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Formaldehyde and TVOC Emission of Bio-Composites with Attached Fancy Veneer*[1]

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ABSTRACT

This study assesses the formaldehyde and TVOC emissions from bio-composites with attached fancy veneer manufactured using wood flour and polypropylene (PP) measured using the Field and Laboratory Emission Cell (FLEC) method and 20 L small chamber method. To determine and compare the effects of the adhesive, samples were prepared with different manufacturing methods. In the FLEC result, the formaldehyde emission level of the bio-composites with attached veneer by hot-press was the lowest than pure bio-composite and bio-composite attached veneer using adhesive. The TVOC emission levels are similar to the formaldehyde emission. The TVOC emission level is very low in all of the samples except fancy veneer that is attached with bio-composites using adhesive. The TVOC emission varies depending on how attaching fancy veneer. The results of the 20 L small chamber method were very similar to those obtained with the FLEC, but the correlation was not perfect. However, the FLEC method requires a shorter time than the 20 L small chamber method to measure the formaldehyde and TVOC emissions. The internal bonding strength exceeded the minimum value of 0.4 N/mm^2 specified by the KS standard. All of the bio-composites with attached veneer satisfied the KS standard.

Keywords : formaldehyde emission, TVOC, 20 L small chamber, field and laboratory emission cell (FLEC), bio-composites

1. INTRODUCTION

In recent years, bio-composites have increasingly been used for household furniture, car interiors and various housing construction materials. They combine the favorable performance and low cost attributes of wood and plastics. In recent years, their utilization has developed rapidly, especially in Europe and the American continent, because of the growing recognition worldwide of the need to reduce global environmental pollution (Demir *et al.*, 2006; Kim *et al.*, 2005; Arbelaiz *et al.*, 2005).

Many building interior materials, which were

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previously made from natural resources, were substituted with artificial resources such as PVC, PS and PP as the industry developed. Many building interior materials emit volatile organic compounds (VOCs) which affect human health (Kim and Kim, 2005). Formaldehyde is a suspected human carcinogen that is known to be released from wood-based composites used in housing construction. Particleboard (PB), hardwood plywood, medium density fiberboard (MDF) and panels are made with urea-formaldehyde (UF) resin and softwood plywood and oriented strand board are made with phenol-formaldehyde resin, owing to the emission of formaldehyde and the associated risk to human health (Gustaffson, 1992). For the sake of human health, various countries have already, or are about to, impose regulations limiting the emission of formaldehyde from building interior materials and from the materials used for the manufacture of furniture and fittings (Kavvouras *et al.*, 1998).

The standard test method for measuring emissions from wood-based composite panels is to use a chamber. In Europe, the standard test chamber method (ISO 16000-10, 2004) uses chambers with three different sizes, ≥ 12 m^3, 1 m^3 and 0.225 m^3, for the determination of formaldehyde emissions. However, measuring the formaldehyde emission in a chamber takes time and requires specialized and expensive equipment (e.g. the chamber itself, HPLC and GC/MS).

The field and laboratory emission cell (FLEC) is a small portable device used for the determination of volatile organic compounds (VOCs) and semi volatile organic compounds (SVOCs) emitted from indoor materials/products (prENV 13419-2, 1998). The FLEC differs from the 20 L small chamber in the sense that it has one open wall or face which is placed onto the planar surface of the material under test such that the material surface effectively becomes part of the emission cell. The FLEC can be used for materials/products with a planar surface. Typical applications include flooring materials (wood-block, carpeting, vinyl flooring, etc.), wood-based panels, sealants, textiles, adhesives, paint, coatings, plastic beads, concrete leveling compounds, wallpaper, plastic sheeting and structural foams. The cell of the FLEC can be placed directly onto rigid products/surfaces and is held in place by the weight of the cell itself compressing the sealing gasket or o-ring. The air inlet of the emission cell is designed such that the flow of air is directed over the entire surface of the test specimen before exiting the cell through a central exhaust point.

The objective of this study was to investigate the emission of formaldehyde and TVOC from wood-based composites with fancy veneer using the chamber and FLEC methods. The 20 L small chamber and FLEC were used to measure TVOC and formaldehyde emissions from wood-based composite panels. The TVOC and formaldehyde emission was compared in two different manufacturing methods of attaching bio-composites to veneer with or without adhesive.

2. EXPERIMENTAL

2.1. Materials

In the present study, polypropylene (PP) was used as the matrix polymer. To make a uniform blend of the matrix polymer with wood flour, PP pellets with a melt flow index (MFI) of 12 (230°C/2,160 g) and a density of 0.91 g/cm^3 were used. The PP polymer was supplied by LG Chem Ltd. Wood flour obtained from Saron Filler Co. was used as the reinforcement material for the bio-composite. The particle size of the wood flour was 100 μm. Modified Ethylene-Vinyl Acetate (EVA) for the adhesive which is

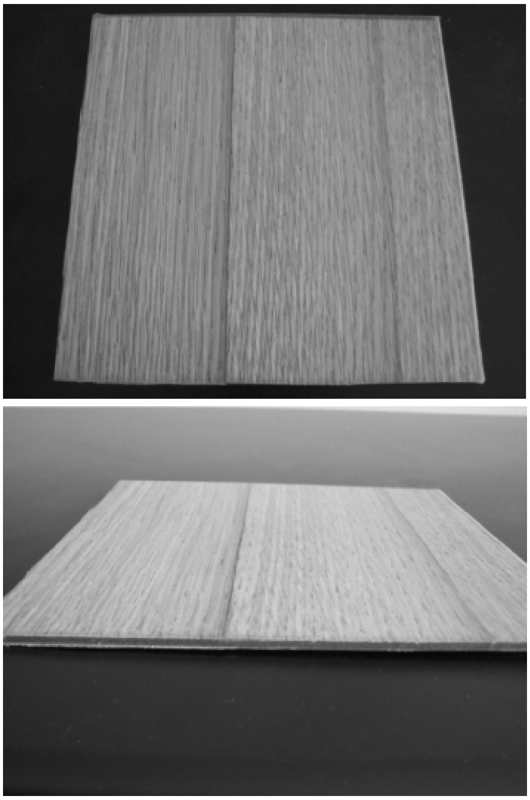


Fig. 1. Structure of bio-composites with fancy veneer.

low TOVC and formaldehyde emission grade than other normal adhesive was donated by Okong Co. Fancy veneer with a thickness of 0.5 mm was attached to the bio-composite. The fancy veneer was dried at 80°C for 4 h in an oven.

2.2. Sample Preparation

The bio-composites of wood flour/PP were prepared using a twin screw extruder machine which makes uniform blends of the wood flour with the polypropylene pellets. The bio-composites in pellet form after extruding were pressed by hot plates. The bio-composites were transferred into a hot press, wherein they were pressed under a load of 50 kgf/cm^2 at 200°C for 5 minutes. At this time, the fancy veneer was attached directly by the hot-press. Note that in the blending of the wood flour and matrix PP, the weight ratios of PP to wood flour were 100 : 0, 90 : 10, 80 : 20, 70 : 30, 60 : 40. The size of samples for 20 L small chamber test was 150 × 150 × 3 mm length, width and depth, respectively. For the FLEC test, the size of samples was 200 × 200 × 3 mm. After the manufacturing of the bio-composite with fancy veneer, the specimens were wrapped with aluminum foil. The structure of the bio-composites with fancy veneer is shown in Fig. 1.

2.3. Field and Laboratory Emission Cell

The TVOC and formaldehyde emissions from the surface of the bio-composites were measured by the Field and Laboratory Emission Cell (FLEC) method. The test conditions and structures are shown in Table 1 (Kim *et al*., 2007) and Fig. 2, respectively. Before the start of the test, the inner surface of the emission cell of the FLEC was washed with methanol. After cleaning the cell, the pure air used as a carrier gas was supplied for approximately 24 hours to clean the cell completely. The sampling conditions are shown in Table 2. Throughout the measurements, the air temperature and relative humidity inside the test chamber were kept constant at 23 ± 2°C and 50 ± 5%, respectively. The sample gas was supplied by a Tenax-TA and 2,4-DNPH (dinitrophenyl hydrazine) cartridge half an hour after the installation of the samples.

2.4. Chamber Method : 20 L Small Chamber

A 20 L small chamber was developed in

Table 1. The properties of the FLEC method

Test condition	FLEC
Sample area	0.0177 m^2
Volume	0.035 L
Loading factor (area of sample/Volume, m^2/m^3)	505.71
Air change rate (h^{-1})	428.57
Air supply (L/min)	250
Equilibration time	sampling after 15-30 minutes
Temperature, humidity	23 ± 2.0°C , 50 ± 5%
Compounds, sampling flow and total sampling	High purity air
Inlet air	High purity air
Background concentration	VOC : 2 $\mu g/m^3$, TVOC : 20 $\mu g/m^3$
Cleaning process	Vacuum oven or cleaning by methylene then high purity air for 1 day
Analysis method	GC/MS for VOC, HPLC for formaldehyde

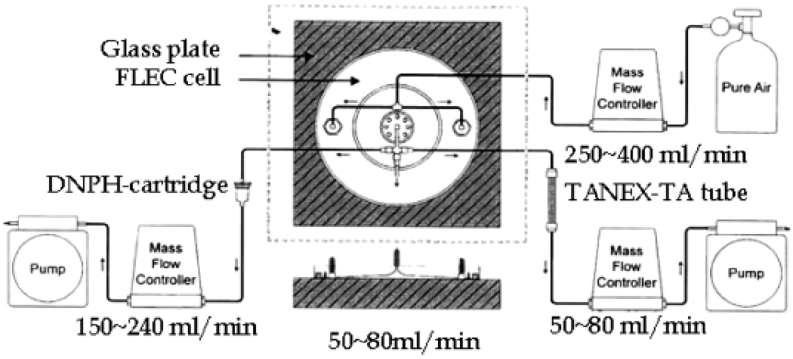


Fig. 2. Schematic of the FLEC (uchiyama *et al*., 2001).

Japan and its performance was in compliance with ASTM (1996), ECA reports (1995) and ENV 13419-1 (1999). The 20 L small chamber is made of stainless steel and is attached to an air control unit. In addition to the 20 L small chamber, four other chambers with volumes of 45, 100, 150 and 180 L also exist, however the 20 L chamber was used in the present study, because it has been standardized in Korea. The air control system has an air supplying unit, a humidifier, pumps and a ventilation system to purify the air. Fig. 3 shows a schematic diagram of the 20 L small chamber structure. A stainless steel sealed box was used to prevent the cut edge effect of the test specimens, by allowing the VOCs or formaldehyde emissions to be measured only from their front surface. The total surface area of the specimens was 0.044 m^2 and the loading was 2.2 m^2/m^3.

Before setting up the chamber and sealed box-

Table 2. Sampling conditions in the FLEC method

	Formaldehyde types	VOCs
Sampler	2,4-DNPH cartridge (Supelco, USA)	Tenax-TA (Supelco, USA)
Air flow rate	167 mL/min	53 mL/min
Total volume	5 L	1.6 L

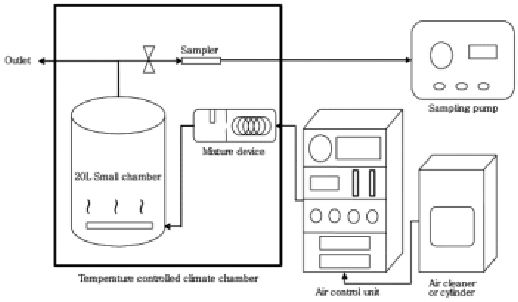


Fig. 3. Schematic diagram of 20 L small chamber.

es, they were washed with dilute water and baked out using an oven at 260°C for 20 min to eliminate any pollutants from the chamber itself. The 20 L small chamber system was supplied with purified and humidified air at a given ventilation rate. The temperature and relative humidity inside the chamber were kept constant. The test conditions are shown in Table 3.

2.5. Internal Bonding Strength Test

Specimens of the bio-composites with fancy veneer with sizes of 50 × 50 mm^2 were used to measure the internal bonding strength as determined by the interfacial adhesion between the bio-composite and fancy veneer according to KS F 3106. To obtain a uniform test result, we used epoxy adhesive to attach the equipment on the fancy veneer. The internal bonding strength was determined using a Universal Testing Machine (UTM, Zwick Co.) at 23 ± 2°C and 50 ± 5% RH. The test speed was 2 mm/min. Each value represents the average of five measurements.

Table 3. Test conditions in the 20 L small chamber method

Variables	Condition
Chamber volume	20 L
Sample size	0.0432 m^2 (0.147 m × 0.147 m × 2)
Air flow rate	0.01 m^3/h
Ventilation rate	0.5 /h
Sampling loading factor	0.4 m^2/m^3
Temperature	23 ± 1°C
Relative humidity	50 ± 5%

3. RESULTS and DISCUSSION

3.1. Field and Laboratory Emission Cell Test Method: Formaldehyde and TVOC Emission Levels

These days, bio-composites are studied by many research workers in an attempt to overcome various environmental problems. These bio-composites have great potential to contribute to the reduction of environmental pollution. Adhesives used to be used to attach the fancy veneer to the MDF, PB and so on. However, adhesive has a very high emission rate of formaldehyde and TVOCs. Therefore, we tried to attach the fancy veneer on the bio-composites without adhesives. Also, to increase the amount of wood material, which is a by-product of wood processing, in the bio-composites, we fabricated wood flour filled bio-composites.

The formaldehyde emission levels are shown in Fig. 4. The results show that PP has a lower emission level than the other samples. However, the formaldehyde emission level of veneer is higher than those of the other materials.

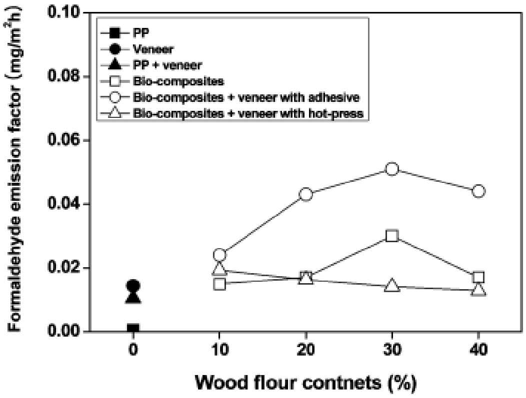


Fig. 4. Formaldehyde emission levels in the FLEC as a function of the sample type.

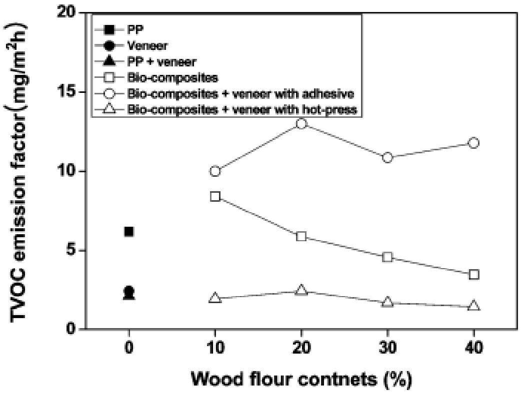


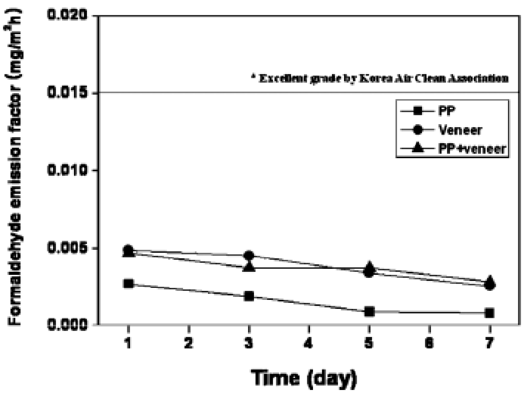
Fig. 5. TVOC emission results in the FLEC as a function of the sample type.

Therefore veneer, rather than wood flour, is the main factor contributing to the emission. Overall, the bio-composites with fancy veneer have much lower formaldehyde emission levels than the other interior materials, such as medium density fiberboard (MDF), particleboard (PB), engineered flooring and laminate flooring (Kim *et al.*, 2006a; Kim *et al.*, 2006b). In the case of the bio-composites with fancy veneer by hot-press, the formaldehyde emission level decreases with increasing wood flour contents. However, the difference is very small. Another important point is that formaldehyde emission level of bio-composites with fancy veneer varies with manufacturing methods. Bio-composites with fancy veneer by adhesive have very high emission level than pure bio-composites or hot-pressed bio-composites with fancy veneer. Therefore adhesive is the main factor contributing to the formaldehyde emission. As a result, bio-composites attached with fancy veneer made by hot-press is very effective in emission reduction.

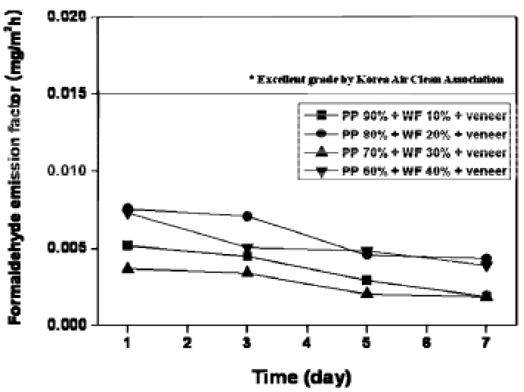
The TVOC emission levels are similar to formaldehyde emission. The results are illustrated in Fig. 5. The TVOC emission level is very low in all of the samples except bio-composite attached with fancy veneer using adhesive. According to the emission results, adhesive is a main factor for TVOC emission. However, veneer, itself, prevents the emission of TVOC. As a result, the surface of the bio-composites which is made of veneer by hot-press has a lot lower emission level than bio-composites attached veneer using adhesive. Thus, from the point of view of the formaldehyde and TVOC emission levels, the bio-composites with fancy veneer by hot-press are good materials.

3.2. Twenty Liter Small Chamber Method : Formaldehyde and TVOC

The 20 L chamber method is generally used for the evaluation of TVOC and formaldehyde emissions in Korea. Fig. 6 shows the formaldehyde emissions which were detected 1, 3, 5 and 7 days after the preparation of the sample. According to these results, the formaldehyde emissions of all of the samples decreased over time. In Fig. 6(a), PP has a lower emission of formaldehyde than the other materials. However, the formaldehyde emission of veneer is higher

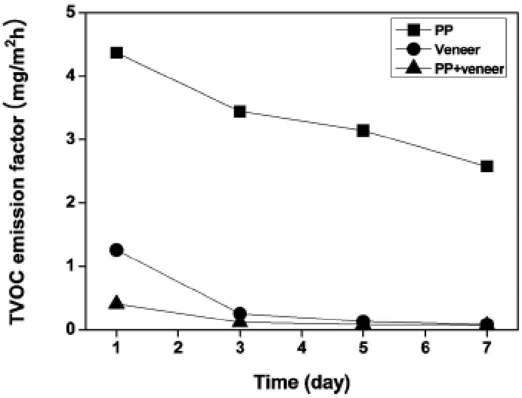


(a)

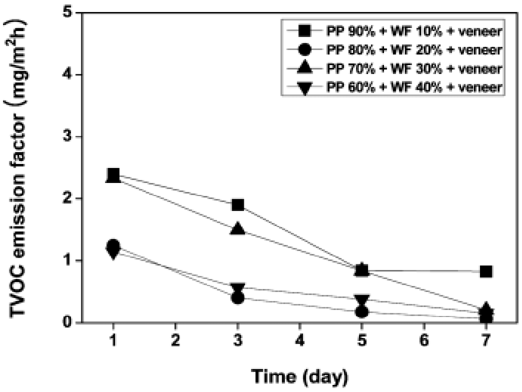


(b)

Fig. 6. Formaldehyde emission levels in the 20 L chamber as a function of time and sample type.



(a)



(b)

Fig. 7. TVOC emission results in the 20 L chamber as a function of time and sample type.

than that of PP. The emission level of PP with attached veneer is similar that of the veneer itself. This means that veneer, itself, emits more formaldehyde than PP. Fig. 6(b) shows the emission of the bio-composite with fancy veneer as a function of the wood flour contents. The results show that the formaldehyde emission level is very weakly correlated with the wood flour contents. However, it seems that the veneer affects the formaldehyde emission of the bio-composites. However, in all cases, formaldehyde emission factor after 7 days was under the 'Excellent' grade as defined by Korea Air Cleaning Association (KACA). The TVOC emission level is shown in Fig. 7. PP has the highest TVOC emission level of about 2.577 mg/m^{2}h and the emission levels of veneer and PP with fancy veneer are 0.084 and 0.772, respectively. The TVOC emission of the bio-composites with fancy veneer is shown in Fig. 7(b). The emission levels of the 10, 20, 30 and 40 wood flour wt.%, filled bio-composites are 0.828, 0.065, 0.206 and 0.156, respectively. TVOC emission factor was under the 'Excellent' grade which range is less than 0.10. 'Superior' grade is ranged from 0.10 to 0.20.

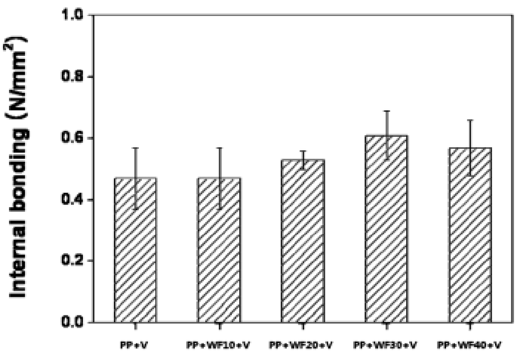


Fig. 8. Internal bonding strength of bio-composites with fancy veneer (V; veneer, WF10; 20 wt.% wood, WF20; 20 wt.%, WF30; 30 wt.%, WF40; 40 wt.% wood flour contents).

And 'good' grade is ranged from 0.20 to 0.40. In some case, the bio-composites were under the 'Excellent' or 'superior' or 'good' grade. According to the results, the formaldehyde and TVOC emissions are only slightly influenced by the wood flour content. For example, PP has a very low formaldehyde emission, but very high TVOC emission. PP with fancy veneer has similar emission levels to PP.

3.3. Internal Bonding Strength

To evaluation the internal bonding strength, we chose bio-composites attached fancy veneer without adhesive that low formaldehyde and TVOC emissions materials. Fancy veneer was directly attached to the bio-composites. This is a very simple method of combining these two materials. The evaluation of the internal bonding strength between the bio-composite and veneer is very important to measure the interfacial bonding. The internal bonding strengths of the bio-composites with fancy veneer are illustrated in Fig. 8. Note that the internal bonding strength tended to increase as the wood flour contents increased. This means that the internal bonding strength depends on the wood flour contents. We estimated that hydrogen bonds were formed between the wood flour and fancy veneer as they are hydrophilic materials. As the wood flour contents were increased, the amount of wood flour visible on the surface of the bio-composites increased. The internal bonding strength of the wood flour filled bio-composite is higher than that of the PP plate with veneer. However, an internal bonding strength of 0.4 N/mm^2 is required to satisfy KS F 3106. The internal bonding strength of all of the specimens exceeded 0.4 N/mm^2. Therefore, the bio-composites with fancy veneer can be used as the interior materials of structures from the standpoint of their internal bonding strength.

4. CONCLUSION

In Korea, standard test methods have been developed to determine the formaldehyde and TVOC emission levels from building products. The 20 L small chamber test was developed for use as an emission test in Japan. However, this method requires a long testing time of 7 days. On the other hands, the FLEC has been successfully applied as a test method for formaldehyde and TVOC emissions with the advantage of a shorter test time and much simpler equipment.

The wood flour reinforced polypropylene bio-composites with fancy veneer were fabricated using the usual process followed by hot press compression molding. Hot-press compression molding was found to be effective for uniformly attaching the fancy veneer to the bio-composites. The effect of the wood flour loading content and fancy veneer on the formaldehyde and TVOC emission levels was investigated by the FLEC method and 20 L small chamber method. It was concluded that the fancy veneer emits more formaldehyde than pure PP and the bio-composites with veneer. And we concluded that the fancy veneer prevent the emission of the formaldehyde and TVOC emissions. Manufacturing method using hot-press has good effect on reducing the formaldehyde and TVOC emissions. The internal bonding strength of materials used for interior construction must exceed 0.4 N/mm^2 according to the KS standard. The internal bonding strengths of the bio-composites with attached veneer having wood flour contents of 10, 20, 30 and 40 wt.% were 0.47, 0.53, 0.61 and 0.57, respectively.

All of the bio-composites with veneer have satisfactory values of the formaldehyde emission, TVOC emission and internal bonding strength. However, further tests need to be conducted before using the bio-composites with fancy veneer as building construction materials.

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