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RESEARCH ARTICLE

EFFECT OF PEG AND PVA BINDERS ON THE CNC MILLING OF HYDROXYAPATITE FOR BIOMEDICAL APPLICATIONS

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Abstract. Hydroxyapatite (HAP) is widely used in biomedical and dental applications due to its unique properties. However, the machining process is important in giving attention to parameter materials and machines to produce a near-net shape for those implants with appropriate surface roughness. It is a challenge due to their high brittleness and hardness. In this context, understanding machining parameters and sample preparation is an essential factor in producing machinable HAP. In the present study, powder compaction with different binder content has been used to produce a sample for machining. This research prepares a sample by dry mixing, pressing, and sintering. HAP powder is granulated with water-soluble binders, Polyethylene Glycol (PEG), and Polyvinyl Alcohol (PVA) in amounts ranging from 1% to 4% by weight. PEG, as a soft binder, contributes to compaction, and PVA, as a hard binder, contributes to green strength. A CNC milling machine with an end mill cutter and constant parameters is used for machining. The samples were characterized using X-ray Diffraction (XRD) for phase identification, Scanning Electron Microscopy (SEM) for morphology, and a Surface Roughness Tester for surface roughness. XRD analysis shows that HAP with different binder ratios did not change the HAP structure. SEM analysis shows that different binder percentages create different surface properties, such as pore size and surface finish. HAP mixed with 4% PEG and 1% PVA (PEG4 PVA1) has a smooth surface finish after milling with a surface roughness (Ra) of 0.988 µm. Based on the machining outcome, it shows that a combination of binder and parameter machine can alter the surface finish and geometrical accuracy for biomedical applications.

Keywords: Hydroxyapatite, machining, binder.

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1. INTRODUCTION

Hydroxyapatite (HAP) is a main component of bone mineral and is widely used in medicine and dentistry because it is bioactive and supports body growth. Its excellent biocompatibility and ability to integrate with living tissues make it a popular choice for bone replacement in orthopaedics, dental procedures, and facial surgery [1]. Before implantation, the implant needs to be processed into a specific size and shape according to the patient's requirement [2]. It is essential to explore the machining of HAP and study the effect of different parameters (sample preparation and machining technique). Machining of HAP (bioceramic) materials is the most significant challenge due to their high brittleness and hardness. Based on this fact, parameter processing, such as binders for powder processing, was considered.

Polyethylene glycol (PEG) and polyvinyl alcohol (PVA) are water-based polymeric binders that are widely used in medical applications due to their biological compatibility and excellent performance [3]. In general, the mechanical properties of polymers depend on the temperature. In particular, the glass transition temperature, Tg, plays a significant role in determining the behaviour of the organic polymers. When the temperature is lower than 0.75 Tg (T< 0.75 Tg), the polymer is brittle. The Tg of PVA is higher than room temperature, and it forms rigid granules. This will confer higher green strength but does not contribute to efficient packing (i.e. lower green density). Consequently, PVA, as a hard binder, will not allow the deformation to take place easily. A polymer becomes viscoelastic at temperatures higher than Tg (T>Tg). Thus, T> Tg is suitable for compaction processes because the soft binder deforms easily. The Tg of the PEG binder is around -20 °C, whereas for PVA the Tg is > 60 °C. Thus, the soft PEG binder would provide a higher compact density but a lower green strength, which may not be adequate for large parts or parts requiring machining in the green state [4]. In order to maximise both contradictory effects of PVA and PEG, an ideal binder system would be one where both binders are mixed together [5].

Conventional bioceramic processing mainly involves pressing, slip or gel casting that uses a molding process limited to small and simple part shapes. Machining offers better interest that is able to fabricate tailored bioceramic implant that fits the shape of the implant. Machining processes like milling are commonly used to fabricate bioceramic materials like hydroxyapatite (HAP) for bone implants. These methods enable precise shaping of the material, ensuring high accuracy and superior surface finishes. According to Ramesh and Bhuvaneswari [6], surface roughness in milling processes can be controlled by optimising several machining parameters, such as feed rate, cutting speed, tool material, and depth of cut.

In creating HAP-based implants, surface roughness is a critical factor directly impacting the implant's functionality by optimising its integration with bone tissue. It can be seen that controlling the roughness enables the enhancement of: (i) osteointegration via promoting osteoblast adhesion and proliferation, (ii) increasing protein adsorption essential for cellular interactions, and (iii) creating an optimised microenvironment conducive to bone regeneration. In addition, surface roughness influences the remodelling process of the surrounding bone, improving implant stability and providing long-term performance. Nevertheless, excessive roughness may introduce risks, such as forming fibrous tissue or inflammatory reactions, highlighting the importance of balance in surface design [7]. Therefore, this study aims to elucidate the effect of surface finishing via the machining process on the sintered sample from the powder compaction at different binder compositions. It was revealed that the smooth surface roughness properties were induced by lower PVA content. It can be concluded that the binder composition has a significant effect on the surface finishing after CNC milling on sintered HAP.

2. MATERIALS AND METHODS

2.1 Material Sample Preparation

Four samples of hydroxyapatite powder (Sigma-Aldrich, #04238), measuring 102 mm in length, 12 mm in width, and 10 mm in thickness, were prepared for compaction and sintering. Each sample incorporated varying percentages of polyethylene glycol (PEG) and polyvinyl alcohol (PVA) as binders (Table 1). The compaction process was conducted under a load of 10 tons for 5 minutes, forming green bodies. Subsequently, these green bodies underwent sintering at a temperature of 1200 °C for 2 hours [8,9].

Table 1: Samples of HAP powders mixed with PEG and PVA percentage by weight

Sample	PEG %	PVA %
PEG1 PVA4	1	4
PEG2 PVA3	2	3
PEG3 PVA2	3	2
PEG4 PVA1	4	1

2.2 Machining Parameters

CNC milling machine (MAZAK NEXUS 410A-II, Yamazaki Mazak, Japan) uses a spindle with cutting tools to remove material from a workpiece. Milling was performed using a four-flute end mill cutter with a diameter of 6 mm. Cutting parameters, including speed, feed rate, and depth of cut, are detailed in Table 2. The parameters for milling were chosen after many trials were done.

Table 2: Cutting parameter for machining

Cutting Speed, *V*	Feed Rate, *f*	Depth of Cut, *d*
(27 *m/min*)	(40 *mm/rev*)	(0.1 *mm*)

2.3 Phase Identification

The HAP sample's chemical composition was characterised using a high-resolution Bruker Advance D8 XRD diffractometer, and the HAP sample powder's phase composition and crystalline structure were determined. X-ray diffraction in the Bragg-Brentano configuration using Cu-Kα (λ = 1.5405 A) radiation at the specific current (40 mA) and voltage (40 kV). The step counting method was used to collect intensity data in the range 2θ between 10° to 90°, with a step of 0.02° and a time of 0.5 s to examine the crystallinity of the HAP.

2.4 Surface Morphology

Scanning Electron Microscopy (SEM SU1510, Hitachi, Japan) was used to investigate the morphological properties of hydroxyapatite (HAP) samples mixed with various binders. The HAP samples were coated with a conductive material before imaging under high vacuum conditions to prevent charging effects, which can degrade the quality of the magnified images.

2.5 Surface Roughness Test

A surface roughness tester (SJ-400, Mitutoyo, Japan) was used to determine a material's surface texture or surface roughness. The measurement was done by evaluating the texture of the surface through physical methods. The average roughness, R_a, represents the arithmetic mean of deviations from the mean line of a surface profile.

3. RESULTS AND DISCUSSION

3.1 Surface Morphology

Figure 1 shows an SEM image of HAP powder at low magnification with a small size of the particle beside the granule. Before mixing with binders, the pure HAP powder samples were sieved to ensure a particle in the acceptable range of 2 µm to 10 µm. The image, captured at low magnification, highlights the variability in particle size. As indicated in Figure 1, some granules range from 25 µm to 63 µm. Figure 2, at a higher magnification, provides a clearer view of granules below 63 µm. These granules were produced after the sieving process. The target granulation for the HAP is below 63 µm to achieve high-density compaction.

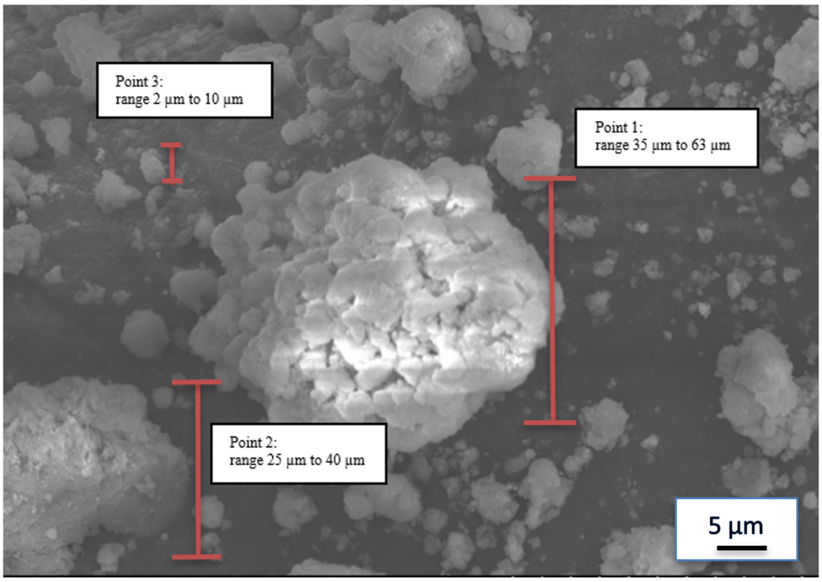

Figure 1: SEM micrograph of HAP powder and granules indicates differences and variations in size

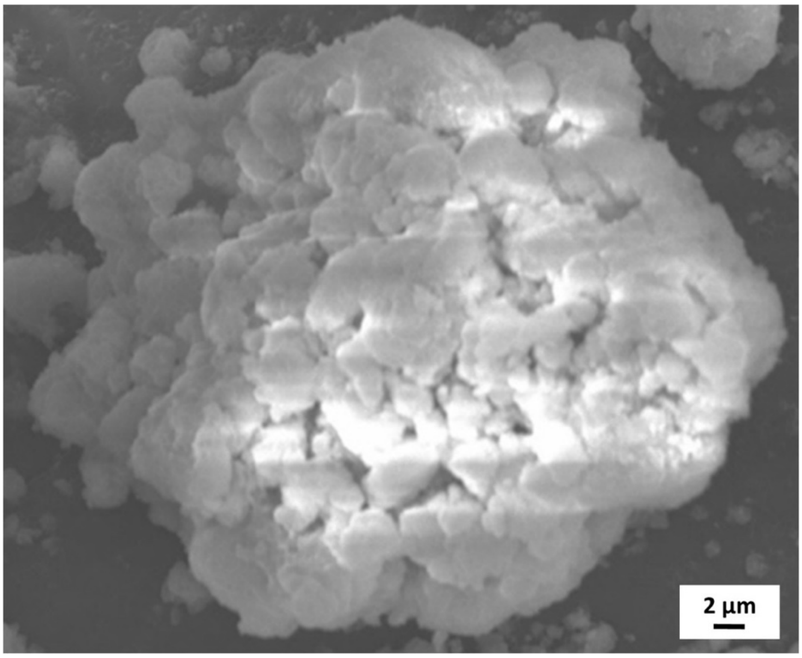

Figure 2: SEM micrograph of the HAP granule at high magnification with a porous structure

The fine particle is essential to produce a fine surface finish after machining. PVA and PEG combinations influence the finished surface, especially for green body machining. The machining process will be done along the granule boundary or through the granule [10]. After sintering, machining is also influenced by the combination of the binder and the size of the granules. The machining process will break through the granule or through the granule boundary. This is due to the compaction process, binder, and granule size. PEG will contribute to good compaction, and machining will break through the granule, not the granule boundary. A small granule size will contribute to the smoothness of the surface after machining. It is not much different from breaking through granule or granule boundaries.

3.2 Phase Identification

X-ray diffraction analysis of the samples revealed sharp, well-defined peaks, indicating a high degree of crystallinity. The XRD patterns confirmed the presence of nano-crystalline hydroxyapatite ($Ca_5(PO_4)_3(OH)$) in all samples. The XRD pattern of the raw HAP powder (Figure 3) displays characteristic peaks, marked in blue, corresponding to the HAP phase. The pattern shows a rise in intensity starting at 25°, with the most prominent peak at 33°. The presence of these peaks confirms the structure of HAP. Phase analysis was conducted by using JCPDS card no. 74-0565 [11,12] for HAP, which covers a 2θ range of 10.835-81.704 degrees, further confirmed the presence of all significant HAP peaks in the powder.

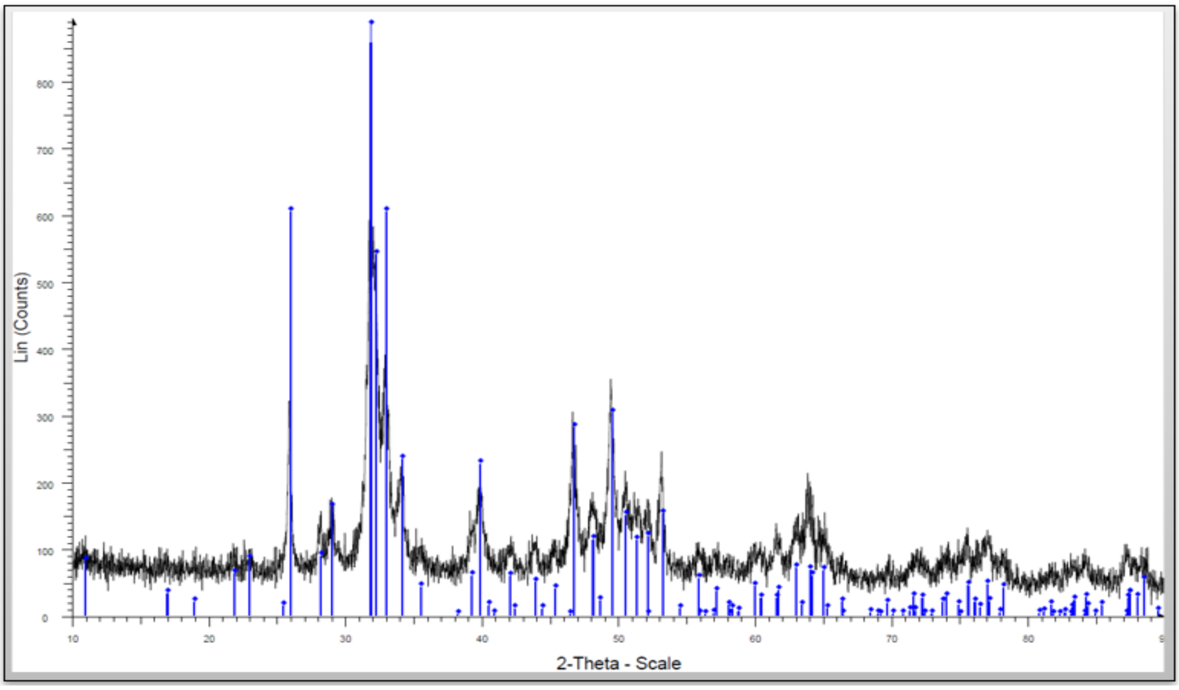

Figure 3: The XRD pattern of HAP powder by referring to JCPDS card no. 74-0565

3.3 Surface Roughness Test

Table 3 and Figure 4 show data on surface roughness (Ra) values before and after machining for different binder compositions (combinations of PEG and PVA). Figure 4 shows the SEM micrograph of the samples before or after machining. Sample PEG1 PVA4 and Sample PEG2 PVA3 show the Ra values increased after machining, indicating that the process caused surface roughening. PVA contribute to less compaction and low strength after sintering [10]. It will affect the surface roughness after machining. For Sample PEG3 PVA2 and Sample PEG4 PVA1, the Ra values decreased after machining, implying that machining smoothed the surface. Samples with higher PVA content

(PEG1 PVA4) started with relatively low initial roughness but increased after machining. Samples with higher PEG content (PEG4 PVA1) began with low roughness and became smoother after machining.

Table 3: The surface roughness values before and after machining

Sample	Before machining R_a (µm)	After machining R_a (µm)
PEG1 PVA4	1.412	1.543
PEG2 PVA3	1.262	1.997
PEG3 PVA2	2.628	2.006
PEG4 PVA1	1.054	0.988

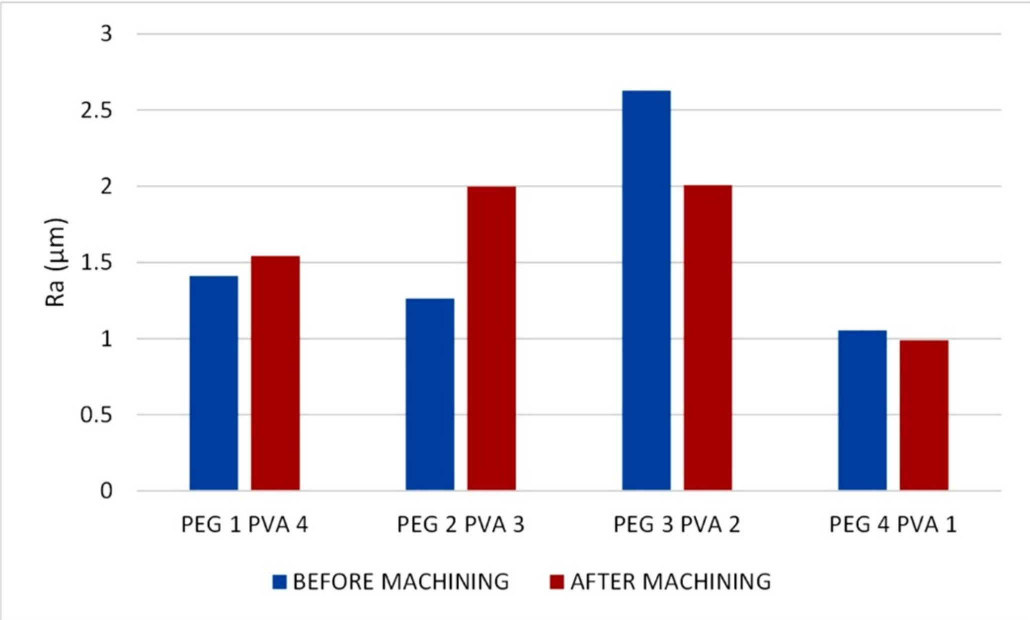

Figure 4: The surface roughness Ra (µm) of all the samples before and after machining

Figure 5 shows the SEM micrographs of the surface before and after machining. It clearly indicates surface roughness increases with the increases of the PVA and a small amount of the PEG. PVA and PEG play a prominent role in the surface finish after machining. Due to the Tg of PVA being higher than room temperature, it will form rigid granules. This will not contribute to efficient packing (lower density), and sintered strength will be decreased. The surface roughness increases the consequences of the strength. The Tg of the PEG binder is around -20 °C, whereas for PVA the Tg is > 60 °C. Thus, the soft PEG binder would provide a higher compact density. It will contribute to the high strength and decrease the surface roughness [4].

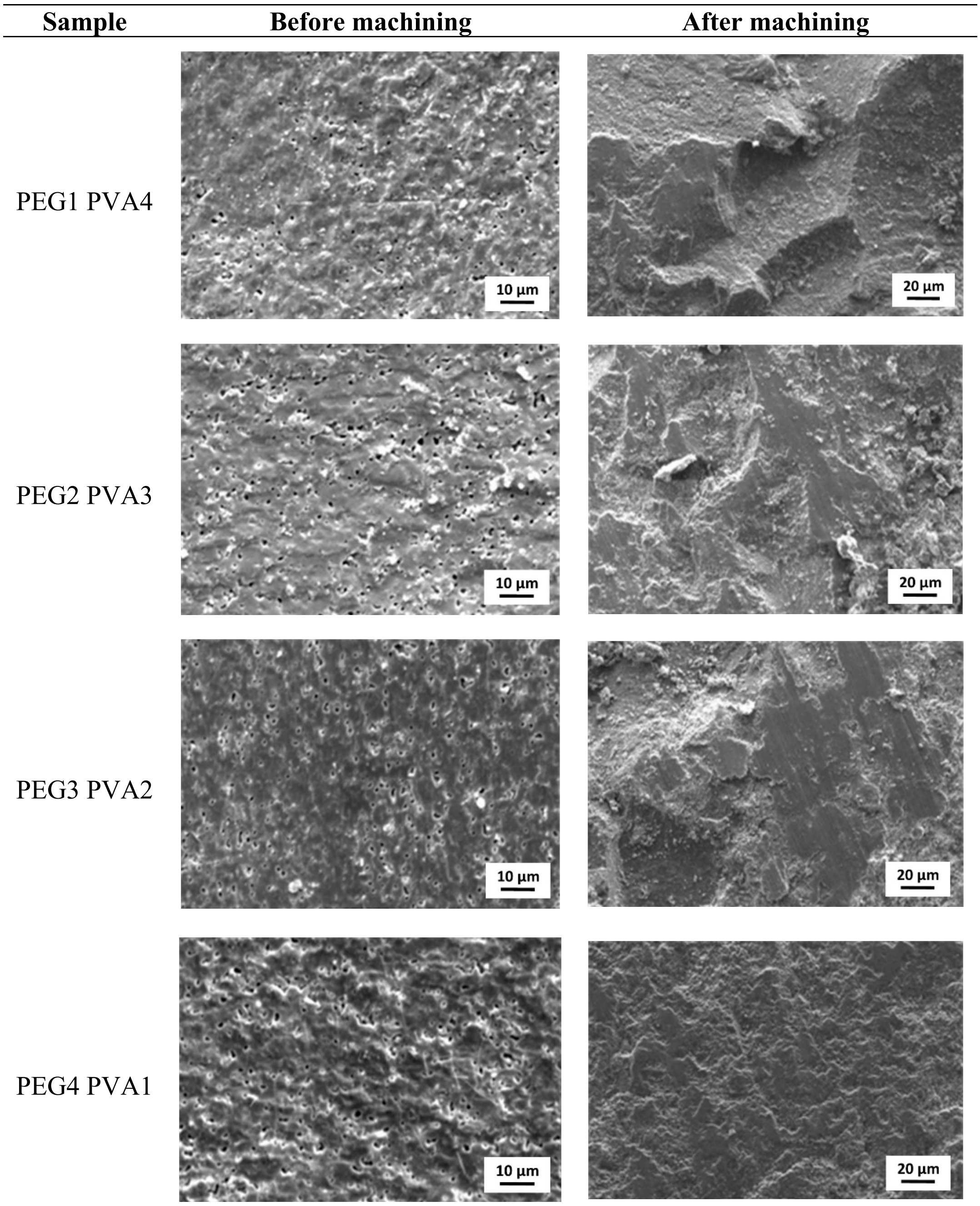

Figure 5: SEM micrographs of the surface morphology of the sample with different combinations of PEG and PVA binders before and after machining

4. CONCLUSIONS

Machining of hydroxyapatite (HAP) by using CNC milling is a new application of manufacturing in biomedical engineering. Milling operations and powder processing offer fast processing time, high efficiency and good surface finish. This study demonstrates that binder composition significantly affects the surface quality of sintered HAP after machining. The ratio between PEG and PVA in the powder compaction could determine the mechanical response during machining. Increased PEG may result in smoother finishes due to its high density and compaction, while higher PVA may increase the porosity, leading to rougher outcomes. The combination of binder samples PEG4 PVA1 produced a machined smooth surface.

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Author Contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of Conflict of Interest

The authors have no disclosures to declare.

Compliance with Ethical Standards

The work is compliant with ethical standards.

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