Application of Hydrogels in Textile Industry

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ABSTRACT

Hydrogels are cross-linked, three-dimensional (3D) networks of polymers that can absorb and hold a lot of water. Loosely cross-linked hydrophilic polymers known as superabsorbent polymers (SAP) are capable of swelling, absorbing, and holding huge volumes of water or other biological fluids. Hydrogels are classified on various basis i.e. source, configuration, polymeric composition, cross linking, physical state, morphological and charge. Hydrogels have several properties such as mechanical, stimuli effect, self-healing, biodegradability. Hydrogels are used for drug delivery systems, tissue engineering, wound healing, gene delivery, electrical conducting, purification of water, agricultural sector, decontamination of organic waste, artificial skin. Hydrogel materials have various applications in biomedical and engineering applications, from wastewater treatment and soft robotics to regenerative medicine, due to their customizable characteristics and adaptable production techniques in textile industry. Lamination of hydrogel onto the fabric makes it fire retardant. Heavy metal removal/Dye removal from aqueous solutions is another application for smart Polymeric Hydrogel (PHG) materials. The global hydrogel market size is expected to be worth around US$ 37.98 billion by 2030 from at US$ 22.45 billion in 2021, growing at a CAGR of 6% during the forecast period 2022 to 2030.

INTRODUCTION

New materials with distinctive features are being introduced as a result of ongoing advancements in polymer research. Hydrogels are one of those that have attracted the attention of researchers. This advancement has opened up new methods for making hydrogels and produced new, more desirable qualities. Hydrogels are water-absorbing polymeric networks and are developed to mimic many of the inherent properties of soft tissue. The first reported hydrogel can be traced back to 1960, when Wichterle and Lim synthesized poly hydroxyethyl methacrylate (PHEMA) and utilized it in the contact lens industry with the ability of imbibing moisture while asserting its network structure, demonstrating the modern hydrogel.

According to E. M. Ahmed "Hydrogel is a water-swollen and cross-linked polymeric network, produced by the simple reaction of one or more monomer/polymer/cross-linker units." It is a polymeric material that exhibits the ability to swell and retain a large amount of water in its three-dimensional network, however, will not dissolve in water. **(Ahmed *et al.*2015)**

A new class of Polymeric Hydrogels (PHGs) reported by US as it is loosely cross-linked hydrophilic polymers that can swell, absorb and retain a large volume of water or other biological fluids. **(Laftah *et al*. 2011)**

Gels and Hydrogels are often confused as same term but they are different. Gels are defined as a substantially dilute cross-linked system and these are categorized, mainly as weak or strong depending on their flow behaviour in steady-state. Gels are materials composed of a three-dimensional crosslinked polymer or colloidal network immersed in a fluid. They are usually soft and weak, but can be made hard and tough. Whereas Hydrogels are hydrophilic polymeric network of three-dimensionally cross-linked structures achieved from a class of natural/synthetic polymeric materials that absorbs a substantial amount of water. Hydrogels are gels that have water as their main constituent. **(Gulrez *et. al.*2010)**

Absorbent materials, usually made of hydrophilic natural or synthetic polymers, and is crosslinked hence having a 3-dimensional structure. It swells in the presence of water and shrink in the absence of water. In dried Hydrogel, the swollen network of the hydrogel is collapsed, hence is smaller in size and is called Xerogel. It is tissue like polymer that mimic many of the inherent properties of soft tissue. It is insoluble and retains its shape while swelling and deswelling according to its environment. (Figure 1).

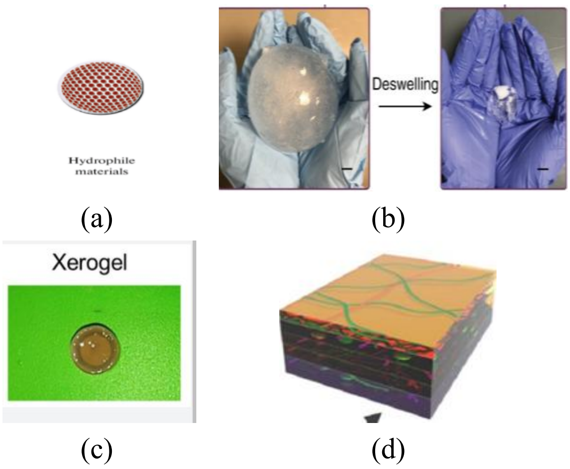

Figure 1: (a) Hydrophilic material of hydrogel, (b) Swelling and deswelling of hydrogel. (c) Xerogel and (d) Hydrogel mimicking tissue

1. Classification of Hydrogels

Classification of hydrogels can be done on various basis according to the end use or requirements. The classification can be done as follows:

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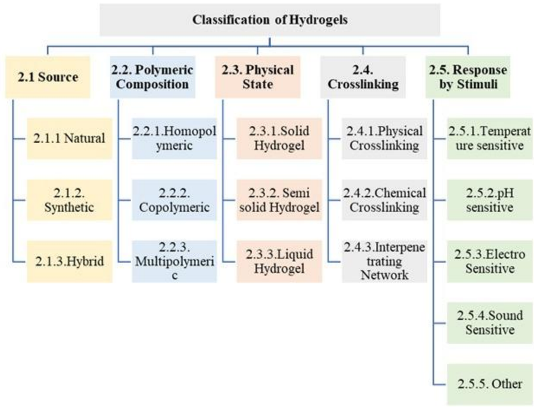
1.1 According to **Ahmed (2015) classification on the basis of Source**



1.2 Classification on the basis of Polymeric Structure (Figure 3c):

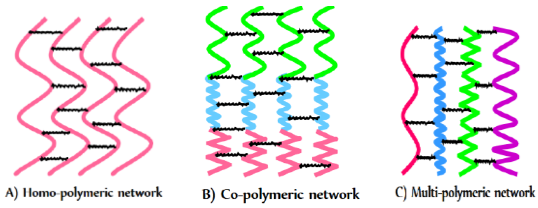


Figure 3: Structure of a) Homopolymeric, b) Copolymeric and c) Multipolymeric networks

1.3 Classification on the basis of Physical State:

1.3.1 Solid: Solid hydrogels have strong cross-linked network structure with ionic or covalent cross-linkers and they are solid in nature at room temperature, but can swell in water.

1.3.2 Semi-solid: Semisolid hydrogels have strong adhesive interactions with interfacial (van der Waals, hydrogen bonds and electrostatic) forces and soft tissue networks.

1.3.3 Liquid: Liquid hydrogels Liquid hydrogels, at the room temperature, are liquid in phase, but at a specific temperature, they have a soft tissue-like elastic phase with good functionality. **(Sharma & Tiwari 2020)**

1.4 Classification on the basis of Cross linking:

1.4.1 Physical Cross linking: In physical cross linking, bonds are joined by secondary forces i.e. non covalent bonds.

1.4.2 Freeze-thawing: Physical cross-linking can be achieved by using repetitive freeze-thaw cycles. This mechanism involves the formation of microcrystals in the structure due to freezing and thawing. These hydrogels are inter-connected by hydrogen bonding, exhibit more porous, spongy, rubbery and higher elastic properties. Poly vinyl alcohol (PVA) hydrogels are made by this method. (Figure 4)

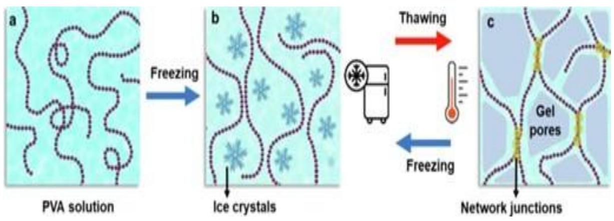


Figure 4: Freeze thawing method

a. Ionic interaction b. Hydrogen Bonding

1.4.3 Chemical Crosslinking: In chemically cross-linked hydrogels, cross-linkers, such as glutaraldehyde, epichlorohydrin, adipic acid dihydrazide and polyaldehydes, etc., are widely used to obtain cross-linked hydrogel networks based on synthetic and natural polymers.

1.4.4 Interpenetrating Network: Crosslinked polymer networks can be supplementarily reinforced by interlocking secondary polymers within the entangled networks. A polymer comprising of two or more networks, which are at least partially interlaced at a molecular scale but not covalently bonded to each other. (Figure 5c) **(Sharma &Tiwari 2020).**

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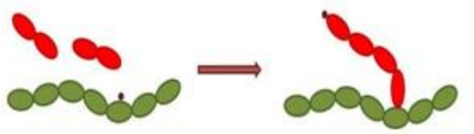
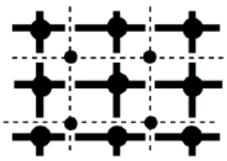


(a)

(b)



(c)

Figure 5: (a) Grafting reaction, (b) Enzymatic Reaction and (c) Interpentrating Networks

1.5 Classification on the basis of Stimuli Sensitivity:

These hydrogels are functional polymers, which respond to an external stimulus and adjust their physicochemical character, especially their water solubility. These hydrogels are called “smart” or “active” hydrogels. The environment stimulants are different. They can be pH, temperature, ionic strength, electrical and magnetic fields, and light, pressure and chemical and biochemical compounds (e.g. glucose). The changes in hydrogel properties are usually reversible and when the stimulant is removed, the system returns to its original state (**Bashari *et al.* 2018**).

1.5.1 Temperature Sensitive: This kind of PHGs is defined by its ability to swell and shrink when the temperature changes in the surrounding fluid which means the swelling and deswelling behaviour mostly depend on the surrounding temperature.

(a) Positive Temperature PHGs: Positive temperature PHGs are known by the upper critical solution temperature (UCST).

(b) Negative Temperature-PHGs: This kind of PHGs which has critical parameter called low critical solution temperature (LCST) (Figure 6).

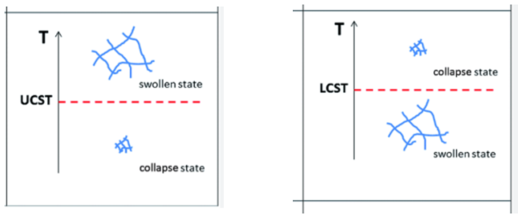


Figure 6: USCT and LCST of hydrogels

1.5.2 pH Sensitive: pH-sensitive hydrogels are materials that respond to pH values of the surrounding medium and they exhibit swelling and de-swelling according to pH of the environment.

1.5.3 Electro Sensitive: This class of PHGs is similar to pH response because they are made of polyelectrolytes. Electric sensitive PHG undergo swelling and de-swelling depending on the applied electric signal (Figure 7).

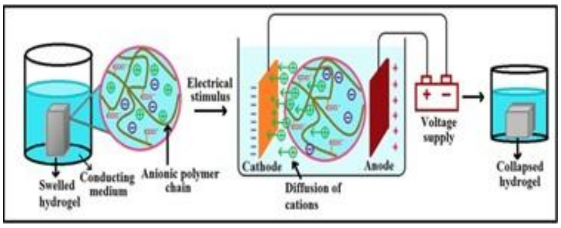


Figure 7: Electro sensitivity of Hydrogel

1.5.4 Sound Sensitive: Among different environmental stimuli, smart hydrogels are also responsive to sound or ultrasound. Particularly in the biomedical field (e.g., drug release, cancer therapy), its applications with hydrogels are prevalent. Polymers or hydrogels can be activated and allowed to burst due to their interaction with ultrasound waves, thereby releasing drug loads into specific tissues.

1.5.5 Light-responsive hydrogels: Photo-responsive hydrogels change their properties when irradiated with light of the appropriate wavelength. Light-sensitive hydrogels can expand and contract upon exposure to ultraviolet (UV) or visible light.

1.5.6 Magnetic responsive Hydrogel: Magnetic responsive behavior can be imparted by incorporating magnetic Nano Particles (MNPs) as dispersion in a crosslinked polymeric matrix rendering responsive behavior against magnetic stimuli. With the change of magnetic state, the mechanical, thermal, and acoustic behaviors are also affected simultaneously as the magnetic part behaves as a composite along with the hydrogel matrix.

1.5.7 Enzyme responsive hydrogels: All the major changes occurring in living cells are because of enzymes, in the field of artificial materials enzymes are being used as a trigger to create biomimetic responsive materials. These include hydrogels that not only undergo structural changes but also interact with the environmental components upon exposure to different enzymes **(Sikdar *et al.* 2021).**

2. Raw Material Used for Hydrogels

Various monomers used are Hydroxyethyl methacrylate (HEMA), Hydroxyethoxyethyl methacrylate (HEEMA), Hydroxydiethoxyethylmethacrylate (HDEEMA), Methoxyethyl methacrylate (MEMA), Methoxyethoxyethyl methacrylate (MEEMA), Methoxydiethoxyethyl methacrylate (MDEEMA), N-isopropyl AAm (NIPAAm), Vinyl acetate (VAc), Acrylic acid (AA), Ethylene glycol (EG), Polyethylene glycol l(PEG), PEG acrylate (PEGA) etc. (Laftah *et al.*2011)

3. Polymers used for Hydrogels

1. *Chitosan:*
2. *Cellulose*:
3. *Gelatin*:
4. Mechanism of Polymeric Hydrogels (PHGs)

Laftah *at el.* (2011) stated that hydrogel in a dehydrated state is referred to as the glassy state, and in swollen form, as the rubbery state. Free spaces in the chains permit the solvent molecules to find spaces when glassy or dry hydrogel makes contact with the aqueous medium. When enough water has entered into the hydrogel matrix, the glassy state turns into the rubbery state, named as swelling. The diffusion process is responsible for the entrance and removal of water from the hydrogel matrix.

4 Hydrogel Fibre: Hydrogel fibre is a hydrogel made into a fibrous state, where its width is significantly smaller than its length. As a water swollen network with usually low toxicity, hydrogel fibre can be used in a variety of biomedical applications such as drug career, optical sensor, and actuator. To make hydrogel into a fibrous state, the pregel solution must be made into fibrous form and then crosslinked while maintaining this shape. (Figure 8)


Figure 8: Hydrogel Fibre

5. Properties of Hydrogels

The preferred mechanical properties of hydrogels may be attained by incorporating specific polymers, co-monomers and crosslinkers and by changing the crosslinking degree. A strong gel network can be obtained with increasing the degree of crosslinking.

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Elasticity is very significant to give increased flexibility to the crosslinked network and to assist in the movement of incorporated therapeutic moieties. Therefore, an optimal degree of crosslinking for hydrogels is essential in order to retain the compromise between mechanical strength and elasticity.

Numerous hydrophilic natural and synthetic polymers can be classified as biodegradable polymers. The degradation of these polymers depends on several factors, such as hydrophilicity, molecular weight, and polymer–water interaction. Hydrogels containing more hydrophilic groups swell more as compared to hydrophobic groups. Crosslinking affects the swelling ratio of hydrogel, as highly crosslinked structures have a lower swelling ratio and vice versa. The swelling of hydrogels is also affected by temperature and pH, environment and surrounding material (Bashir *et al.* 2020).

6. Requirements of Functional Features of an Ideal Hydrogel Material

1. Highest absorption capacity
2. Highest absorbency under load
3. Desired rate of absorption depending on the application requirement
4. Highest biodegradability without formation of toxic species
5. Re-wetting capability
6. Colorless, odorless, and absolute non-toxic
7. Highest durability and stability in the swelling environment and during the storage
8. Lowest price
9. Lowest soluble content and residual monomer (Ahmed 2015)

7. Applications of Hydrogel in Textiles

7.1 Wound Healing Applications

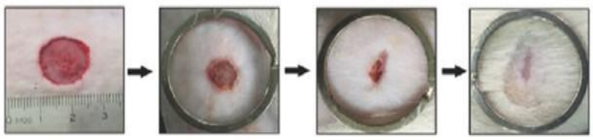


Figure 9: Hydrogel nanofibrous scaffold being used for wound healing

7.2 Environmental Sensitive Hydrogels in Deodorant Fabrics

Lee *et al.* (2000) used formic acid as a catalyst to copolymerise N-methylol-acrylamide (NMA) and β-cyclodextrin (β-CD) (CD-NMA). The fragrance of CD-NMA-grafted cellulose fibres treated with vanillin was retained even after prolonged storage, initially at room temperature for 7 days, following holding at 80 °C for 7 days. In contrast, the untreated cotton fibres only retain the fragrance for less than two days.

7.3 Environmentally Sensitive Hydrogels in Nutrient/Drug Delivery Fabrics

Ishida *et al.* (2003) synthesised a temperature-sensitive copolymer (EOVE200-HOVE400) consisting of poly-2-ethoxy-ethyl vinyl ether (EOVE200) and poly hydroxyethyl vinyl ether (HOVE400).

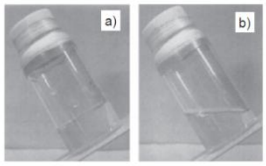


Figure 17. Visual observation of sol and gel states of EOVE200-HOVE400 at 30 °C a) and 10 °C, b) [26].

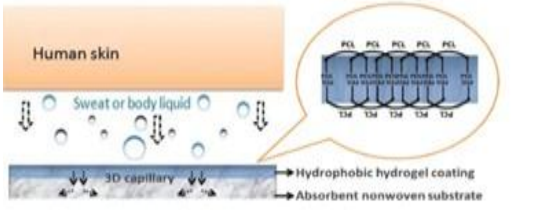
Figure 10

EOVE200-HOVE400 was in sol-state and gel-state at 10 °C and 30 °C respectively. The sol-gel transition is also reversible. When vitamin E was dissolved in EOVE200-

HOVE400 solution, a controllable release of vitamin E could be realised by a temperature-induced sol-gel transition. (Figure 10) It was apparent that there was no release of vitamin E from EOVE200-HOVE400 at 30 °C owing to the gelation of the solution. When the temperature was reduced to 10 °C, vitamin E was released from EOVE200-HOVE400.

7.4 Hydrogel-functionalized Textile System with Moisture Management Property for Skin Application

Huawen *et al.* (2014) studied a functional textile-based material for topical skin application. It was fabricated by coating a thermoresponsive hydrogel onto one side of absorbent nonwoven fabric. The thermoresponsive hydrogel was synthesized easily through coupling of poly ethylene glycol (PEG) and poly ε-caprolactone (PCL) with hexamethylene diisocyanate (HMDI) as a chemical linker. (Figure 11).



. Schematic diagram of the hydrogel functionalized-nonwoven fabric with smart moisture management property.

Figure 11

7.5 Fire- resistant Hydrogel- fabric Laminates

Hydrogel-fabric laminates were prepared by sewing the hydrogel samples to a commercial aramid fabric, fire-resistant wool, and an oxidized polyacrylonitrile fabric (OPAN) (Figure 12).

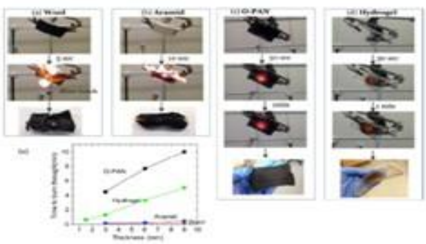


Figure 12: Shows burning of a) wool b) aramid c) OPAN and d) hydrogel

7.6 Hydrogels in Personal Care

Product Groups	Products
Feminine sanitary protection	Sanitary napkins, pant liners, panty shields.
Baby diapers	Baby diapers, pant diapers, training pants, swimming pants.
Adult incontinence products	Insert pads (needs additional product for fastening) pants/briefs, liner pads, mesh briefs supports, bed protection, under pads.

7.7 Hydrogel Eye Patch and Hydrogel Mask

Eye patches are specially designed with hydrogel layer to ensure they stick to skin like glue and adhesive back layer that stick well to hold throughout lash extension session as well as provide moisture to skin and reduce dark circles. The latest cosmetic mask technology introduced is new Hydrogel Mask, an innovation improving on traditional sheet masks.

7.8 Agro-textile Cultivation Bed

Scientists developed a system to cultivate the plants in a soil-less agro-textiles bed. Reduction of agrochemicals, maximization of crop production on minimum land are getting prime issues in case of agriculture nowadays. They presented agro-textiles based cultivation where plants are grown on textile fabric basements. Superabsorbent Hydrogel (from diapers) was introduced within the textile fabric to make root support to grow plants. Organic fertilizer was used to provide the required nutrients (micro and macronutrients) and integrated with the beds. (Figure 13) (**Zhou, *et. al*. 2015**).

Figure 13: Agro textile-based cultivation bed for soil-less farming using hydrogels for wheatgrass

7.9 Natural fibres woven fabric reinforced hydrogel composites

Koc *et al.* (2022) prepared PVA (Poly vinyl alcohol)/Cotton, PVA/Flax and PVA/Wool blended woven fabrics and the borax/water solutions were spilled on the fabric samples to transform PVA yarns into hydrogel form by crosslinking PVA molecules in the fabric structure.It was found that wool fabric reinforcement for PVA based hydrogel composites was better for mechanical enhancement.

7.10 Strong Hydrogel induced with Fibre

Glass fibre fabric was added to polyampholyte (PA) hydrogels that contained high levels of water. Though the fibres were no bigger than 10µm in diameter, slightly thinner than the human hair, the resulting composite material proved to be very strong. It was tested to be five times stronger than steel. (www.zmescience.com) (Figure 14)

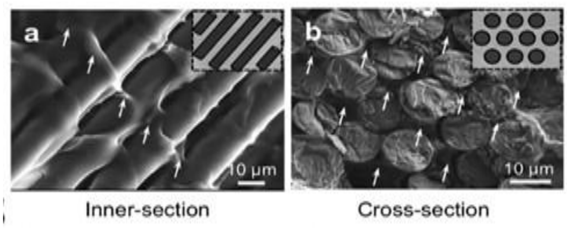


Figure 14: Inner and Cross section of Polyampholyte hydrogel with glass fibres

7.11Removal of Dyes and heavy metal by Hydrogels

Scientists from Indian Association for Cultivation of Sciences (IACS), Kolkata, have developed a new gel that can remove toxic organic dyes and metal ions from waste water. They found the hydrogel began absorbing various commonly used dyes within 15 minutes. The hydrogel can be washed with sodium bicarbonate and ethyl acetate and reused. As the dyes and metal ions are soluble in water they get washed out from the gel and the hydrogel can be used for up to four cycles.

CS-based adsorbents that are usually used in the form of hydrogel beads have shown the highest adsorption capacity for numerous dyes. **(Agarwal *et al.* 2016)**

8. Market Size

- Hydrogel market size was valued at USD 25.4 bn in 2021 and the hydrogel market revenue is expected to grow at 7.2 % from 2022 to 2029, reaching nearly USD 44.3 bn.
- The Polyacrylate segment is expected to grow at the highest CAGR during the forecast period.
- The developing countries are increasing market investments. Large-scale investments are being made by nations like China, Japan and India.
- The market was negatively impacted by COVID-19 in 2020 due to sharp fall in demand for various end-user industries and lockdown imposed across the world.

9. Advantages and Disadvantages of Hydrogels

Advantages

1. Hydrogels possess a degree of flexibility very similar to natural tissue, due to their significant water content.
2. Entrapment of microbial cells within Hydrogel beads has the advantage of low toxicity.
3. Environmentally sensitive Hydrogels have the ability to sense changes of pH, temperature, or the concentration of metabolite and release their load as result of such a change.
4. Timely release of growth factors and other nutrients to ensure proper tissue growth.
5. Hydrogels have good transport properties and biocompatible.

Disadvantage

1. Hydrogels are expensive and causes thrombosis at Anastomosis sites.
2. The surgical risk associated with the device implantation and retrieval.
3. Hydrogels are non-adherent; they may need to be secured by a secondary dressing.
4. Hydrogels used as contact lenses causes lens deposition, hypoxia, dehydration and red eye reactions.
5. Hydrogels have low mechanical strength and difficulty in handling.
6. Difficulty in loading and sterilization

CONCLUSIONS

The development of smart fabrics not only represents a research advancement in the textile industry, but will also bring convenience to people's lives with their use. Smart polymers show capabilities of responding to external stimuli and have significant potential applications in a variety of fields. Hydrogels with unique properties will be appropriate candidates for electronic, sensing, cell imaging, drug delivery and tissue engineering applications. Hybrid hydrogels can be extended to produce artificial skin, soft robotics, tissue generation, 3D printing etc. Therefore, hydrogels having magnified mechanical strength will be the most focusing goal of research for the coming decades. Extensive research is going to achieve new kind of hydrogels for future better findings; novel conceptual assimilation of hydrogel preparation may lead to remarkable properties, translating its innovative applications in different fields. Among all, easy, smart and economically friendly way to improve the efficiency of advanced hydrogel will be most effective.

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