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Polymer-MOF Hybrid Materials in Future Separation, Flame Retardancy and Sustainable Packaging

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Abstract. Polymeric materials offer advantages such as low density, facile processing, and low cost, yet they still face key bottlenecks in advanced applications—e.g., the permeability–selectivity trade-off in membrane separations, the loss of mechanical performance caused by high flame-retardant loadings, and insufficient room-temperature ionic conductivity and electrochemical stability in solid polymer electrolytes. Metal–organic frameworks (MOFs), featuring high surface area, tunable pore structures, and tailorable functional sites, provide an effective route to introduce molecular-sieving channels, adsorption/catalytic activity, and char-forming/smoke-suppressing effects into polymer matrices. This review summarizes the classifications and fabrication strategies of polymer/MOF composites (physical blending, covalent linking, in-situ growth, core–shell architectures, etc.), clarifies the synergistic—and potentially adverse—structure–property relationships, and highlights progress in separation, flame retardancy, and sustainable packaging. Remaining challenges are discussed, including interfacial characterization, pore blockage, scalable manufacturing, and environmental/health risk assessment.

1 Introduction

1.1 Performance bottleneck of polymer materials

Practically, the wide range of applications of polymeric materials, including membrane filtration, electronic parts, energy storage, and fireproofing (among others) has taken place, in part, due to the perceived ease of combining low density, good processability, and economic viability that is difficult to achieve with other material groups. And yet, even these very materials, concurrently, present a series of inherent restrictions which have become even harder to overlook in practice. As an example, in the case of gas separation membranes, their operating capabilities are inherently limited by the so-called Robeson boundary in which an increase in permeability generally causes a corresponding loss of selectivity. The core of most of these problems literally is the molecular structure, whose polymer chains are flexible and only weakly polar to give them comparatively low glass transition temperatures, resulting

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in a lack of sufficient stiffness and solubility to heat and to resist chemicals in challenging environments. Besides that, the materials are quite easily burnable and produce a lot of smoke, which poses severe safety issues in practical application. Conventional flame-retardant additives would typically require a relatively high concentration to be effective, which in turn reduces the overall mechanical characteristics of the polymer. When used in applications as an energy storage, polymer-made solid electrolytes usually exhibit significantly lower ionic conductivity at room temperature than their liquid counterparts do, and also have a relatively small voltage stability window, also limiting their practicality.

One of the ongoing challenges regarding the use of conductive polymeric materials is the attempt to balance processability with mechanical robustness, as the two processes are in reality antagonistic to each other. The issue is particularly knotted when scholars provide one or two single techniques of modification, such as cross-linking, forming a composite, or high load level, in that they tend to increase one characteristic and at the same time peer directly weaken the other. These trade-offs tend to create additional complications, including an increase in the level of melt viscosity, a decrease in fracture resistance, and the material degrading at an accelerated rate. All these associated issues eventually put a cap on the effectiveness of the material in terms of the production that could possibly be achieved and the cost-effectiveness.

Metal-organic frameworks (MOFs) are a relatively new area of materials science that seems to offer a remedy to this old problem. The hybrid materials themselves are built of three-dimensional structural networks based on inorganic networks, which are connected by organic molecules, and this makes them have remarkably high surface areas of up to 7000 square meters per gram. Moreover, they may be precisely tuned in size (between 0.5 and 5 nanometers) and thus have pore dimensions, which can be tuned to suit a given application. The addition of MOFs to polymer matrices creates efficient transportation technology of transportation or special adsorption sites. This can possibly allow simultaneous optimal increase in both permeability and selectivity, which is not typically effectively combined. This way, they assist in breaking the performance bottlenecks unique to the trade-off relationship between the said properties.

Once high modulus fillers are added, they result in observable increases in both thermal and mechanical properties, and what is particularly interesting is that the results are apparent at extremely low loading contents. More to the point, this increase is done without causing any significant density increment. A very useful property comes in during MOF thermal degradation in which a garner of metal oxide/carbon composite forms that can perform two functions: It not only acts as an active carbonizing portion, but also prevents the formation of smoke. This material has an intrinsic micro-mesoporous nature, thus able to trap smoke particles and dangerous gases, and therefore enables it to act as a flame retardant due to such a small loading (1-3%). This is because of its dual ability, and thus, the material meets the demands of mechanical performance and environmental safety standards. Going to electrical properties, as conductive polymers are prepared within the non-conductive channels within MOF through in-situ synthesis, the conductivity could be boosted up to five orders of magnitude, and at the same time maintain the necessary porous architecture of the material.

Metallo-organic frameworks (MOFs) possessing Lewis acid characteristics are highly compatible with lithium salts, and the specified interaction is beneficial to help implement the effective reduction of the overall level of crystallinity that prevails among the surrounding polymeric materials. This interaction in turn facilitates the formation of continuous ion transport pathways in the material, which in turn causes significantly increased ionic conductivity in even the common ambient temperatures, and moreover allows the operational voltage range of the system in a range where it would not be operational otherwise. It can also be stated that cheaper aluminum variants of MOFs have already been produced at scale through using aqueous-phase techniques with the synthesis performed under conditions of normal atmospheric pressure, and have reached the levels of true kilogram-scale synthesis, and have been capable of maintaining costs of materials below 3 per kilogram. This highly cost-efficient manufacturing process also shows ideal agreement with the traditional manufacturing techniques that prevail across the industry at large, including traditional routes such as melt extrusion and solution casting. More so, to the extent that the chemical modification potential of the materials is versatile, via the addition of different functional groups such as amino, sulfonic acid and phosphazene, it allows a broad scope of multifunctional applications, which can start with the catalytics processes, up to biological sensing and antimicrobial purposes, which in turn helps reduce the potential compatibility problems that have regular occurrence in multi-component material systems.

The challenges associated with polymer materials through deep-rooted trade-offs are becoming a solvable problem with metal-organic frameworks (MOFs). These issues are, at the center, balancing several opposing pairs of properties: permeability/selectivity, strength/toughness, flame resistance/mechanical performance, and conductivity/porosity. The most useful aspect of MOFs to such issues is that they combine three key properties in a material system: pore structures that can be designed to suit particular purposes, chemically stable structures, and the ability to modify the material after synthesis. Thanks to this combination, MOFs are becoming an increasingly popular target of active research in high-performance polymer composites, and they have real potential to allow real progress in a variety of important technology domains, such as gas separation membranes, solid-state batteries, flexible electronic devices, and fire-resistant materials.

1.2 Definition and classification of polymer/mofs hybrid materials

Polymer/MOFs composite materials are a comparatively recent type of practical material that encapsulates essentially the structural properties of porous metal-organic materials (MOFs) with the functionality benefits of organics of the polymer. Such hybrid systems fundamentally combine the form of ordered pore structures and large surface areas that MOFs are identified with, with the mechanical flexibility and the simple processing characteristics that polymers provide. Differently put, they attempt to bind the high surface area and finely defined pore structure of MOFs to the ability to handle and the mechanical resilience that polymers usually offer. Regarding practical considerations of fabrication and interfacial properties, however, they can broadly be divided into four main types: physical mixtures, chemically bonded systems, in-situ synthesized composites, and core-shell structures.

1.2.1 Physical mixture type

The category of this is the direct blending of MOFs with polymers by physical blending methods, usually by a solution-based approach, a melt-based approach, or a mechanical blending approach. In reality, the contact between these two aspects is not achieved by stronger chemical bonds but rather secondary forces, namely hydrogen bonding, van der Waals forces, or attractive forces. Although this method has significant ease of preparation and rather high versatility in terms of choice of components, it is often faced with the challenge of incompatible interfaces, which in turn may lead to the problem of particle aggregation or phase segregation.

It is commonly initiated by the isotopic addition of chemically reactive functional groups (i.e., amino, carboxyl, hydroxyl, etc.) to either metal-organic structures (MOFs) or to polymer chains. These groups are introduced and then undergo covalent bonding by a range of chemical reactions (such as condensation reactions, click chemistry, or ring-opening reactions), and eventually lead to immobilization at the molecular scale. Practically, this design has the benefit of guaranteeing high interfacial bonding, stability to dispersion, and performance to durability, as well as the ability to easily incorporate specific functional sites whenever the specific modification is needed.

1.2.2 Within-the-solid crystallization method

The metallic ions or organic linkers are initially dispersed in the polymer meshwork of a random pattern prior to the formation of MOF crystals under carefully controlled conditions, actually starting- this, of course, is done by creating a constrained environment that will inform the latter crystallization process. With the progressively developed crystals, the polymeric chains effectively control the size of the particles and the space geometry of the MOF crystals that in turn reliably guarantee the intimate interfacial contact between the components throughout the material. This generalized system allows the immediate production of flexible membranes, hollow fibers, as well as nanofiber assemblies and various other structured apparatuses all within the same processing procedure and this simplifies the complete production process greatly.

1.2.3 Core-shell configuration

In cases where the base material is a metal-organic framework (MOF), or polymeric microspheres, other materials can be added to their surfaces with a great degree of precision using well-developed methods like sequential self-assembly, sol-gel reaction, or atomic layer deposition. With this broad methodology, one is able to produce relatively advanced architectures, such as core-shell architectures, yolk-shell architectures, and multi-layered composites, including "MOF@polymer\" structures and alike designs where the shell is made of polymer and the core is made of MOF or the contrary, which makes it clear that that layer is the shell and that layer is core. Hybrid structures are effectively able to decouple the unusual porosity properties of the core material with the protection and functional benefits of the outer layers in that the core component undertakes the performance role, and the shell component adds extra stability and functionality. These composite materials are used extensively in many fields such as controlled drug delivery systems, catalytic microreactor systems, and other developers of hi-tech sensing gastronomy, where each utilisation scenario capitalises on the individual combination of core porosity and shell performance.

1.3 Research purpose and overview of size

During the last few years, hybrid materials that incorporate polymers and metal-organic frameworks (MOFs) have received much focus and demonstrated an overall potential in a broad range of functional directions. These compounds combine several impressive properties: they offer high surface area, tunable porosity, catalytic functionality, and keep the natural pliability, processability, and mechanical strength of polymers with which they are typically associated. This review provides a broad overview of the recent developments in three areas of particular interest in application such as the development of more sophisticated separation methods, enhanced fire-resistant characteristics and the growth of eco-friendly packaging systems. The suggested primary goal here is to systematically gather the existing information of the design procedures, performance processes, and structure-function relationships of such materials in various situations, as well as to determine the common scientific difficulties that commonly arise and the ways to resolve them so as to assist in achieving the experimental investigations to actual applications.

To be more exact, this review is aimed at the achievement of the following objectives: 1. Build a multi-disciplinary scientific platform: This basically consists of showing how polymer-MOF composite materials overcome common performance trade-offs that are often faced in practice-such as; a balance between "selectivity versus permeability," a trade-off between "fire resistance versus mechanical strength" and the trade-off between "barrier properties versus degradation resistance"-by primary manipulation of pore architecture, tri-phase characteristics, and functional composition on the material design level. 2. Compare three effective processes: Systematically assess the effect of MOF selection, MOF concentration, spatial structure, and interfacial interconnection on separation efficiency, fire retardation performance, and protective barrier performance. 3. Design principles of hybrid materials: This basically refers to the systematic analysis of the advantages and disadvantages of all these fabrication methods available: physical mixing, chemical conjugation, direct synthesis, and layered construction, whilst being keen on the performance and practical manufacturability of these new techniques. It is also required to prescribe design solutions, which are specially selected depending on the needs of application cases. 4. Identify what research has already been done and what obstacles are still there: In this part, we should capture the key challenges that are yet to be addressed in assuring food contact material safety. More specifically, these are also the relatively small number of flame-retardant solutions that are already available on the market, and the challenges that accompany the mass production. In perspective of the future working process, investigations should focus on improving safety testing of materials as well as advancing greener production methods. 5. Incorporate sustainability considerations: Although much attention might be paid to material functionality, one should also consider ecological considerations, reusability, and efficient consumption of resources based on a life cycle assessment (LCA) paradigm. This strategy in practice guarantees full assessment of environmental compatibility and long-term sustainability, considering the way these components interrelate throughout the entire product lifecycle.

Regarding scope, this review focuses on the key developments in research in the last decade, though it will also focus on the achievements that have been made since 2023. The discussion is on composite materials in which the continuous matrix phase is composed of polymers, and the active components are metal-organic frameworks or MOFs, which are dispersed throughout the continuous matrix phase. It also investigates the MOF-derived substances that do not lose their structural characteristics during thermal treatment. In terms of functional properties, the review is a systematic discussion of gas/liquid separation capabilities, fire-resistant properties, and attributes of packaging.

2 Structural-performance correlation analysis

2.1 Functional contributions from MOF components

MOF structures have received wide acclaim over their exceptional surface properties and this acclaim is largely due to their highly porous and ordered framework architecture. As detailed illustrations, substances like ZIF-8, UiO-66 and the MIL family have outstanding surface areas which are generally between 2000 and 4000 m^2/g. As a practical matter, the aromatic interfaces of these large scales are active in supporting a number of processes of paramount importance, these being gas adsorption, radical trapping, and formation of carbon layer(s).
The pore structure is designed so that it has hypotension adjustables, on which it is possible to modify the diameter of the pore to range between 0.5 and 5 nm allows rapid uptake of volatile hydrocarbons at the very point of combustion. This absorption, in its turn, has the effect of postponing the time at which it actually reaches the peak of the combination of combustible substances. Simultaneously, the same pore structure performs a similar task of limiting the intrusion of the polymer segments that assist in maintaining generally clear paths of mass transfer. Going to the metal active sites, they are used particularly in the temperature

regime of 250-400 ℃. Metal species are converted into oxides or carbonates in this window, including Co^{2+}, Zn^{2+}, Fe^{3+} as well as Zr^4+. These newly obtained species in turn serve as triple functionality catalysts that account for the carbon formation effected by Lewis acids, CO oxidation, and radical suppression. These sites in real-life situations become the main sources of kinetic activity, which leads to three effects: creating a thermal barrier, inhibiting smoke, and facilitating detoxification. Reviewing the literature, cobalt-based MOFs usually demonstrate a reduction in peak heat release rate (pHRR) that is 10 to 20 percent greater than can be achieved using iron-based MOFs. This comparison, in turn, throws light on the highest importance of the choice of the metal center to the total performance.

The case of the contribution of the polymer unit is as follows:

Mechanical adaptability: Addition of flexible aliphatic amine functional groups or reinforcement of the cross-linked polymer framework can be used to address the brittle nature that rigid particles of MOFs are known to cause, and still retain thermal stability at the same time. Practically, this method will maintain over 90 percent of the original resistance to impact and this implies that the material will retain most of its shock-absorbing capabilities. Flexibility in manufacturing: The ability of different processing methods to form films with solvents, or through vacuum-assisted resin infusion and photopolymerization at controlled temperatures, can be used to conveniently work around thermal limitations that most MOFs are subject to. When these strategies are implemented, the processing conditions become much more desirable. This, in its turn, assists in the maintenance of the structural integrity of the framework materials in the very process of manufacturing it. Interfacial bonding properties. In this specific system, the epoxy functional groups may either react during ring-opening reactions or form hydrogen bonds with the surface functional groups ($-NH_2$, -COOH, H_2PO_3) on MOFs. Such an interaction between interfaces results in strong interfacial anchors of the molecules immediately at the interface. Practically, this always leads to a lower content of voids of less than 2 percent, which not only provides effective stress transfer but also prevents the formation of particle aggregates.

2.2 Positive synergy: Strengthened properties that are stronger than mere additive effects.

Mechanical property improvement: By fixing the intrinsically rigid structure of MOFs with the flexible epoxy polymer chains, an interlocking network structure of nature that is hybrid is obtained and exhibits what is what can be termed as a rigi inflexible nature. This architecture scales to a 30-60 percent enhancement of material stiffness, and at the same time maintains (in some cases even slightly improves) the fracture elongation property of the material. Also, the purposefully designed functional interface at the interface between components contributes greatly to it, which increases the shear resistance three times. Synergy between thermal decomposition and flame retardancy MOFs can serve as a catalytic agent to enhance the initial stages of carbonization, which actually initiates the entire process and occurs at temperatures up to 20 to 40 ℃, or approximately 20-40 ℃ lower than otherwise. Simultaneously, the epoxy matrix prevents the volatilization of the ligands excessively, and one of the positive sides of this issue is that it leads to 50-90% increment in the char yield. The thin carbonaceous coating thus formed has solid thermal protection, and in practice, forms a 40-70% decrease in peak heat release rate (pHRR). Multifunctional composite design is based on the porous architecture of MOFs, and different functional small molecules, such as DOPO, ionic liquids, and HCCP are common examples that can be introduced into one structure. This in practice, means that flame retardancy, smoke suppression, toughness improvement, and electromagnetic shielding are all capable of being incorporated at the same time as one filler system. This will effectively reduce the complexity of formulating materials by a large margin, as many of the functions will be incorporated into one component.

2.3 Counteractive effects: Performance trade-offs

Pore obstruction phenomenon: Due to the conditions of a real process, namely, extrusion of molten epoxy or high-viscosity surroundings, it is likely that the chains of polymer epoxy can enter the interior cavities of metal-organic structures. Such intrusion of structure normally introduces a significant decrease in surface region, typically in 40-60 range and as a direct fit result in approximately 20% loss of adsorption catalytic efficiency, in addition to smoke suppression powers. Thermal degradation of organic ligands is a serious situation that usually arises in two conditions, namely, when processing temperatures exceed 250 ℃, or when acidic curing agents are incorporated into the formula. In both instances, hydrochloric acid degradation takes place, which in turn initiates the creation of the ligand bond rupture. This framework destruction results in the end in breakdown of the structure, loss of the metallic active centers and deterioration of the flame retardant attribute of the V-0 rating to V-2. The brittleness caused by particle aggregation is a typical problem of unmodified MOF materials, which inherently tend to have a high surface energy profile. Practically, this results in particle clustering at concentrations more than 5% by weight. Since the aggregation also forms stress points within the material in a localized way, the overall outcome is the loss of impact resistance of between 15 and 25 percent [1].

3 Dimensional regulation and fabrication method of polymer/MOF hybrid materials

3.1 Mechanical mixing method

The creation of polymer/MOF composites is usually based on physical blending methods, and the more popular ones are solution-based mixing and melt processing. MOF particles are dispersed in a polymer solution by using appropriate solvents in solution blending, then by evaporating the solvent or precipitating the mixture, the composite is obtained. Such a technique is attractive to researchers due to its simple design and wide applicability in a wide range of polymer-MOF interactions, but it encounters both practical challenges: the distribution of the particles becomes uneven, and it is always hard to fully eliminate any traces of solvents. In the meantime, melt extrusion consists of the combination of MOFs with molten polymers at high temperatures, and the extrusion of the product. The method is particularly effective with thermoplastic substances and can be adapted to continuous production, although the nature of thermoplastic substances dictates that the high temperatures needed to deposit the material tend to damage the MOF structure, or to reduce its performance, so the thermal stability of the MOF is a critical consideration that must be considered carefully.

3.2 On-site/one-pot polymerization

In situ polymerization is a method that fundamentally entails the combination of metallorflexible-organic structures (MOFs) and polymers, which involves the combination of both actions into a unified procedure. In the real synthesis, they are instead simply added into the reaction mix, thereby enabling the precursors of MOF to grow or polymerize inside the polymer network itself. Consequently, this method enables high effectiveness in incorporating the MOF and polymer fragments on the molecular scale. This causes distinctly superior MOF distribution in the polymer medium, intensifies the interphase bonding, and, as a result, improves both the mechanical properties and the functional behavior of the resulting composite materials. Nevertheless, reaction parameters, such as temperature and concentration, still require close regulation to ensure the reproducible development of MOF and the correct progression of polymer formation.

3.3 Post-Synthesis Grafting

In materials chemistry, post-synthetic modification refers to the chemical functionalization of existing metal-organic frameworks; that is, creating a means of modifying their characteristics once already synthesized. Practically speaking, the method provides scientists with the means to fine-tune the properties of MOFs in two major directions: by adding new functionalities where the frameworks have not had them initially or by improving the ability of the structures to integrate with other polymers. Several different chemical reactions can be used to accomplish this modification, with the most common being radical polymerization, ring-opening polymerization, and condensation reactions. By judicious choice of the technique of modification procedure and defining parameters of reactions, it is possible to control the density of affixed functional groups and the chain length of polymers rather precisely, and this, in its turn, can be used to adjust the overall performance properties of the resulting composite material to a considerable level.

3.4 Interface-oriented assembly

In materials science, interface-directed assembly is a method of essentially the joint assembly of metal-organic frameworks (MOFs) with other polymeric substances by exploiting interfaces between them. This method allows the attainment of exact spatial organization of MOF components in polymer media, and this control is normally achieved by a thorough control of both chemical composition and physical parameters at the interface. Practically, there are various outlines of implementation on such an assembling process, such as spontaneous self-organization and template-aided approaches, and external field-driven alignment. These interfacial-engineered materials may show observable gains in strength and thermal resistance of their materials as well as functional activity, yet such gains may require complex fabrication criteria and microscopic control of processing conditions.

3.5 Green amplification

Discussing the concept of green large-scale production in the said context, we simply mean to apply to the production of polymer/metal-organic framework (MOF) composites the central tenets of green chemistry. The point is to streamline the whole process in such a way that it minimizes or even avoids the use of harmful solvents and reagents, in addition to decreasing the consumption of energy and environmental pollution. To be more specific, in mechanochemistry, instead of chemical energy, mechanical energy is employed to create the reaction, which has such practical benefits as solvent-free processing, high efficiency, and reduced impact on the environment. Secondly, the spray drying technique is capable of drying and molding polymers and MOFs in a very short period, and this reduces a lot of energy consumed. In the meantime, continuous flow synthesis consists of flow reactors that are utilized to obtain the efficient synthesis of the material and formation of a composite that enhances the production efficiency without interfering with the quality of products. Altogether, this green production concept not only contributes to the sustainable development of polymer/MOF composites but also provides improved conditions for their industrial manufacturing and practical use.

4 Polymer/MOF Composite application.

4.1 Flame-retardant polymer

4.1.1 Imidazole or carboxylate ligand Flame-retardant MOFs

Some of the sturdy metal-organic structures, including the ZIF series, UiO compounds and the MIL compounds can be included in polymer lattices through simple physical blending, giving rise to new composite materials with enhanced fire resistance. The literature has pointed out certain examples [2], such as cobalt-based ZIF-67, zinc-based ZIF-8 and iron-based MIL-53(Fe), that have all demonstrated a discernible flame suppression when added into the framework of epoxy resin. Comparative analysis showed that the cobalt and zinc variants were more successful in the control of the smoke production and the release of thermal energy. In other words, as far as the minimization of the peak heat release rate (PHRR) and the average mass loss rate (AMLR) is concerned, the cobalt MOF should be listed first, then the zinc MOF, iron MOF. Based on reference [1], the research team sought to answer what would intervene on the performance of epoxy resin on three main dimensions, namely thermal properties, smoke generation patterns as well as carbon monoxide emissions of different types when different metal components were used and when ligands were designed with different configurations. By comparing, they found that cobalt-based MOFs exhibited greater resistance to fire compared to other organic ligands of the same organic ligands being the same. Further on studying MOFs containing rare earth metals in them, in particular, y-mof, La MOF, and Ce MOF, the y-mof proved to have significantly enhanced fire suppression properties. Lastly, computational modeling revealed that Y2O3 had the highest radical scavenging ability compared to all the other compounds tested.

4.1.2 MOFs of other ligands

A viable method of making MOFs that actually happen to be good flame retardants is to introduce specialized ligands, in their turn, endowed with fire-resistant properties, as a result of which the resulting material will be able to call upon those familial protective elements. As an example, let us refer to [3], where the researchers succeeded in synthesizing phosphorus-containing MOFs (or P-MOFs), combining functional ligands: bis(p-aminobenzoic acid) phenyl phosphate amide (DAAPA) and binding them to the cobalt ions, which serves the purpose of weaving the phosphorus-based components into the MOF framework. As this specific strategy was experimented in epoxy resin composites, it demonstrated significant changes in catalytic oxidation capacity, namely, CO emissions were reduced by a considerable 52 percent and CO 2 release was increased by 6.25 percent, meaning that the P-MOFs were aiding in the conversion of carbon monoxide into carbon dioxide. Another good illustration of this concept can be found in reference [4], which explains how yet another version of phosphorus-rich MOF was synthesized. Tris(p-aminobenzoic acid) phenyl phosphate amide (tri(PABA)PA) ligands were used in this study and they attached to cobalt ions, producing the resultant P-MOF. When this material was brought into the epoxy resin composites, it showed excellent flame-retardant behavior, and a UL-94 V- 0 test was performed successfully, reaching a limiting oxygen index (LOI) of 29.0 percent at the normal test condition. Moreover, in combustion, the substance produced a stronger and smaller layer of char, which also increased its overall resistance to fire several-fold.

4.1.3 MOFs were obtained as flame retardants

In practical laboratory procedures involving the work with layered double hydroxides (LDHs), the traditional synthesis pathways, including the ion exchange pathway, co-precipitation pathway, and hydrothermal pathway, usually face real-life challenges. To be more precise, it is often rather difficult to regulate the particle sizes and structure, and on the surface characteristics, and so on, to a considerable degree in reality. Metal-organic frameworks (MOFs), in turn, have proven useful as templates towards the development of LDHs with designed architectures and specifically the hollow three-dimensional structures that have become of interest to researchers. With the help of reference [1], a research team employed graphene oxide-supported, acid-sensitive ZIF-67 composites as these were the starting precursors. By using a three-dimensional assembly method, they were able to produce a type of sandwich-like structure referred to as rGO renewed. This new design brought significant positive changes in a variety of performance indicators, and the thermal conductivity of epoxy composites actually achieved the value of 0.421 Wm K^{-1}, and the glass transition temperature and total mechanical performance of those final materials were significantly enhanced. As mentioned in reference [5], scientists have come up with a new type of dual-layered LDH comprise of material named MgAl-LDH@NiCo-LDH (abbreviated as MgAl). Precursors to the NiCo-LDH nanosheets are the ZIF-67 nanosheets, and upon deposition on MgAl-LDH substrates, the nanosheets are quite well distributed. This type of architectural construction significantly improves the dispersion of the building material and the fire-resistance of the LDH. Of particular interest is that at 2.5% by weight of MgAlSequestration rate of MgAl NI Co incorporation, the resultant composite manages to pass the tough UL-94 V-0 classification criterion of the flame resistance.

4.1.4 Flame retardant obtained as MOFs derived from aluminum hydroxide

Based on reference [6], the researchers could synthesize the aluminum hydroxide nanomaterials that exhibit the closed structure in the form of a honeycomb-like mesoporous architecture (ATH) using acid-sensitive ZIF-8 as a structural template. The resulting engineered materials in this form have controllable dimeric pore sizes and interlocked networks of nanopores, both of which can permit a significantly increased loading capacity of phosphorus-containing small molecule flame retardants such as DOPO. In comparison analysis that was conducted between various formulations, the findings revealed that epoxy resin composite with 10 wt DOPO-loaded ATH produced the same level of flame retardancy as with 20 wt DOPO-modified aluminum hydroxide, in addition to producing better mechanical performance properties.

4.1.5 Phosphorus-modified MOF hybrid

A study has developed a new flame-retardant substance with an eco-friendly approach where the researchers synthesized a new substance labeled as PA-UiO66-NH_2 [1], which they prepared through the modification of UiO-66-NH_2 with phytic acid (PA). This composite was then combined with epoxy resin in order to test its fire-resistant properties and smoke-reducing properties. The thermo-degradation behavior of the hybrid material was fairly comparable to that of the epoxy resin matrix, and the gases that were emitted by the heating environment reacted with the filler by radical recombination. Such an interaction improved the density of cross-linking and the formation of an aromatic structure in this material. The test results revealed that the addition of 5 wt% of PA-UiO66-NH_2 resulted in significant changes; the peak heat release rate (pHRR) was reduced by 41 percent, and the total smoke production (TSP) was reduced by 42 percent compared to the unadulterated resin. Based on the study conducted by the researcher [7], researchers have achieved a phosphorus functionalized bimetallic organic structure referred to as W-Zr-MOF-DOPO, and its structural characteristics are multi-level porous. In this novel material, it is evident that there is an enhancement in the capture of both trigger catalytic carbonization byproducts as well as gases, which are generated through a thermal decomposition process. Simultaneously, the complex three-dimensional structure of such composite material is effective to shelter the flow of organic vapours and thermal energy and to inhibit the production of combustion particulates as well.

4.1.6 Silicon-modified MOF composites

One of the studies, as reported in [1], explains how researchers were able to prepare a SiO2@UiO-66 composite, which exhibited a clear core-shell structure. Their synthesis protocol entailed in-situ crystallization of UiO-66, rather, UiO-66-NH_2, to the epoxy-functionalized silica microspheres (E-NaO_2). The resulting engineered material had significant thermal resistivity and retained the properties of catalytic activity. In the meantime, parallel work on ZIF-8@S1O2 hybrids made by sol-gel coating methods is also reported in publication [8], in which silica coats were deposited onto existing ZIF-8 crystals. Due to this core shell design, epoxy resin blends could reach UL-94 V-1 fire rating category by only loading 2 percent additives.

4.1.7 Enhanced MOF Composites of Phosphorus and Silicon

Originally, a new flame-retardant material named MPOFs-P was first introduced in study [9], it combines polysiloxane (POSS), phosphorus and transition metal components within the same system. Of particular interest, however, is the fact that the addition of 2% by weight of MPOFs-P increases the limiting oxygen index (LOI) of the composite to 27.0% and UL-94 V-0 certification is gained simultaneously. Practically the material also exhibits considerably superior performances in decreasing the peak heat release rates (pHRR), total smoke production (TSP) and carbon monoxide emissions in combustion.

4.1.8 MOF Hybrid Systems that contain Boron

A study assembled a state-of-the-art flame retardant by coating the surfaces of ZIF-8 with a polymer coating that takes two flame-retardant agents simultaneously - boron and nitrogen [10]. The researchers made a further step with this system since they incorporated cobalt ions to finally integrate it into the material known as ZIF-8@BP-Co. At a loading level of 7 percent, when they incorporated this material into epoxy resin, the composite passed the UL-94 V-O classification, and, practically speaking, they also recorded better mechanical properties than untreated base materials.

In the study [1], scientists report the application of hollow nanocage structures (ZNs-B/CP) into which they loaded ZIFs nanodots using a step-by-step etching strategy, whose produced materials demonstrated good thermal stability and smoke-reducing properties. In practice, the even spreading of the ZIFs nanodots on the nanocage surface, in its turn, facilitated the promotion of the decay of the epoxy resin substrate, underlying the uniformly spread material.

4.1.9 Modified MOF hybrid and graphene oxide

In one of the studies described under [11], the research team was able to develop a composite material of ZIF-8/RGO by first depositing the ZIF-8 nanoparticles on RGO sheets, which was carried out, followed by a reduction step. The design method in question is, in fact, rather effective in reducing the restacking and aggregation issues that quite often come up in GO-based materials. Simultaneously, it has managed to integrate the positive thermal conductivity of the reduced graphene oxide with the catalytic carbonization that is offered by ZIF-8 itself. The most interesting thing is that the addition of even 2 percent of the weight of this type of hybrid was enough to allow the composite to meet the UL-94 V-1 standard, and, at the same time, a much lower rate of heat production and smoke was also recorded. Another method, which is presented in [12], is the method in which the iron-based MOF crystals are grown directly on RGO surfaces. This process results in the formation of multifunctional composites, whereby the composite possesses the abilities of fire resistance in the event of a fire breakout and the ability to absorb electromagnetic waves. The findings of that study in an experimental study, revealed that the materials sustained their structural integrity when in direct exposure to flame within 20 s, which can be regarded as impressive fire-resistant work.

4.2 Membrane separation

4.2.1 Gas separation

In bubble separation processes, mixed matrix membranes using polymers along with metal-organic frameworks (MOFs) have proven to have exemplary capacity, usually surpassing those of standard materials. This development is especially important considering the emerging need for a more efficient CO_2 capture and purification system of hydrogen in the industrial environment. An exception in this list is the ZIF-b-PIM-1 composite membrane that was designed based on HSP theory and exhibits superior CO_2 capture as well as H_2 purification. Hansen solubility-based design strategy enabled achievement of high compatibility factors between the MOF filler and polymer based on the polymer, a factor that is vital in the performance. This particular membrane achieves a 31.5 CO_2/N_2 separation factor, a 20.9 H_2/N_2 selectivity, and a CO_2 permeability rate of 8409 Barrer, and increases the transport coefficients of H_2 significantly. These parameters measured are relatively large in comparison with the original Robeson upper limit that has long been used in the field as an important parameter to trade off membrane performance. This high performance is because the MOFs have a high surface area and clear-cut pore structures, together with enhanced interfacial adhesions and a distribution of particles that the HSP-based design facilitates, thus permitting effective molecular sieving and a significant increase in the rate of gas transportation [13].

4.2.2 Water treatment

Composite membranes containing metal-organic frameworks (MOFs) and polymers have been shown to be of particularly high performance in the area of water purification and have become the alternative of choice in removing contaminants. One tangible case is a composite of ZIF-8/PD-TPU that yielded remarkably high results with varying dye contaminants, i.e., methylene blue, carmine, orange G, and 4-nitrophenol, which is why this composite drew the attention of a wide range of applicants. It opened up an impressive 99 percent removal ratio of these pollutants, coupled with a water permeation rate of 3 290 liters per square meter per hour during vacuum filtration conditions, which is a very good trade-off between purification efficiency and processing speed. Such a good catalytic effect is attributed to the honeycomb structure of the membrane and the high surface area that MOFs offers and which facilitates the rapid movement of reactants and the active interaction between catalysts and pollutants to be broken down in an efficient way. Moreover, it was demonstrated that the durability of the membrane allowed it to sustain the constant flow rates following ten consecutive treatment rounds, preserving approximately 90% of catalytic activity, meaning that it is highly robust to operate and has the potential to be reused again in practice [14].

4.2.3 Preservation and modified atmosphere packaging

The use of polymer-based composite materials has received a lot of attention in recent years, primarily due to the fact that they actually have the potential of enhancing food packaging. To be more precise, the integration of the metal-organic frameworks (MOFs) with polymers has proven to be a promising avenue to expand the time interval of the food longevity, as the PVA-CNF-MOF films are a good case. These hybrid materials demonstrate unusual detection of microbial contaminants, ethylene gas and oxygen molecules and it is with the help of their enormous surface area, adaptable porosity, and the abundance of catalystic metal centers. All this helps in retarding food spoilage which is the primary reason for using state of the art packaging materials. The experimental data have indicated clearly that adding MOF framework and cellulose nanofibers into polyvinyl alcohol frameworks significantly enhances various essential properties of films, including mechanical strength, gas barrier, and light-absorbing properties. To be more particular, a PVA-CNF-MOF-801 type of material demonstrates tensile resistance increase by 130 percent over the standard PVA films, along with half of the moisture permeability, as well as the serving capacity amplified by 168 percent in terms of its ability to protect against the ultraviolet radiation. Moreover, other positive characteristics of these composite membranes are also exhibited, which contribute to their overall hygiene. Practically in the food supply chain, PVA-CNF-MOF composite film has been shown to have a definite health benefit of prolonging the shelf life of perishable agricultural products. As an example, in experiments with banana storage under normal market conditions, the film showed a wide decrease in the rate of spoilage as well as the length of freshness in the product. These conservation effects are explained by the fact that several mechanisms are acting in concert, such as; microbial activity suppression, oxidative reactions retardation, and regulating ethylene. Moreover, the approach to creating this scaffolded composite film is quite simple and easily scalable, whereas the materials are highly biocompatible and environmentally-friendly, which correlates with the opportunities of a wider approach to sustainable development. Thus, the PVA-CNF-MOF composite film, as an innovative active packaging system with multiple preservation mechanisms, has great potential in large-scale applications in the preservation of food [15].

5 Key challenges

Although polymer/MOF hybrid materials have exhibited in a few instances truly commendable features and are still going on proving useful features in a very broad field of fields, there are still several acute problems that are yet to be solved and which still appear as authentic problems as far as their practical application is concerned. Among the key aspects in this respect are the interfacial attachment of the different parts that have to be included, and this factor is very critical in the sense that it is the factor that determines whether the actual performance of the composite in practice can be successfully granted or not. The completely accurate determination of interfacial shear strength within the complete range of bonding conditions, between hydrogen bonds and covalent bonds, remains a technical challenge that is yet to be overcome. The other difficulty is based on the nature of a trade-off that exists between the processing requirement and the structural integrity. This basically implies that tradeoffs between the two are often made at the literal cost of the other of which designs must make hard decisions. Although an addition of the MOF content would definitely increase the functional properties of the material, the increase would be at the cost of film flexibility and mechanical performance. This generates a processing-structure dilemma that complicates the overarching process of material design quite a bit. In a pragmatic perspective, scalability and economic viability are the two biggest impediments that can impede commercial deployment. Recent technologies of the environmentally friendly synthesis of MOF at kilogram scales face significant challenges, and the key bottleneck is the solvent recovery systems, which are comprised of around 5% efficiency. This ineffectiveness increases the cost of production, making it, consequently, much more complicated to produce on any industrial scale and making the effective implementation difficult. In addition to these economic and technical issues, the possible environmental and health risks of these materials deserve careful attention, and the strategy of mitigation should be developed. When nano-scale metal-organic structures (MOFs) are operationally implemented, they can find their way to the ecosystems in several ways. Nevertheless, their ecological threats and their biological accumulation characteristics are not adequately studied; that is, we do not have a clear picture of their possible effects. In the meantime, the lack of standardized testing procedures by OECD also complicates the overall environmental and health assessment, a fact that renders systematic evaluation of a subject more complicated for the researcher and the authority.

6 Conclusion

These days, Polymer/MOFs have reached well beyond the period when the primary aim was merely to demonstrate that the underlying concept might be practical. Rather, the industry is getting into a newer stage where there is a practical integration of performance optimization, manufacturing efficiency, as well as environment consideration into the industry. In the next five years, it will be of particular significance to have interfacial engineering correct and to have large-scale production to have a viable opportunity of being adopted by real industries. Through the systematic exploration of structure-property mechanisms, synthesis, and other technical obstacles, these composites have real potential to be implemented in real applications in a number of applications, such as flame resistance, selective membrane filtration, controlled atmosphere packaging, and other similar applications. With such progressive development, it can potentially have a significant beneficial effect on the building of next-generation high-performance polymeric materials.

Based on the given structure and chosen literature, this review incorporates a variety of aspects of polymer/MOF composites. The basic properties of these materials and the relationship between structure and performance are discussed in detail, the manufacture of these materials and their applications in practice are discussed, and limitations which are currently being encountered and potential future research directions are also discussed. In other words, this is aimed at providing the researchers in this interdisciplinary field with some useful insights that they can use.

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