International Invention of Scientific Journal
Online ISSN: 2457-0958
Available Online at http://www.iisj.in **Volume 8, Issue 02(April-May-June)|2024**|Page: 149-155
Original Research Paper-Basic Sciences

Polymer Nanocomposites

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Article Received: 24-April-2024 Revised: 14-May-2024 Accepted: 04-June-2024

ABSTRACT:
Nanocomposites became commercial in 1980 when Toyota Company produced the first polymer nanocomposite parts for use in cars. The progress made in the area of the ability to determine the characteristics, production, and manipulation of nanoscale materials has caused them to be used as fillers in new types of nanocomposites. Nanocomposites obtained from polymer have very good tensile strength, modulus, and heat distortion temperature. Additionally, nanomaterials have improved some properties of composites such as color and transparency, conductivity, resistance to fire, insulation, and magnetic properties. These characteristics have made the global consumption of polymer nanocomposites increase day by day. The goal of making polymer-based nanocomposites is to achieve a cheaper, lighter, more resistant, higher quality, and more efficient product. The presence of particles and fibers in the structure of nanocomposites mostly causes strength in the base material. Nanocomposites have been introduced to the food packaging industry to be a bigger barrier against the penetration of gases and to reduce corruption. Nanocomposites have been applied in spaceships, commercial airplanes, and even rocket technology, bedding, and products such as polymer pipes, tennis rackets, rubber, tissue engineering, construction, etc.
The present study tries to provide information about polymer nanocomposites, their synthesis, and their applications in brief.

Keywords: Polymer nanocomposites, Nanocomposite, Polymer

INTRODUCTION:

People and especially scientists throughout human history believed that materials can be divided into small enough to reach indestructible particles and these particles form the basis of material. The world of nanomaterials is an exceptional opportunity for a revolution in composite materials. A composite is a material consisting of two or more components so that these components together create properties on a macroscopic scale that are not available in any of those components alone. If one of the components is on a nanoscale, the composite material will be a nanocomposite (1).

Composites can be classified into 3 categories according to what the base material or primary phase is composed of:
-Metal-based nanocomposites
-Ceramic-based nanocomposites
-Polymer-based nanocomposites

Among these nanocomposites, the most attention is paid to polymer-based nanocomposites.

The unique mechanical, chemical, and physical properties of polymer nanocomposites are some of the reasons for their expansion. Polymer nanocomposites mostly have high strength, low weight, high thermal stability, electrical conductivity, and high chemical resistance. The discovery of carbon nanotubes in 1991 is another reason for the development of polymer-based nanocomposites and increasing research in this area. The strength and electrical properties of these nanocomposites are significantly different from graphite nanolayers and other filler materials. Polymer nanocomposites have been widely used in aerospace, automotive, food packaging, biomedicine, tissue engineering, and cell therapy, thanks to their unique properties. The global consumption of nanocomposites is increasing rapidly, so its market value was over $2 billion in 2017 and it is estimated to reach $7.3 billion by 2022(2).

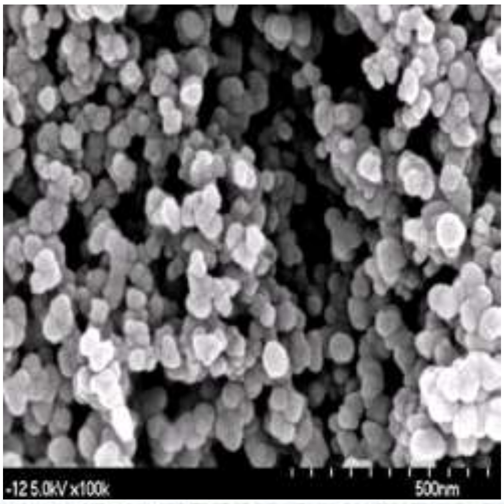
What is composite?

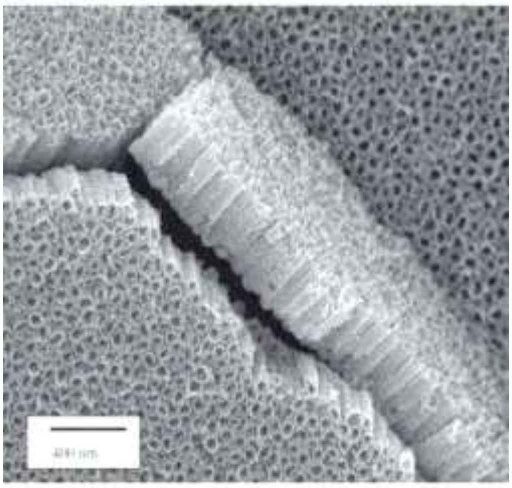
The term “composite” is derived from the English root “To compose”, which means to combine and mix. A composite is a compound that is macroscopically made from the physical mixing of several distinct materials with different physical and chemical properties so that these components can be easily distinguished from each other.

Composites have 3 primary characteristics:

-Solid (liquid compounds are worthless in terms of mechanical properties)
-Synthetic (natural composites such as wood and bone are not considered)
-They consist of two or more components (phases) that are chemically or physically different and are placed together in a regular or dispersed manner and there is a common layer between them or the mechanical properties of one of the phases are different compared to the phase or phases (1).

Nanocomposites
Nanocomposites are a special class of composites that at least one of their components is nanoscale. Most nanocomposites have a small amount (generally less than 5% by weight) of lamellar mineral fillers or carbon nanotubes with a single structure (3).



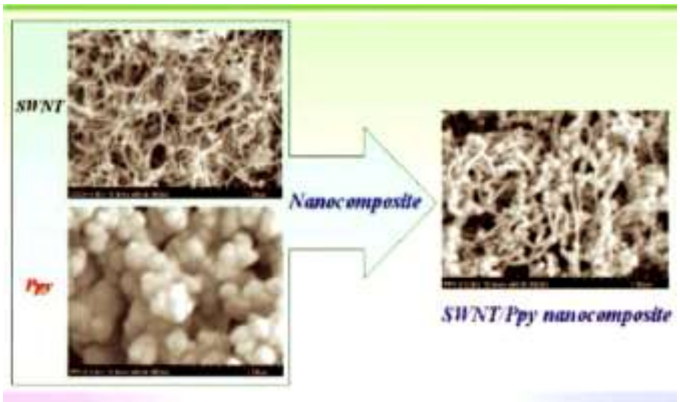


An image of a nanotube structure An image of the structure of nanoparticles

Primary components or phases of each nanocomposite
Each nanocomposite includes two phases. The first phase (matrix), which includes the second phase and has a higher weight percentage than it, contains a crystal structure that is considered as the composite base.
Metal fields (high-impact resistance), ceramic fields (high-heat resistance), and polymer fields, especially plastic fields (high-chemical resistance) are among the most used fields.
The second phase also includes particles or fibers that are distributed as fillers to achieve certain characteristics such as strength, heat resistance, electrical conductivity, magnetic properties, etc. in the first phase (base material), and to improve its properties (4,5,7)

Matrix materials
Polymers are organic (carbon-containing) molecules composed of identical repeating monomer units. Rubber and cellulose are examples of synthetic polymers. A wide range of synthetic polymers are applied in various composites.
Structurally, particles and fibers mostly cause inherent strength, and the polymer matrix (first phase) can uniformly transfer the forces applied to the composite to the filler or reinforcement by sticking to the minerals. In this state, characteristics such as hardness, transparency, and porosity of the materials inside the composite will change. The polymer matrix can also protect the filler surface from damage and keep the particles separated, so crack growth is delayed. In addition to all these physical properties, the components of nanocomposite materials can have a combination of the properties of both components, and perform better due to the interaction between the matrix surface and the filler particles (4, 5, and 7).

Fillers
Fillers (second phase) are nanoscale materials small amounts of which are added to a polymer substrate to obtain a nanocomposite with special properties (tensile resistance, fire resistance, etc.). Due to the nanoscale dimensions of the fillers used in nanocomposites, the interaction between the fillers and the matrix is different from the interaction in conventional composites. These interactions affect the physical properties of nanocomposites differently. The impact of placing the second phase on the background of the first phase is so much that we will see a significant increase in the physical and mechanical properties of the nanocomposite by adding 5 to 10 volume percent of the second phase to the matrix phase (4,5,7). The following figure schematically displays the placement of the second phase (polypyrrole particles) on the first phase (single-walled nanotubes (SWNT)) in the polypyrrole-SWNT nanocomposite (3).



Classification of nanocomposites
-Nanocomposites are divided into 3 primary groups based on the type of their primary phase:
-Metal-based nanocomposites
-Ceramic-based nanocomposites
-Polymer-based nanocomposites
Polymer-based nanocomposites are the most significant category of nanocomposites. Polymer-based nanocomposites are used in a wide range of high-end industries, such as the production of airplane parts, to low-end industries, such as the production of sinks, etc. Currently, they include about 65% of the composites market, so they are considered the largest subset of composite materials.
Nowadays, most industries enjoy the unique benefits of these materials. The trace of composites can be found in the following areas (7):
• Transportation industries including air, road, and sea transportation
• Military and aerospace industries
• Energy industries in the areas of electricity production and transmission and oil, gas, and petrochemical industries
• Construction industry including infrastructure and building industry
• Urban furniture industries
• Household appliances
•Sports equipment and goods

General characteristics of nanocomposites
Tensile strength, modulus, and heat distortion temperature are the primary characteristics of components used in the construction industry. Tensile strength indicates the level of force required to cut a piece under tension. The modulus indicates the level of bending of a piece under load. Heat distortion temperature indicates the working temperature of a piece. Nanomaterials mostly increase the heat distortion temperature of a polymer without changing its low-temperature impact properties. However, conventional fillers reduce their plasticity at low temperatures by increasing the heat distortion temperature of a polymer, leading to failure under impact. Fire resistance is required for some polymers with special applications (such as plastic insulation of electrical wires and cables in buildings). Most nanocomposites are not fire-resistant, but they can be used as part of a fireproof set. Reinforcing polymers using organic and inorganic materials is very common. Reinforcements are nanometer-sized particles in nanocomposites, unlike conventional reinforcements that are on a micron scale. Tensile strength, yield strength, and Young's modulus increase significantly by adding a small percentage of nanoparticles to a pure polymer(4).
For example, Young's modulus of the material will increase by 58%by adding only 0.04% by volume of mica (a type of silicate) with dimensions of 50 nm to epoxy.

Structure of polymer-based nanocomposites
In polymer nanocomposites, the matrix is a polymer material referred to as resin and includes two general categories of thermoplastics. Reinforcing fibers also include types of glass, aramid, carbon, and boron. In this composition, fibers primarily play the load-bearing role. The resin is responsible for distributing the load applied to the fiber matrix and keeping the position of the fibers in their place. Nowadays, using natural fibers in conventional nanocomposites to green nanocomposites has also become popular (5).

Composite pipe industry
One of the primary fields of using composites is the production of pipes with different diameters using composite materials. Composite pipes, consisting of glass fibers and thermoset resins, provide a strong, corrosion-resistant, and light structure, which are considered a very suitable alternative to metal and concrete pipes. The most significant characteristic of composite pipes is the resistance to corrosion caused by fluids (liquids and gases) in both inner and outer walls. Due to their polymer structure, composite pipes are safe from this phenomenon and can work without repair in chemically and electrochemically active environments for 25 to 50 years. For this reason, the oil, gas, water, and sewage industries are the primary areas of penetration of these products. The most significant factors that have made composite pipes surpass their other traditional competitors are eliminating the heavy maintenance costs of corroded pipes transporting oil or gas and the damage caused by service interruption to industrial centers (6).
A composite pipe primarily weighs 25% of cast iron pipe, 33% of metal pipe, and 10% of concrete pipe. This issue is associated with the following advantages:
• Reducing loading and transportation costs
• The possibility of nesting pipes with different diameters inside each other
• Low installation cost
• Smooth and polished inner surface

Synthesis of polymer nanocomposites
Nowadays, polymer-based nanocomposites include more than 90% of the global consumption of

nanocomposites. Their metal and ceramic types are used very limitedly. In other words, when nanocomposites are talked about, the polymer type is meant (5,7).
Generally, there are 3 methods for producing polymer-based nanocomposites:

Direct mixing: In this method, nanoparticles prepared as a suspension are first dissolved in a solvent and then added to the polymer solution, and the resulting mixture is extruded by a hydraulic press in a mold. Finally, thin plates are formed. In this method, selecting the polymer substrate, selecting the type of particles, the compatibility of these two types with each other, and the way the particles are distributed are crucial points that should be considered. This method is mostly applied to produce polymer nanocomposites containing carbon nanofibers. The limitation of this method is the amount of reinforcing phase or filler material. For example, the maximum amount of silica nanoparticles can be 20% by weight for the production of silica nanocomposite (polypropylene). Agglomeration is also another limitation of this method.

Solution processing: Some of the limitations of the direct mixing method can be overcome using this method. Additionally, the amount of agglomeration of nanoparticles in the polymer material can be reduced. Polymer nanocomposites can be produced in two ways in this method. The resulting solution can be poured into the mold and the nanocomposite can be produced if the polymer-based material and its reinforcing nanoparticles can be dissolved in each other. Otherwise, the mixture of nanocomposite materials is dissolved in a solvent and finally, the desired nanocomposite is obtained by evaporation of the solvent.

In situ polymerization: In this method, the polymer substrate is polymerized in the presence of nanoparticles, and the monomer includes the filler particles during growth. The distribution of nanoparticles in the monomer is the key point in this method. The desired distribution can be obtained by controlling the bonding between nanoparticles and the substrate. Many polymer-based nanocomposites can be produced by this method. For example, nanocomposites containing graphite nanolayers, with high electrical conductivity and low permeability, are produced by this method. To produce these nanocomposites, graphite layers are first distributed uniformly in the monomer with ultrasonic waves, and finally, polymer nanocomposite is obtained by in situ polymerization.
The proper distribution of the filler material is a significant point in the production methods of polymer nanocomposites. By modifying the surface, it is possible to distribute it uniformly to prevent the agglomeration of the nanometer components of the filler material and provide a proper distribution of the reinforcement phase. In other words, the interface between polymer and nanoparticle is modified in all these processes. The use of surface processes leads to the uniform distribution of the reinforcement phase in the polymer substrate and will increase the modulus and strength of the nanocomposite (5,7).

Clay-polymer nanocomposite
The clay-polymer nanocomposite is the most widely applied polymer nanocomposite whose production and consumption technologies are commercialized easily. This nanocomposite causes significant improvement in many physical and engineering properties of polymers in which a small amount of filler is used. Major developments in this field have been made during the past 20 years. Smectite-type clays such as hectorite, montmorillonite, and synthetic mica are used as fillers to improve the properties of polymers in this type of material. Smectite-type clays have a layered structure, and each layer is made of silicon atoms in the form of a tetrahedron connected to an octahedral plane with common edges of Al(OH)3 or Mg(OH)2.
Given the nature of bonding between these atoms, these materials are expected to show excellent mechanical properties in the direction parallel to these layers. However, the exact mechanical properties of these layers have not been clarified yet. Using modeling methods, it is estimated that the coefficient of Young's modulus along the layers is 50 to 400 times higher than that of a normal polymer. The layers have a high aspect ratio and each layer is approximately 1nm thick, while its radius varies from 30 nm to several microns. Hundreds of thousands of these layers are stacked together by a weak van der Waals force to form a clay component. It is possible to put clays in various shapes and structures in an organized form within a polymer with a suitable configuration. Studies have indicated that many engineering properties such as heat resistance and strength are significantly improved when small amounts of filler are used (mostly less than 5% by weight). When a small amount of clay filler is used in polymers such as nylon 6, it shows a 103% increase in Young's coefficient, 49% in elastic strength, and 146% in deformation caused by heat resistance. Other improved properties include resistance to fire resistance, reduced permeability to gases, ionic conductivity, and increased biodegradability. Another advantage of clay-polymer nanocomposites is that they do not have a significant impact on the optical properties of the polymer. The thickness of a single clay layer is much less than the visible wavelength. Thus, well-laminated clay-polymer nanocomposites are optically transparent (7).

Synthesis of clay-polymer nanocomposites
Several Many methods have been utilized in the production of clay-polymer nanocomposites, but

the 3 methods that have been more developed since the beginning include:
- In situ method
- Solvent method
Melting method

The in situ method involves inserting a polymer precursor between the clay layers and spreading and then spraying the clay layers into the base material with polymerization. This method was innovated by Toyota's research group when they wanted to make polymer-clay nanocomposites. This method is very useful for thermosetting polymers (polymers that become stronger against heat).

In the solvent method, a solvent is used to load and disperse the clays in the polymer solution. This method still has many problems and barriers in the commercial production of nanocomposites. The high price of required solvents and the problem of separating the solvent phase from the produced solution phase are among these barriers. Also, there are health and safety concerns in this method. For example, the polyamide-montmorillonite nanocomposite is obtained in this method in a bed of dimethylacetamide solvent. In the melting method, the clay and polymer are combined during melting. The efficiency of this method is not as high as the in situ method and the produced composites have little lamination. However, this method can be used in old polymer production industries where methods such as molding and injection are used. Polypropylene-montmorillonite nanocomposites have been synthesized in this method.

In addition to these methods, other methods such as vulcanization, sol-gel, and solid composition are being developed (5,7)

Combination of nanocomposite with various polymers
Nanocomposites can be produced with thermoset polymers or thermoplastics. The chemical behavior of the special versatility of the resulting nanocomposites is a function of the chemical behavior and physical characteristics of the host polymer.

The primary types of commercial clay nanocomposites, their characteristics, and important applications (5)

Matrix / filler	Primary characteristics	Applications
Nylon / Montmorillonite	Heat resistance Obstructive features Elasticity of tensile strength Impact resistance	Auto Parts packing Medical instruments Electrically conductive materials non-combustible materials Multipurpose applications
TPO / montmorillonite	Shock resistance Heat resistance	Auto parts
EVA / Montmorillonite	Fire resistance Chemical resistance Thermal stability and easy construction	Covering cables and wires
PP / montmorillonite	High flexibility module High impact resistance Low bulk density Scratch resistance	Auto Parts packing non-combustible materials office equipment Home Appliances
PE (including LDPE, HDPE, UHMWPE) / Montmorillonite)	High flexibility module High impact resistance Low bulk density Scratch resistance	Auto parts and packing

Applications	Primary characteristics	Matrix-filler
Auto parts and electronic	High flexibility module Heat resistance	Montmorillonite
Auto parts	Heat resistance Obstructive features Elasticity of tensile strength Impact resistance	Nylon / mica fluoride
Sport good \tires	Barrier to air penetration	Butyl / vermiculite

Application of polymer nanocomposites in Iran
Based on the international standard of the development index from the composite industry viewpoint, per capita consumption is 3 kg per citizen. 95.8% of the composites used in Iran are polymer-based composites, and they are largely applied in the construction and transportation industries. The nanocomposites in industries are used to protect against corrosion in the form of pipes and tanks. Most of the country's industries face the problem of

corrosion and its cost consequences. Corrosion in Iran in 2000 was estimated to be 2700 billion Rials based on 5% of the gross national product. Nanocomposite materials refer to those materials whose reinforcement phase has dimensions on a scale of 1 to 100 nm. These materials have been introduced to the field of science and technology over the last decade of the 20th century and have made significant progress in these years.
Polymer nanocomposites are combinations of polymers and 2 to 10 percent by weight of nanometer particles, such as clay and carbon nanotubes. Thanks to its very small dimensions and very high surface compared to conventional reinforcements at the leading surface, the nanometer reinforcement improves the desired properties, and the problems related to conventional ones such as weight increase, surface defects, and processability problems are less seen in them. Thus, nanocomposites are a good alternative to conventional composites since they have better performance and less weight. (5)

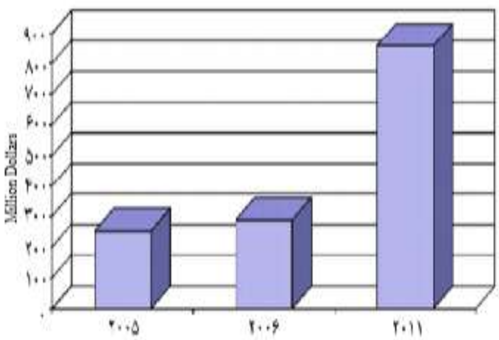
Global market of polymer nanocomposites
The global consumption of polymer nanocomposites is increasing rapidly, so that the market value reached 2 billion dollars in 2017 and it is estimated to reach 7.3 billion dollars by 2022 (2).

The necessity of paying attention to polymer nanocomposites
Given the large volume of use of conventional composites in Iran and the high volume of polymer production by the National Petrochemical Industry Company and the need to increase the use of these polymers, the production of polymer nanocomposites is one of the most appropriate ways to meet the needs of the market, improve the properties, and expand the range of application of domestic polymers. Unlike conventional reinforcements that are on the micron scale, the reinforcement phase is on the nanometer scale in nanostructured composites. The uniform distribution of these nanoparticles in the polymer matrix phase makes the interface of the matrix phase and the reinforcing phase have a very high area per unit volume. Required performance, mechanical properties, cost, and processability are vital in composites. Polymer nanocomposites have overcome these limitations. For example, consider the rapid development of layered polymer-silicate nanocomposites. Efforts in recent years have doubled the tensile modulus and strength of these composites without reducing their impact resistance.
These properties can be achieved by increasing a small amount of layered silicate in a large number of thermoplastic resins such as nylon, olefin, and thermoset resins such as urethane and epoxy. General Motors Company has used nanocomposites with thermoplastic olefin base and layered silicate reinforcement in the external parts of the car. An olefin nanocomposite with 5.2% layered silicate is much stronger and lighter than the conventional talc particles used in making conventional composites. A weight reduction of about 20% can be achieved based on the type of part and the reinforcing material in an olefin nanocomposite (8). These advantages will have positive impacts on environmental issues and their recycling. Based on the reports, the use of polymer nanocomposites with silicate layers in the American automotive industry will save 5.1 billion liters of diesel over the life of the car produced in one year. Thus, the release of diesel Carbon dioxide will decrease by about 10 billion pounds. Regarding polymer nanocomposites, we are still at the beginning and there are many areas for their development given the final application (10).

The importance of polymer nanocomposites
Nanocomposite demand in America (thousand tons) (5)

	2005	2010	2020	Percentage of annual growth
Total nanocomposites	70	156	3190	29
Thermoplastic-based nanocomposites	69	149	2540	27
Nano composites-based thermostats	1	7	650	55

Global consumption trend of polymer nanocomposites 2005-2011 (million dollars)



Advantages of polymer-based nanocomposites

The advantages of structures of polymer-based nanocomposites compared to traditional, wooden, and metal samples, which have caused them to be used extensively in different industries, can be summarized in the following cases:

• Reducing the weight of the built structure based on the architecture
• Being safe against corrosion
• Capable of bearing cyclic loads and very good resistance
• The simplicity of production methods and the possibility of producing very complex shapes with very easy, efficient, and cost-effective methods
• Ease of repair and troubleshooting processes
• Low thermal expansion coefficient and suitable thermal insulation
• Electrical insulation
• Improved connections and the possibility of integrated production
•Reducing the permeability to gases, high sintering, solvent resistance, transparency, and colorlessness are other advantages of polymer nanocomposites (9)

Disadvantages of polymer-based nanocomposites

There are significant process problems in making these nanocomposites. The most important of these problems include:

The non-uniform distribution of the second phase in the base phase and thus the accumulation of very fine powder particles in nanocomposites reduce the mechanical properties of nanocomposites.

Also, using expensive chemicals for the uniform distribution of the second phase in the matrix phase and preventing the nanocomposite powder particles from sticking together and making nanocomposites with a homogeneous microstructure and high mechanical properties makes the process uneconomical and complicated (9)

CONCLUSION

Thanks to their very good properties, polymer nanocomposites can have many applications in different industries. Their most important property is the improvement of their properties compared to other types of materials. Hence, the weight of the parts is reduced significantly and the abrasion and tensile resistance and strength are increased significantly using this method. Also, we cannot overlook the biological applications of this material the construction and repair of body bones, and its biocompatibility. The issue of nanocomposites is very broad, up-to-date, and practical. Researchers have recently been able to combine the hardest material known in the world (diamond) with carbon nanotubes and obtain a composite with new properties. Diamond is very hard, but normally it is not a conductor of electricity. Also, carbon nanotubes are incredibly hard and conductors of electricity. A composite with special properties will be obtained by integrating these two forms of carbon at the nanometer scale (10). In Iran, light-cured dental composites have recently taken a special place among restorative dental materials thanks to their impressive beauty and color as real teeth, appropriate physical and mechanical properties, and lack of side effects for the patient. The development of technology for the production of polymer-based composites has made it possible for most industries to benefit from the unique advantages of these materials. We hope that this material will find more diverse applications and that its synthetic aspects will be discussed as it deserves.

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