

Influence of the Nanoparticles Chitosan High Molecular on the Degradation of Nanofill and Nanohybrid Composite Resins in Various pH Saliva

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Abstract:- Composite resin is a filling or restoration material that has a similar color to the teeth, is insensitive to dehydration, and is relatively easy to manipulate. One of the nanotechnology developments in dentistry is nano fill and nanohybrid composite resin with minute particle sizes, which has a different value in its physical, mechanical, and optical properties. In the oral cavity, composite resin restoration material comes in contact with various salivary pH, acidic or alkali that can affect physical property changes, including surface roughness. Chitosan is a biomaterial continuously being developed because it has many medical benefits and has proven safe to use on people. This study analyzes composite resin restoration strength when nanoparticle chitosan high molecular is added 1% to its surface degradation. Samples are 36 human premolar teeth randomly classified into 12 groups ($r=3$). Each group is classified based on different filling materials and salivary pH. Scanning Electron Microscopy (SEM) samples are tested to see the surface degradation. The result of this study shows that using composite resin, either nanofiller or nanohybrid, will go through salivary degradation on pH 3, 5, 7, dan 10. The lower the pH, the higher the degradation, Adding 0,1% chitosan on nano fill and nano hybrid shows that there is still degradation in the restoration surface. 0,1% Chitosan added in nano hybrid composite resin on pH 7 offers surface stability, although degradation is still found. The 0,1% chitosan added into nano fill composite resin shows a different value although still lower than nano hybrid composite added with 0,1% chitosan on surface degradation. Adding 0,1% high molecular Chitosan to both nanocomposite resins shows a better value when compared to the composite resin that is not infused with Chitosan.

Keywords:- Composite resin, Degradation, Nanohybrid, Nanofill.

I. INTRODUCTION

Composite resin is a filling or restoration material with a similar color to the teeth, is insensitive to dehydration, and is relatively easy to manipulate (Olsburgh et al., 2002). Advance in nanotechnology has produced nanocomposites with more advantageous properties. Nanocomposites are classified into two types: nanohybrid and nanofiller. Nanohybrids are composed of glass fillers and 40-50 nm-sized nanoparticles. The combination of nanometers and nanoclusters forms nano fill types (Mocanu et al., 2019).

Composite resin surface changes in a specific range of time and will affect the mechanical properties of composite resin. The term for this is composition resin degradation. Mechanical degradations are sliding, abrasive, and fatigued. In contrast, chemical degradation can be caused by hydrolysis or catalyst enzymes in saliva and oral cavity enzymes, weakening composite materials enough to reduce restoration age (Dennis and Abidin, 2013).

Hydrolytic degradation of composite resins is mainly caused by moisture accumulation.⁴ Inside the oral cavity, resin composite restoration materials are in contact with saliva, either in acidic or alkali pH, affecting composite resin's physical properties, including changes in surface roughness. Furthermore, other factors can cause damage to hybrid resin fillers. Low salivary pH (about pH 4) is caused by diet and false teeth brushing (Pribadi and Soetojo, 2011). A study examined the breakdown of nano fill and nanohybrid composite resins after polishing using artificial saliva with different pH levels. The results showed that nano fill and nanohybrid composite resins broke down in artificial saliva with pH 3.5 and 10 ($p<0.05$) (Oliveira et al., 2012).

This study also shows groups that release the most fillers. For example, Aluminium (Al^{+3}) dan Strontium (Sr^{+2}) is a nano hybrid composite resin in the immersion of artificial saliva of pH 3.5. At the same time, the group that released the minor fillers is nanofiller composite resin immersed in artificial saliva of pH 7 (Ahmed Hesham Ahmed, 2017).

An example of dentistry natural biomaterials is high molecular Chitosan. Chitosan is a continuously developed biomaterial because it has many medical benefits and is proven safe for people. Sutrisna and Trimurni (2013) studied adding 0,15% chitosan in RMGIC (*Resin Modified Glass Ionomer*) in vitro. The result shows much better compressive strength on a class 1 cavity and better flexural strength on a class 2 cavity when compared to RMGIC on its own. The study by Qi (2014) shows that adding high molecular chitosan nanoparticles weighed 0,015% b/v on glass ionomer cement variants (RMGIC danRMGICn) increases bonding between materials and dentin (Qi et al., 2010). Da Silva (2011) (2017) studied the effects of different pH saliva on nano fill and nanohybrid composite resin degradation. The result showed no significant degradation on both nano fill and nano hybrid composite resin. Insignificant degradation difference is also found in nanofiller and nano hybrid composite resin immersed in the same saliva pH, which is 3,5, 7, 10 (Da Silva et al., 2011).

A difference in the pH of the saliva could affect a filling made of composite resin. If the pH goes down, the surface of the composite resin will start to break down. If the pH goes down, the surface of the composite resin will begin to break down. Degradation could happen at a higher pH (alkali) level, but it would be less than at a pH level. The use of Chitosan addition on composite resin will decrease the surface degradation of composite resin caused by salivary pH and will not damage dentin collagen. Hence, tooth fillings will bond better on cavity walls (Lobato et al., 2017).

Degradation happening on long ranges on time, on restoration material surface will cause the surface to become rough and might decrease the aesthetic value of the teeth. *Scanning Electron Microscope* (SEM) and Energy-Dispersive X-ray (EDX) are considered optical devices that are easy to use on surface characterization topography (Cazzaniga et al., 2015). SEM EDX can obtain surface images with very high resolution that will be computerized with software to analyze material components, both quantitative and qualitatively. But, there are not many studies observing how different pH of saliva and immersion time affects polished composite resin (Gniadek and Dąbrowska, 2019). This study aims to determine the effects of nanocomposite chitosan addition and its ability to increase the physical properties of the composite resin.

II. MATERIAL AND METHODS

A. Research Materials

The study used a laboratory experiment with a posttest-only group design. The ethics committee agreed with this study to implement health research No. 704/TGL/KEPK FK USU-RSUP HAM/2019 on nano hybrid and nanofiller composite restoration materials immersed in different salivary pH which are 3.5, 7, dan 10. An evaluation is done on the capability of composite resin degradation in all aspects of the restoration, rigidity, heat release, tensile bond strength, and surface roughness. Tools that are used in this study are beaker glass (Pyrex®, USA), colored adhesive, light-curing unit (Woodpecker, China), chamber(Kong,

China), Syringe, Tissue culture test plate(SPL, Korea), Micro Motor (Strong, China), Handpiece (Strong, China), Scanning Electron Microscopy(SEM), Energy Dispersive X-ray(Hitachi, Jepang), Aluminum oxide disk medium, fine, extra-fine (3M, USA). Materials used are high molecular chitosan powder, Filtek™Z350 XT nano fill composite resin (3M, USA), Filtek™Z250 XT nano hybrid composite resin(3M, USA), phosphoric acid etch 37%, Scotch Bond (3M, USA), pH 3.5, pH 7, pH 10 saliva.

B. Preparation sample of tooth

This study uses 36 maxillary premolar teeth extracted and obtained from dental practitioners free of cracks or fractures. The crowns are in good condition, clinically and macroscopically whole, and have no discoloration on the enamel. The tooth is planted in a mold, prepared with a Class I design. Nanocomposite resin and high molecular chitosan powder mix are prepared using 0,1% nano chitosan mixed with composite resin warmed up to 35-60 until it is homogeneous for 15 minutes in a dark room. The composite resin is then applied to the cavity that has been made. The Nanofiller is used in groups A, B, C, and Nanofill+chitosan is used in groups D, E, and F, and nano hybrid composite is used in groups G, H, I, and nano hybrid + Chitosan is used in groups J, K, L. Polishing is then done with an aluminum oxide disk. The oral cavity is then simulated by immersion of samples in saliva. In groups A, D, G, and J, 12 teeth are immersed in pH 3,5. Groups B, E, H, and K have 12 teeth immersed in pH 7; in groups, C, F, I, and L, 12 teeth are engaged in pH 10.

C. Heat Release, Tensile Bond Strength, and surface degradation Tests

Measurement of heat release uses Differential Scanning Calorimeter (DSC). Tensile bond strength measurement is done at the Physic Laboratory, Faculty of Mathematics and natural science, UniversitasSyiah Kuala, Aceh, Indonesia, also evaluated using Torsee's Electronic System Universal Testing Machine. The measurement of surface roughness uses Vickers methods done by grinding sample surfaces that are going to be given treatments, and then it was given 6 kg load for 20 seconds, and then test samples are measured to get the values and calculated with the formula: $d_1 = (a_1x 0,1)+(b_1x 0,002)$; $d_2 = (a_2x 0,1)+(b_2x 0,002)$; $D = d_1 + d_2/2$; $Hv = 1,8544.P/D^2$. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) are used to check how many samples have broken down on the outside.

D. Statistical Analyses

Analysis statistics of the tooth rigidity, heat release, and tensile strength were used in the nonparametric Friedman test

III. RESULTS AND DISCUSSION

Nanoparticle chitosan high-molecular 0,1% was added tonanohybrid and nanofilm composite restoration material immersed in different salivary pH, namely 3.5, 7, and 10. Evaluation is then done related to the degradation of composite resin restoration, whether in terms of rigidity, heat release, tensile bond strength, or surface roughness. The statistical analysis of this research is done to obtain the

Mean value of one variable with the other in one treatment method and to observe the correlation of the variables simultaneously. The result of this research is reported below based on the working method analysis of each research group.

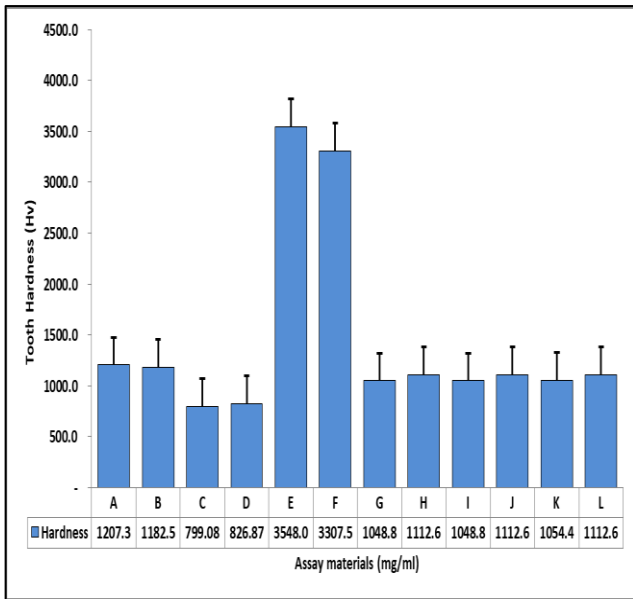


Fig. 1: Vickers profile filled tooth area with nanofiller, nanohybrid, and chitosan mixed composite. Groups E and F have the best rigidity compared to other groups. Group A (Nanofill pH 3,5); B (Nanofill pH 7); C (Nanofill pH 10); D (Nanofill +Chitosan pH 3,5); E (Nanofill +Chitosan pH 7); F (Nanofill+Chitosan pH 10); G (Nanohybrid pH 3,5); H (Nanohybrid pH 7); I (nanohybrid pH 10); J (Nanohybrid +Chitosan pH 3,5); K (Nanohybrid +Chitosan pH 7); dan L (Nanohybrid+Chitosan pH 10). Bar (rigidity) error bar (standard deviation)

In Figure 1, it is shown that group E and F has the best rigidity out of all the groups. Chitosan as a mixer material gives better bond viability for the composite as in groups E and F. These groups show that pH significantly affects the rigidity of this material mix. Neutral pH (7) gives good stability compared to pH 10 (Alkali). Hence it is apparent that if the pH of the oral cavity is always controlled to neutral pH, it is possible to give a more considerable tension to the material and has an active phase and extended material time. It shows that groups E and F are better as filling material. From table 1, it is shown that there is a significant difference ($p < 0,005$) between all of the samples treated with the strength test.

Figure 2 shows that group H (Nanohybrid pH 7) and group K (Nanohybrid + chitosan pH 7) has a high heat release compared to the groups. Group E (Nanofill + Chitosan pH 7) dan J (Nanohybrid + Chitosan pH 3,5) have the lowest heat release. Statistical tests show a significant difference between treatment groups on heat release properties ($p < 0,05$), which means every composite mix material as a filling material can release heat at different levels. Statistical tests show a significant difference between treatment groups on heat release properties ($p < 0,05$), which means every composite mix material as a filling material can release heat at different levels.

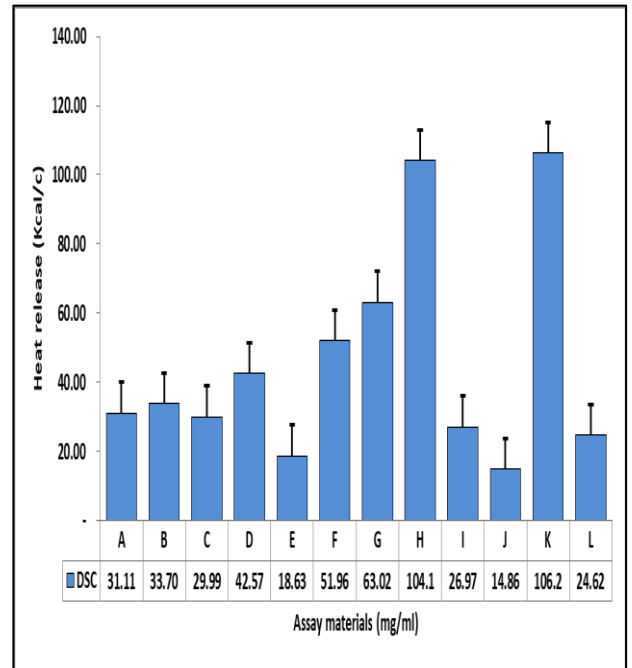


Fig. 2: Differential Scanning Calorimeter (DSC) heat release of the tooth that has already been filled with nano fill, nano hybrid, and Chitosan mixed composite restoration material. Groups D, F, H, and K, have a heat release that is relatively better than other groups. Group A (Nanofill pH 3,5); B (Nanofill pH 7); C (Nanofill pH 10); D (Nanofill + Chitosan pH 3,5); E (Nanofill + chitosan pH 7); F (Nanofill + Chitosan pH 10); G (Nanohybrid pH 3,5); H (Nanohybrid pH 7); I (nanohybrid pH 10); J (Nanohybrid + Chitosan pH 3,5); K (Nanohybrid + chitosan pH 7); dan L (Nanohybrid + chitosan pH 10). Bar (heat release) error bar (standard deviation)

Analysis Variables	Statistical description					Friedman Test
	N	Min	Max	Mean	SD	P
Heat Release	1	14,9	106,3	45,6	30,9	$p < 0,05$ (0,001)
Test samples	2	1,00	12,00	6,50	3,61	

Table 2: Friedman analysis test towards tooth heat release with sample materials (Nanofill, Nanohybrid, dan chitosan)

Analysis Variables	Statistical description					Friedman Test
	N	Min	Max	Mean	SDV	P
Rigidity	1	799,0	3548,	1446	934,9	$p < 0,05$ (0,001)
Test samples	2	0	,9	,9	3,606	

Table 1: Friedman analysis test on the rigidity of Sample tooth (Nanofill, Nanohybrid, and Chitosan)

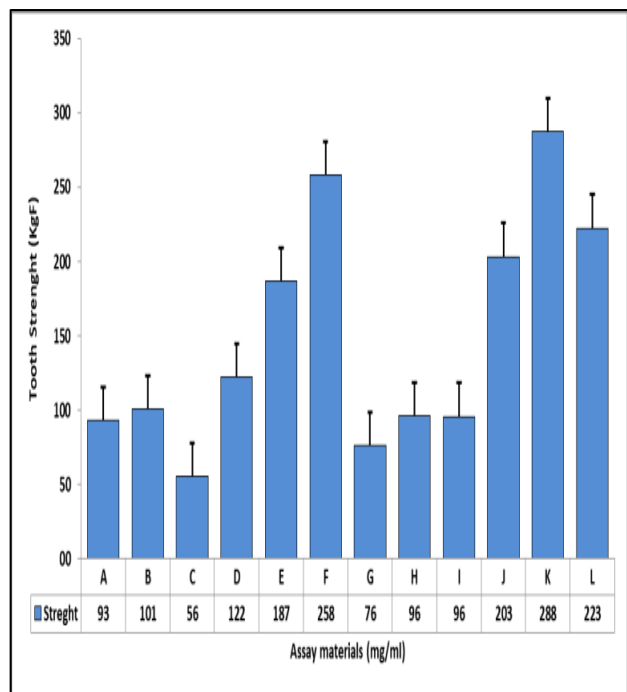


Fig. 3: The scanning electron microscope of porosity profile on the tooth root canal wall. In the SEM images, each treatment with Lerak fruit extract 6.25% (A), Lerak 12.5% (B), Lerak 25% (C), NaOCl 2.5% + EDTA 17% (D), Saline (E) with different incubation time variations after interaction with *F. nucleatum*.

Figure 3 shows the group K (Nanohybrid + Chitosan pH 7); F (Nanofill + chitosan pH 10); L (Nanohybrid + Chitosan pH 10); J (Nanohybrid + Chitosan pH 3,5) has a better strength when compared to other groups. Statistical analysis with the Friedman test shows a significant difference between every test group ($p < 0,05$).

Analysis Variable	Statistical description					Friedman Test P
	N	Min	Max	Mean	SD	
Transversal strength Test samples	1 2	55,5 0	287, 60	149, 73	77,9 7	$p < 0,05$ (0,001)

Table 3: Friedman test analysis on tooth tensile strength on composite resin restoration material. (Nanofill, Nanohybrid, dan chitosan)

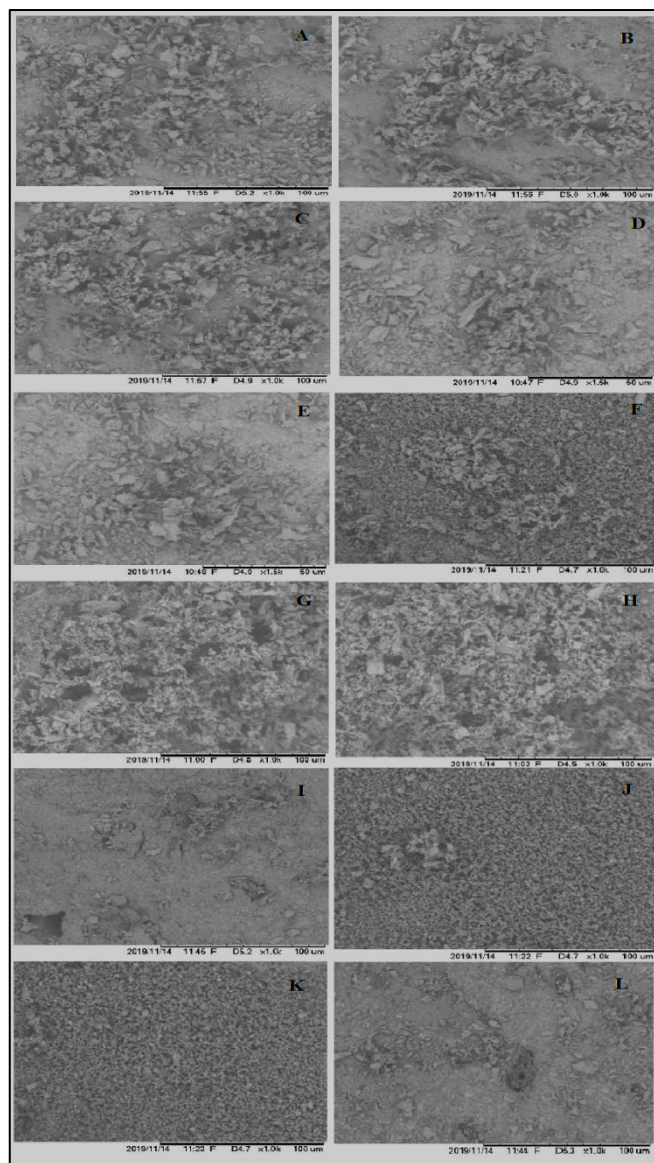


Fig. 4: SEM profiles of the filling surface. Generally on every treatment group shows different surface profiles on the filling. A (Nanofill pH 3,5); B (Nanofill pH 7); C (Nanofill pH 10); D (Nanofill + Chitosan pH 3,5); E (Nanofill + Chitosan pH 7); F (Nanofill + Chitosan pH 10); G (Nanohybrid pH 3,5); H (Nanohybrid pH 7); I (nanohybrid pH 10); J (Nanohybrid + Chitosan pH 3,5); K (Nanohybrid + chitosan pH 7); dan L (Nanohybrid + Chitosan pH 10).

In this study, the rigidity of nanohybrid and nanofiller added with high molecular 0,1% chitosan as material mixer gives better viability on the bonding of the composite like groups E and F (Figure 2). Both groups show that pH significantly affects the rigidity of the material mix. Neutral pH (7) gives excellent stability compared to alkali pH (10). Hence, if the oral cavity pH is always controlled on neutral pH, applying more tension on the material and has an active and elongated phase.

Acid or base salivary pH can affect composite resin's physical properties, including surface roughness. One of the factors that can cause damage to composite resin filling material is the effects of low salivary pH (Prakki et al., 2005). Other than that, Curtis (2018) said there is a

significant difference in Nanofill composite resin degradation on synthetic salivary immersion pH 3.5 and 10. It is also known that nano fill releases the least filler material on pH seven synthetic salivary immersion (Curtis et al., 2008).

Saliva has a normal pH of 6-7 that can change based on salivary flow. The pH of saliva can be anywhere between 3.5 (low) and 7.8 (high) (high). If there are a lot of H⁺ ions, the pH and other properties could go down (Anderson and Orchardson, 2003). The H⁺ ion is known for releasing composite resin filler materials, which is an inorganic metal that tends to dissolve when reacted with acid. The release of filler materials will cause porosity that will cause hydrolytic degradation (Namgung et al., 2013). Hydrolytic degradation, known as surface roughness in this restoration material, is caused by the severance of functional molecular groups generated by a reaction with water. Factors that usually push the kinetics of hydrolysis involve the composition of materials with hydrophilic properties and cross bonds on material structures (Buzalaf et al., 2012).

Groups added with Chitosan have a better ability on heat release when compared to filling materials that are not added with Chitosan. It is known that Chitosan has a high affinity because it has amino and hydroxyl clusters on its structure that will induce a specific property on the catalyst (Guibal, 2005). Chitosan can be a catalyst to speed up heat release on teeth material (Cicciù et al., 2019).

In the Differential Scanning Calorimeter profile, heat release on composite material is different between groups. The use of basic pH can be one of the variables that cause the level of heat release shown in groups H and K on this image, where neutral pH causes higher heat release than acid or alkali pH. It can be assumed that pH has a significant effect on heat release. Hydrogen ion bond in the smelting process of composite materials has a considerable influence on heat release, which will cause hydrogen ions to bond with rigid composite components, which generates heat in this composite material that is challenging to release. Excessive heat can speed up brittleness because it damages bonds between features (mixes) such as bisphenol-A-glycidyl methacrylate (Bis-GMA) and urethane dimethacrylate (UDMA), and triathlon glycol dimethacrylate (TEGDMA). All three components are used a lot to shape large cross-linked polymer structures on composite and sealant materials (Sideridou and Achilias, 2005).

Angular reported that organic particles (minerals) in Chitosan help stabilize inorganic materials from teeth, so the density of both particles can prevent excessive heat absorption (Aguilar et al., 2019). Mineralization activity between Chitosan and this material, other than reducing heat storage, will also speed up the homogenization of teeth materials to increase stability in the adaptation process during a mechanical and physical response on teeth (Dongre, 2019).

Nano chitosan addition can prevent porosity formation and decrease roughness, preventing cracks from forming and reducing static tooth tension. It can be connected to the perfect homogenization of the mixed materials, including Chitosan, which has caused a decrease in porosity that could disturb the material integrity (Dongre, 2019). It is known that the more porosity formed, the strength of the material will decrease. The high oxygen level stored in the material caused by the amount of porosity has reduced the chemical bond in the material structure (Rouquerol et al., 1994).

The density strongly influences the strength of the material during homogenization. Besides, pH also determines the thickness of the material when homogenization occurs between mixed materials. Groups E, F, J, K, and L in Figure 4 show the highest strength level compared to other groups. Chitosan has adhesive compounds that can help increase the density of the material so that the material becomes intact and will adapt to a neutral pH oral environment.

The polishing procedure is known to affect the surface of the restorative material, such as decreasing roughness, increasing microhardness, and affecting microleakage. Surface roughness can be affected by several factors. The intrinsic factors that can affect the surface roughness of the composite resin are the type of filler, the filler's shape, the filler's size, and the filler's distribution. As is well known, the microhardness of the restorative material can also be affected by the polishing procedure (Alagha et al., 2020).

Chitosan can potentially reduce the susceptibility of the constituent ions of apatite crystals, especially phosphate. It indicates that Chitosan can increase the strength and minimize the microstrain of apatite crystals. Changes in these crystal constituents will affect apatite crystals' size and microstrain (micron strain). Which can directly affect the strength and nanostructure of dental apatite crystals (Nasution et al., 2016). However, it is still necessary to calculate X-Ray Diffraction (XRD) to determine further the degradation of chitosan composite resin in influencing its strength concerning the substitution of ions that make up the apatite crystal.

The Chitosan Nanofill composite resin pH 10 group results show a better surface than other groups, especially in the group with a pH of 3.5. One of the factors that can cause damage to the composite resin filler particle is the effect of an acidic environment, which is a low pH. In addition, the surface of the composite resin restoration can change over a period, affecting the composite resin's mechanical properties, which is described as composite resin degradation.

Results from Figure 5 explain that pH affects surface roughness, as shown in groups E, F, and K. It can be assumed that the chitosan addition and neutral pH can help the homogenization of nanohybrid and nanofiller composites better in neutral pH. So in composite filling material mixed with Chitosan or other materials, pH

becomes an indicator of consideration to obtain the perfection of the filling material.

Degradation is described as composite resin hydrolytic caused mainly by the accumulation of water or saliva (Delaviz et al., 2014). Furthermore, composite resin degradation, which is the loss or release of Bis-GMA chemical structure, can be affected by mechanical and chemical processes. From all the hypotheses that have been offered, the selection of composite resin, both nanofiller and nanohybrid with chitosan addition, will show degradation in pH 3,5, 7, and 10. The more salivary pH decreases, the degradation will increase.

IV. CONCLUSION

This research shows that nanofiller and nanohybrid composite resin will undergo degradation on salivary pH of 3,5, 7, and 10. The lower the pH, the degradation will increase. 0,1% chitosan addition on nanofiller and nanohybrid composite resin show degradation on restoration surfaces. The 0,1% chitosan addition on nanohybrid composite resin treated with pH 7 shows surface stability. However, degradation is found, but in nanofiller composite resin, 0,1% chitosan addition shows a different result, although it is still lower compared to nanohybrid composite mixed with 0,1% chitosan on surface degradation. The addition of 0,1% high molecular chitosan on both nanocomposite resins shows a better result when compared to the composite resin without adding Chitosan

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