the adhesive content provides an adequate and permanent bonding. They also stated that thanks to the HEMA, a hydrophilic monomer, it can wet the composite resin surface better and penetrate more into the retentive areas⁵⁰. Since the PENTA functional monomer in adhesive systems contains polymerizable double bonds, they form various calcium-phosphate complexes and build nanolayer structures that strengthen the hybrid layer of the adhesive and facilitate the spread of the adhesive by wetting the surface⁵¹. In a study conducted by Staxud et al. the bond strength values obtained with universal adhesives were found to be similar to the bond strength of the groups applied post-silane adhesives²⁷. In their study, Fornazari et al. suggested that the bond strength of a silane-containing universal adhesive is as effective as silane + adhesive application and eliminates the need for a separate silane application⁵².

For the adhesive systems to provide sufficient adhesion clinically, the required repair bond strength values should be similar to the bond strength values of the adhesive systems to the enamel (15-30 MPa). Therefore, according to most researchers, repair bond strength should be above 18 MPa⁵³.

Bayrak et al. stated that the solvent and filler content of adhesive systems have more effect on their shear bond strength than their pH⁵⁴. In a study conducted, Teixeira said that adhesive systems containing fillers showed higher repair bond strength than those without fillers⁵⁵. It is thought that the reason for this is that the adhesive systems containing filler have adequate tensile strength and relieve shrinkage stresses between the materials⁵⁶.

NEW APPROACHES IN REPAIRING CERAMIC BASED MATERIALS WITH COMPOSITE RESINS

Nowadays, there is a wide variety of ceramic materials and systems for indirect restorations such as laminate veneers, inlays, onlays². Although ceramics are the most preferred indirect restoration material in clinical practice, there are also hybrid-ceramic

and nanoceramic resin materials developed by different companies. The advantages of dental ceramics such as not being affected by oral chemical events, color stability, high resistance to abrasion, low thermal conductivity, biocompatibility, ideal aesthetic properties, and production techniques facilitated by using CAD / CAM (computer-aided design/manufacturing) have increased its use by dentists 78. Localized fractures frequently appear in indirect restorations applied in the clinic. In this case, restoration should either be wholly refurbished or repaired as a treatment option ⁵⁸.

It is necessary to obtain a strong micromechanical connection between the restoration fracture surface and the different structure of hydrophobic resin-based composite or resin cement for the oral repair to be successful. Since this connection also includes chemical interaction, it is necessary to choose suitable surface treatments for exposed cracked surfaces of different types of materials ⁵⁹. Surface treatments applied mechanically or chemically to the restoration materials; sandblasting with aluminum oxide particles (Al_2O_3), burs, hydrofluoric acid (HF), and phosphoric acid roughening, silane and metal primers application, tribochemical silica coating can be listed ⁶⁰.

Wiegand et al. reported that roughening with burs generally showed the highest bond strength values in their study. Based on this finding, it may be suggested to roughening the surface with diamond burs before repairing hybrid ceramics with composites ⁶¹. Although roughening by bur is a quick and easy method, Jain et al. suggested that roughening with diamond milling creates sharp surface roughness on the ceramic surface and causes microfractures causing an increase in stress concentration and subsequent fracture formation on the ceramic surface ⁶².

It is recommended to use acid roughening on glass-ceramic (silicate materials) surfaces. It is difficult to protect the undamaged surfaces during sanding of the restoration with aluminum oxide particles ⁶³. In surface roughening by acid, HF acid, phos-

phoric acid or acidified phosphate fluoride (APF) gel can be used. Among these gels, HF acid is more durable than phosphoric acid and is the most commonly used agent for porcelain roughening. HF acid can be used for surface roughening of silica-based porcelain. HF acid cannot be used for surface roughening of metal or oxide ceramic materials with a silica content of less than 15% by volume ⁶⁴. As a result of his work, Acar Ö stated that HF acid does not increase the success of connection in hybrid ceramic material (Vita Enamic). This result indicates that the material contains a high proportion of leucite and zirconia crystals and that the entire structure shows a substantially composite formation ⁶⁵.

Tribochemical silica; It is a system used in the clinical environment for repairing metal porcelain and full porcelain restoration fractures to coat silica on the surface. With the tribochemical silica coating process, the silica content of the ceramic increases, and many structures are exposed so that the silane bonding agent can react. The covalent bonds have been reported between silane application and ceramic-composite. Also, silane agents provide to increase the wettability of the glassy structure of composite resins while at the same time strengthening the physical, chemical, and mechanical bonding between composite resin and porcelain ¹⁸. Silanes, by their nature, create a strong connection between ceramics containing silica and composite resins, while they cannot provide strong connections with silica-free dental restorative materials ⁶⁶. Since aluminum, aluminum/zirconium or zirconium ceramics have a high crystal content; silica coating is recommended because acid roughening can not affect their durable structure.

For this reason, the silica coating process; indicated for acid-resistant ceramics with low silica content ⁶⁷. Stawarczyk et al. found the highest value in the group in which they used Universal Bond and tribochemical silica coating in their study, where they applied different surface treatments on CAD / CAM resin nano ceramic (Lava Ultimate) and compared various bonds with composite resin. Some of the universal adhesives contain MDP and

silane, capable of bonding to different surfaces such as glass or non-glass ceramics and metals ⁶⁸.

Metal primer is an agent used to strengthen the bonding between metal and resin. The functional monomers contained in it can be attached to both resin and metal. Metal primers interact differently depending on the type of metal used. The metal primer suitable for the metal type must be selected by the clinician ⁶⁹. Because the bifunctional phosphate monomers (10 methacryloxydihydrogen phosphate-.MDP or 4-.Methacryloxyethyl trimethylate anhydride) in the product, one end connects to the metal oxide or oxide ceramic surface and the other ends to the resin material with a direct chemical connection ⁷⁰.

The bonding resistance of the ceramic and repair composite resin interface depends more on the type of repair composite than the surface treatment. Hybrid composite resins exhibit higher bond strength than composites with microfill fillers. Microfill composites are preferred for repairing superficial fractures at the level of enamel porcelain, and condensable and hybrid composites for repairing deep fractures at the posterior region where chewing pressure is high ⁷¹.

WHAT AWAITS US IN COMPOSITE REPAIR IN THE FUTURE?

While dental materials often fail after a period of use, nature manages to renew most of the biological materials it uses. Nature has inspired new technologies such as self-healing and repair mechanisms that can increase material survival. All self-healing systems have shown promising results for self-repair and crack inhibition, suggesting a long life for dental composite restorations. These new materials can heal cracks, restore load-bearing ability, inhibit oral bacterial pathogens, reduce or eliminate biofilm acids, increase biofilm pH, and regenerate lost tooth minerals. Also, its effects are stated to be durable and long-lasting ⁷².

Self-healing approaches are bio-inspired or biomimetic mechanisms. Nature's self-healing ability inspired engineers and chemists who aimed to restore the mechanical properties of a material by suggesting different healing approaches⁷³. Self-healing composite systems include self-healing hollow fibers and microcapsules. The microcapsules of the dicyclopentadiene (DCPD) monomer in the polyurea-formaldehyde (PUF) shells are dispersed in a polymer host and breaks when exposed to a load causing crack propagation. Healing agents (DCPC) is drawn along the fissure line, where it encounters a faulty chemical catalyst (usually ruthenium-based 'Grubbs') in the polymer matrix. This chemical catalyst initiates polymerization and recovery occur⁷² (Figure 1).

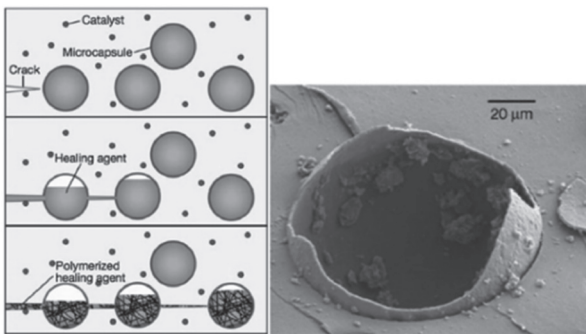


Figure 1: Typical method of microcapsule approach (Left), SEM image showing ruptured microcapsule (Right)

One of the first self-healing synthetic materials reported has some resemblance to resin-based dental materials as it is resin-based. This is an epoxy system containing resin-filled microcapsules⁷⁴. If a crack occurs in the epoxy composite material, some microcapsules are destroyed and release the resin. The resin then fills the crack and reacts with a Grubbs catalyst dispersed in the epoxy composite, causing polymerization of the resin and repair of the crack. Similar systems have been shown to have a longer mission cycle under on-site mechanical stress than similar self-healing systems⁷⁵.

It is clear how effective such an approach is for application in dental composites. Dental composites using this technology can be expected to have a longer mission cycle and improved clinical performance. The problems may arise from the potential toxicity of resins in microcapsules and the catalyst that should be present in the composite. However, the amounts of these agents required to repair microcracks in the dental composite seem quite small and maybe below the toxicity threshold. The self-healing mechanism based on microcapsules may be more promising, so the composites repaired in this way can perform better than those improved with macroscopic repair approaches; some of these have not been shown to cause satisfactory mechanical properties of the repaired composite ⁷⁶.

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