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How Can the Filler-Polymer Interaction in Mixed Matrix Membranes Be Enhanced?

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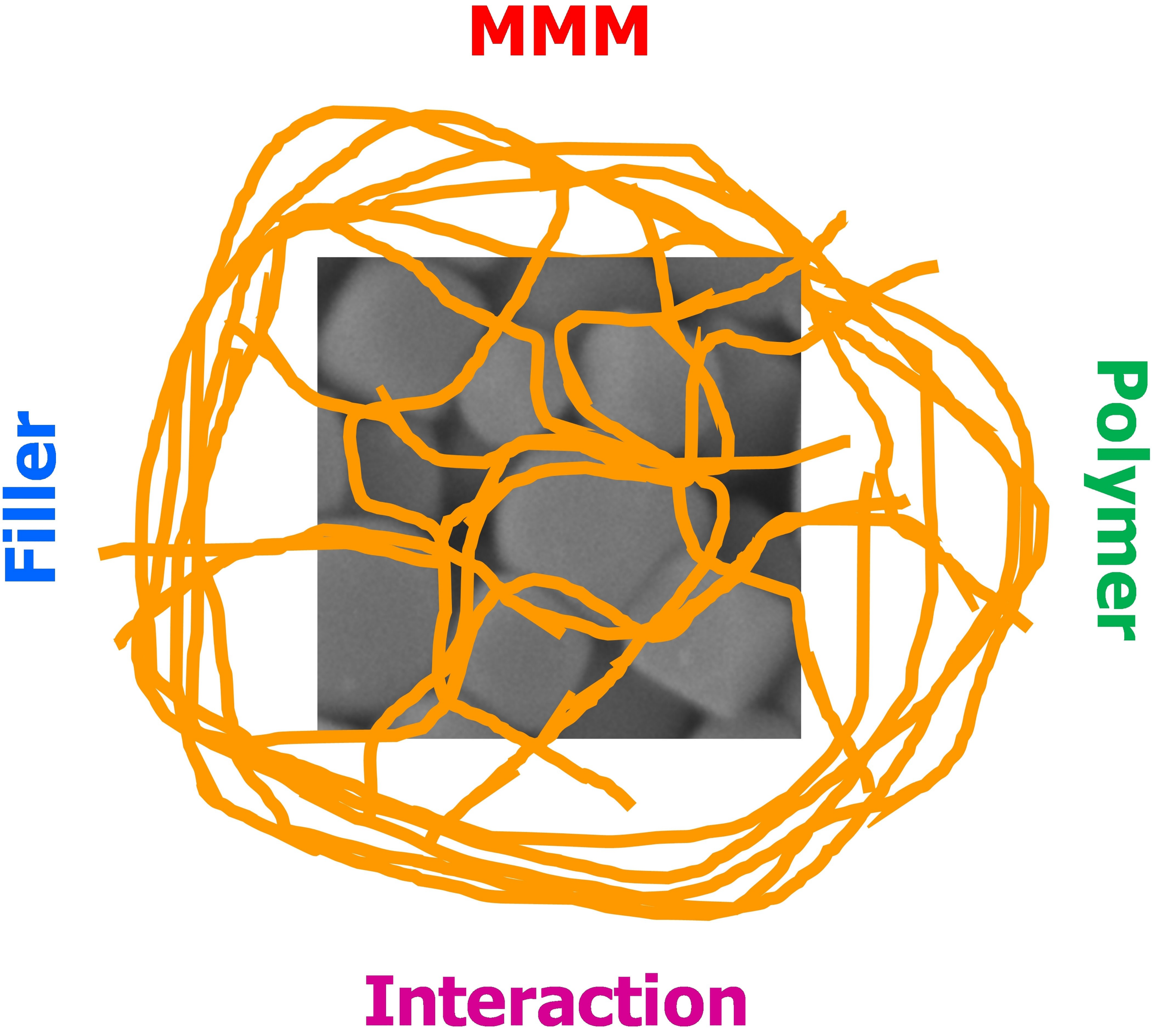

Mixed matrix membranes (MMMs) constitute a type of molecular separation membranes in which a nanomaterial type filler is dispersed in a given polymer to enhance its selective permeation ability. The key issue in MMMs is the establishing of a proper filler-polymer interaction to avoid non-selective transport paths while increasing permeability but also to improve other membrane properties such as aging and plasticization. Along the pass years several strategies have been applied to enhance the physicochemical interaction between the fillers (e.g. silicas, zeolites, porous coordination polymers, carbonaceous materials, etc.) and the membrane polymers: increase of external surface area, priming, use of intrinsically more compatible fillers, in situ synthesis of filler, in situ polymerization, polymer side-chain modification and post-synthetic modification of filler.

1. Introduction

Anthropogenic activities cause diverse effects on the natural environment which includes, releases CO_2 with a 6% increment every year,[1] causing global warming and unpredictable climatic changes to the planet, water pollution by organic and inorganic pollutants. These effects are evident both in developed and developing countries, causing water borne diseases, soil adulteration which reduces its fertility, so that productivity and yield of crops are hampered, among others. Waste discharge from power plants, garment industries, oil refineries, leather tannery industries, residues of applied pesticides and fertilizers, emerging biological (e.g., super bacteria, viruses) and chemical micropollutants (e.g., hormones, toxins, psychotropic substances, drugs), etc. are the pollutants of major concern. Consequently, under the International Initiative for Water Quality (IIWQ), UNESCO marked that water quality degradation directly causes environmental, social and economic problems. Moreover, the general assembly of United Nations at New York in 2015 adopted the agenda 2030 for sustainable development, which consists of 17 sustainable development goals (SDGs) to mitigate the pernicious anthropogenic effect on earth environment. Some of these goals are: SDG6 (clean water and sanitation), SDG7 (affordable and clean energy), SDG13 (climate action) and SDG14 (life bellow water). In line to the proposed SDGs, global entities agreed during the Paris COP21 in 2015 to limit the global temperature rise below 2 °C,[2,3] something confirmed at the Glasgow COP26 in 2021.[4] In this context, membranes appear as an attractive choice to be considered due to their affordable cost of production, easy installation and scale up and diverse field of application to treat both water and gas effluents.

After a long historical lab-based development, membrane technology achieved its placement in industrial application in 1960s. Nevertheless, during the past 70 years, research has improved and diversified membrane application in a significant extend, which cover water and dairy refinement, water desalination, waste-water treatment, beverage production, gas separation, energy conversion and storage, air pollution control, hemodialysis, proteins and microorganism separation, among others. Indeed, these applications have brought significant improvement towards sustainable growth for environment and public health.[5] Membranes can be classified by their morphology, geometry, methods of synthesis, separation methods and the nature of the material, etc.

Gas separation with membranes is characterized by two main parameters, permeability and selectivity. The higher the permeability, the lower the selectivity and vice versa. In consequence, membrane-based gas separation is limited by the so-called permeability-selectivity upper bounds established for the gas mixtures to be separated,[6] e.g. those corresponding to CO_2 and H_2 containing mixtures involved in carbon capture and H_2 purification.[7] On the contrary, solute/liquid separation follows a different phenomenon wherein permeance, permselectivity and rejection are the key parameters which determine the membrane performance.[8] Component gradients between upstream and downstream significant determine the separation efficiency for both class of separations. As main drawbacks, gas separation (e.g. CO_2 separation) may produce membrane plasticization, whereas liquid phase separation suffer from membrane fouling.[9,10] However, commercial membranes for gas separation are usually based on polymeric materials. To try to surpass such upper bounds, these polymers can be modified with fillers constituting mixed matrix membranes (MMMs) or thin film nanocomposite (TFN) membranes, i.e. membranes with a thin MMM as selective skin layer placed on top of a porous support, as shown in Figure 1. However, key challenges in MMMs fabrication are filler incompatibility within polymeric matrix and agglomeration tendency of fillers (due to strong inter-filler interaction).[11] The fillers can be of different nature but mainly are materials like porous carbons, silicas, zeolites, metal organic frameworks (MOFs), covalent organic frameworks (COFs) or graphene and its derivatives. However, MOFs are considered better than the other fillers due to their crystallinity, chemical stability, narrow porosity, specific adsorption features and flexible organic-inorganic structure able to stablish a suitable interaction with membrane polymers for homogeneous dispersion and then high separation performance.[12]

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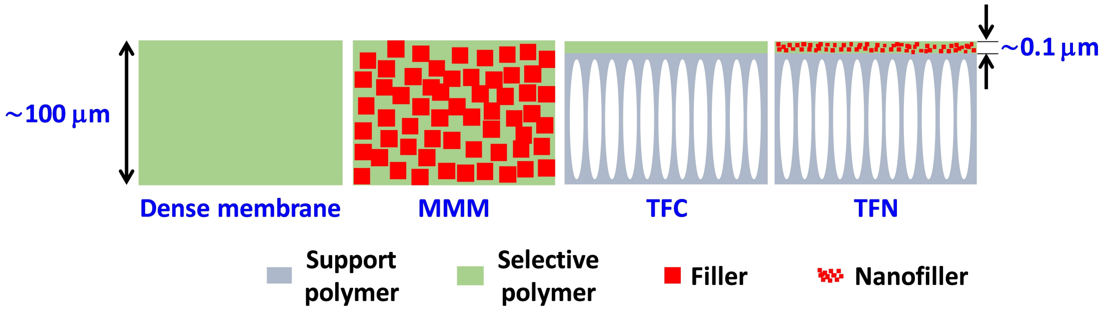

Figure 1. Different types of polymer-based membranes: from left to right, dense membrane, dense mixed matrix membrane (MMM), thin film composite (TFC) and thin film nanocomposite (TFN) membranes.

Even if the term "polymer" can be extended to many systems (including inorganic ones), organic polymers are typically the result of the existence of residual forces (van der Waals forces and hydrogen bonding) among thousands of molecules. When a filler (in principle a material of different nature to that of the polymer) is inserted between the polymer chains to constitute a MMM, a disruption is created, usually translated into an increase of permeability followed by a decrease in selectivity. The goal has been along the years the compensation of such disruption through the creation of a suitable filler-polymer interaction. This interaction has had roughly four key evolutions from the first MMMs based on zeolites (microporous porous materials with low external surface area): from zeolites[13] to non-ordered silicas,[14] then to ordered mesoporous silicas,[15] then to zeolites or related materials with large external surface areas (i.e. colloidal zeolites and delaminated pseudozeolites[16]) and then to porous coordination polymers like MOFs.[17]

All those generally porous materials have contributed to the understanding of the filler-polymer interaction mainly through two aspects: i) enhanced interaction due to external groups like hydroxyls and polymer functionalities, and ii) enhanced compatibility when using a filler (like MOFs and COFs) with organic moieties with a higher affinity (sometimes exacerbated through post-synthetic modifications) to polymers ("like dissolves like").[18] Having said that, this work focusses on the study of the filler-polymer interaction in MMMs. Even if this constitutes a transversal field of research, the short perspective proposed here has yet to be addressed, as shown by the absence of monothematic treatment in recent reviews dealing with MMMs and TFN membranes.[7,12,19–23] Finally, Table 1 summarizes the main strategies used to enhance the interfacial compatibility between fillers and polymers used to constitute MMMs and discussed here.

2. Increase of External Surface Area of Filler

This is perhaps the most expanded approach to improve the filler-polymer interaction of composites, particularly MMMs. It has three versions: i) use of mesoporous materials (where the specific surface area is considered external area because of its easy access), ii) use of nanoparticles (NPs) and iii) use of high aspect ratio nanolaminates. NPs are typically generalized in most MMM and TFN membrane approaches, since it is believed that NPs have the potential of produce ultrathin membranes).[24]

Due to their microporosity and crystallinity and potential synthesis as nanoparticles (colloidal zeolites), zeolites were the first fillers used in MMMs.[13] However, even if their external area increases, and thus the zeolite-polymer interfaces,[25] as their particle size decreases, this advantage was not enough to produce good membrane composites. In some cases, the zeolites need of calcination at high temperature (e.g. MFI-type zeolite) for activation what favors their strong aggregation

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Table 1. Overview of the strategies for better interfacial compatibility in MMMs.

Strategy	Effect
Increase of external surface area of filler	Enhance of filler-polymer interaction
Priming	Enhance of filler-polymer wetting
Use of intrinsic compatible filler	Increase filler loading, enhance filler-loading dispersion
One pot fabrication (same solvent for synthesis and MMM casting)	Avoiding of agglomeration
In situ polymerization of the membrane selective material	Filler intimate interaction with nascent polymer
Polymer side-chain modification	Enhance of filler-polymer interaction
Post-synthetic modification of filler	Enhance of filler-polymer interaction

through the formation of Si-O–Si bonds which in turn is a cause of loss of silanol groups (that usually contribute to favor the filler-polymer interaction in silica-based materials). Besides, their low range microporosity (following the IUPAC classification, micropores are below 2 nm, while mesopores correspond to 2–50 nm) and rigid structure (e.g. only minor changes in cell volume are observed[26] through host-guest interaction as compared to MOFs)[27] do not allow polymer branch penetration. In consequence, ordered mesoporous materials (OMS, MCM-41[15] and MCM-48[28] being the most studied for the purpose) were proposed as replacement of zeolites to produce better MMMs. OMSs have high mesoporosity, evaluated as external specific surface area, upholstered with abundant silanol groups. Thus, a double enthalpic (silanol/Si-OH-polymer functionality interaction through van der Waals forces and hydrogen bonding)-entropic (polymer chain penetration into filler mesoporosity) interaction could be established between the filler and the polymer. Figure 2a shows a MCM-41 spherical particle embedded in a polysulfone matrix.[29] The matching between the sizes of the filler porosity (ca. 3 nm) and the polymer chain diameters (0.9–1.2 nm) enhances the interpenetration of both materials. In turn, this is enhanced with a proper chemical interaction by hydrogen bonding between the abundant silanols on the external surface of the filler and the electronegative oxygen atoms of the polymer (Figure 2b).

Nanosized fillers (i.e. NPs), either porous or non-porous, having high specific surface area which are being widely used and are mostly found compatible with polymers in MMMs. Nonporous nano-dimension fumed silica[14] and nano metal oxides (such as MgO, TiO_2) produce equivalent disruption in polymer chain, creating interchain microvoids which alters gas transport behavior of the pure polymer matrix.[30] However, the dispersion of metal oxide NPs at the optimum concentration improves the permeability of certain gases, while maintaining a considerable level of selectivity. Hosseini et al. reported that the inclusion of highly porous MgO NPs in the Matrimid® polymer matrix increases gas transport properties of the MMM which is a result of both inherent transport properties of porous MgO and the micro-voids observed at the particle-polymer interface.[31] Addition of other conventional metal oxide NPs, carbon nanotubes, graphene, graphene oxides, etc. have shown a similar gas transport behavior in polymer matrix but often suffers from filler-polymer incompatibility.[30] Such drawback can be solved introducing MOFs which carry both organic and inorganic properties, and so better dispersion is secured which reduces the chance of having interchain-particle micro-voids and increases the possibility of overcoming the Robeson upper bound.[6] In this sense, ultra-small MOFs (e.g. 4–6 nm UiO-66 and derivative NPs) can be considered as the most suitable fillers to constitute TFN membranes with relatively low loading due to the maximum MOF-polymer interfacial area in play.[32] If

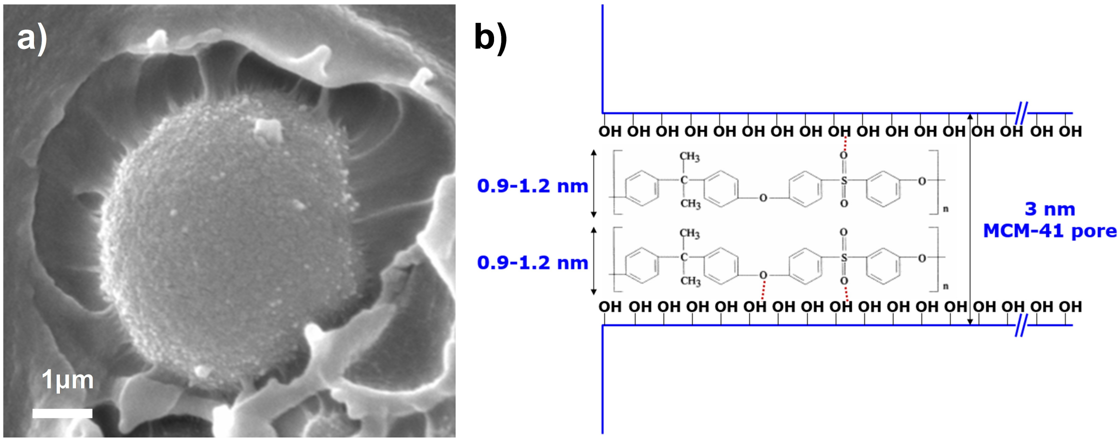

Figure 2. (a) A MCM-41 sphere embedded in a polysulfone matrix. Reproduced with permission, Copyright © 2009 American Chemical Society.[29] (b) Illustration of MCM-41-polysulfone interaction through the formation of hydrogen-bondings.

sometimes 10–50 wt% filler concentrations are needed compromising the membrane mechanical properties, these ultra-small fillers produce important effects on the MMM performance at filler loadings as low as 5–7.5 wt% (see Figure 3).[32]

Delamination of layered materials constitutes a fundamental way to increase the external surface area through the production of high aspect ratio, nanosheet particles of very small thickness. Layered materials like clays, as-available or delaminated,[33] were first used in composites based on their potential for polymer chain intercalation in between the gallery space of the clays. This intercalation changes both the local and global dynamics of the polymer in the hybrids and in the polymer bulk enhancing important properties like mechanical strength and barrier properties to gases. In this sense, Cussler's works[34,35] helped to understand the effect of impervious silicate sheets on the gas transport behavior of certain polymers. However, the first work in which a delaminated porous material was used to enhance the gas separation properties of a membrane was published in 2004 by Jeong et al.,[16] where a layered aluminophosphate (AlPO) with a porous net layer was dispersed in a polyimide generating important increases in O_2/N_2 and CO_2/CH_4 selectivities. Concerning the filler-polymer interaction, the layer AlPO was swollen by the intercalation of a surfactant (an alkylammonium cation) to allow the polymer chains easily penetrate into the interlaying space of the AlPO. As a result, the AlPO was delaminated to 5–10 nm thick laminates, randomly distributed and oriented (parallel to the membrane itself) in the polymer matrix (Figure 4) and improving the molecular sieving ability of the nanocomposite membrane.

Previous approaches are considered top-down. MOFs have made possible the application of bottom-up strategies (i.e. the direct synthesis of the high aspect ratio nanosheets directly from the MOF precursors, avoiding a top-down approach (exfoliation-delamination) needing of post synthetic treatments and purification steps, often not very effective. For instance, to produce nanosheets from the laminar MOF CuBDC, a synthesis medium composed of three liquid layers, with and intermediate liquid separating the metal and ligand solutions, was applied.[36,37] In this case, the MOF nanosheets, with 5–25 nm thicknesses, expose ca. 10 times more external surface than the crystals of the same CuBDC, resulting in increases of the filler-polymer interaction and interaction with permeating CO_2/CH_4 molecules giving rise, at 8 wt% filler loading, to a separation selectivity up to 80% higher than that of the bare polymeric membrane.[36]

Other laminates such as graphene oxide (GO or reduced graphene oxide, RGO) related to the production of high aspect

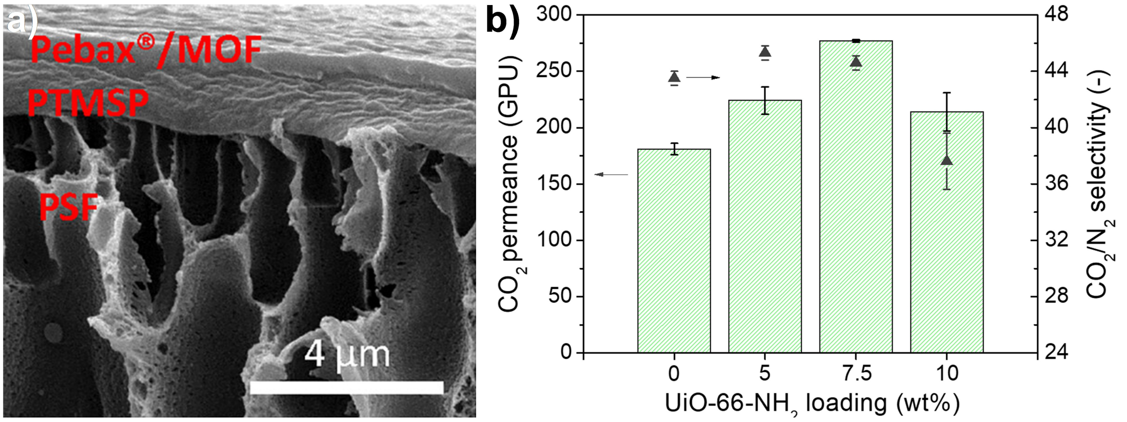

Figure 3. (a) SEM cross-section image of the Pebax® 1657 TFN membranes prepared with 5 wt% UiO-66-NH_2. (b) CO_2/N_2 separation performance at 35 °C of TFN membranes fabricated UiO-66-NH_2. Reproduced with permission, Copyright © 2024 The Authors. Published by American Chemical Society.[32]

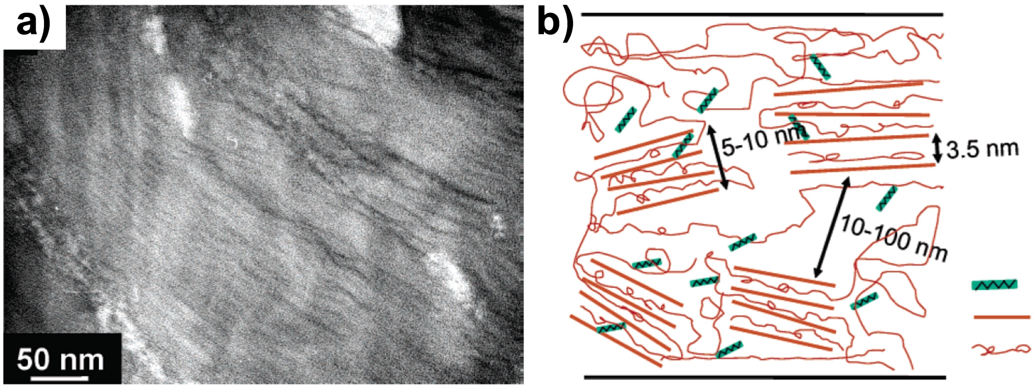

Figure 4. (a) Transmission electronic microscopy image showing intercalated AlPO. (b) Scheme of the layered AlPO-polyimide nanocomposite. Reproduced with permission, Copyright © 2004 American Chemical Society.[16]

ratio particles, sometimes with suitable chemistry due to the presence of oxygenated surface groups, have given rise to improvements in the gas separation of MMMs. An interesting combination is the use of graphite oxide as substrates to the MOF synthesis.[38,39] This heterogeneous MOF growing along the graphite oxide functionalities has two main effects on the resulting material: i) it reduces the particle size of the MOF and helps the exfoliation of the graphite oxide through the intercalation of MOF synthesis precursors in the graphite gallery space, favoring the interaction with the polymer, and ii) it produces hybrid particles with the chemistry of both materials, what can have a positive effect on the MMM performance.

3. Priming

Priming consists of impregnating the filler with a part of the total polymer and solvent to be used creating a relatively diluted suspension to which the rest of the polymer and solvent is subsequently added until completing the target MMM composition (i.e. filler loading).[40–43] With this method, usually helped by sonication, the filler particles are desired to be individualized and totally surrounded by polymer trying to favor more the filler-polymer interaction than the filler-filler interaction and consequently decreasing the undesired agglomeration. In fact, it has been observed, by combining STEM-HAADF and HRTEM techniques, that in ZIF-8-PIM-1 colloidal suspensions ZIF-8 agglomerates of a few hundred nanometers are created having a polymer top layer of ca. 3 nm thick.[44] This agrees with a moderate ZIF-8-PIM-1 affinity (also evidenced in the same work for PIM-EA-TB). Moreover, the priming can lead to success in the preparation of MMMs at higher loadings (above 25 vol%) with low compatibility inorganic fillers like zeolites.[45] Moreover, Dudek et al. have incorporated iron oxide nanoparticle within sulfuric acid crosslinked chitosan following the priming strategy to reduce the swelling effect.[46] The obtained MMM was applied in pervaporation-based separation of ethanol/water mixture, where the 15 wt.% filler based MMM showed 86 times water diffusion coefficient than the pure chitosan membrane.[46] Similarly, Sarinam et al. have reported the effect of the TiO_2 incorporation in polyvinylchloride (PVC), where it was found that MMMs increased their hydrophobicity with a less swelling effect and an increase in pervaporation water flux.[47]

Finally, Canivet et al. analyzed a set of 15 MOFs whose surface was modified with hydrophilic moieties such as amines and aldehydes and inspected their properties towards water adsorption.[48] The authors concluded that the surface modification of MOFs results in a reduction of pore filling pressure.

4. Use of Intrinsic Compatible Filler

MOFs are a promising growing class of porous crystalline materials due to their high porosity and high specific surface area (beyond 6000 m^2/g), which carries properties of both inorganic (metal ions as cluster) and organic (linker) materials.[49] Because of such inherent properties, MOFs have diversified applications: clean energy,[50] catalysis[51] and membrane separation[52] to name a few. For gas separation applications, MOFs should be well dispersed throughout the polymeric phase to produce micro-void free MMMs towards better selective molecular separations. Additionally, MOFs should have high thermal stability, active sites at their internal surface to ensure high adsorption capacity of the target penetrant (e.g. polar sites for CO_2 separation) on the surface and limiting pore diameter to ensure molecular separation.[4]

MOFs can be basically divided into two big families: carboxylate-type and imidazolate-type (zeolitic imididazolate frameworks, ZIFs). Even if the most studied MOF as membrane material is ZIF-8, one of the ZIFs with very attractive features as MMM filler is zeolite imidazolate framework-94 (ZIF-94, also known as SIM-1).[53–55] With the empirical formula of ZnL_2 (L, the ligand, being 4-methyl-5-imidazolecarboxaldehyde), it possesses a SOD topology (same that ZIF-8) and a well-defined 3D pore network, with limiting pore diameter of 2.6 Å and cavity diameter of 9.6 Å.[48,53,56] Its CO_2 adsorption capacity of 2.4 mmol g^{-1} at 100 kPa and 25 °C is far above those of other typical ZIFs (see Figure 5): 0.7–0.8 mmol g^{-1} for ZIF-8 (3.4 Å limiting pore diameter and 11.4 Å cavity diameter), 1.6 mmol g^{-1} for ZIF-7 (2.9 Å limiting pore diameter and 7.5 Å cavity diameter), 1.7 mmol g^{-1} for ZIF-93 (17.9 Å cavity diameter) and 0.8 mmol g^{-1} for ZIF-11 (3.0 Å limiting pore diameter and 14.9 Å cavity diameter) at 100 kPa and 25 °C.[57] Exteberria-Benavides et al. introduced ZIF-94 in 6FDA-DAM copolyimide matrix and the fabricated MMM was applied towards the CO_2/N_2 mixture separation, where a 40 wt % dosing of filler produced maximum CO_2 separation performance which was very close to the Robeson upper bound limit.[58] Moreover, Benzaqui et al. reported a new MOF, MIL-178, which was found compatible with Pebax® 3533 polymer matrix, resulting in the fabrication of a MMM with better gas separation performance over the pristine membrane.[59] Finally, Hasan et al. reported the reuse of

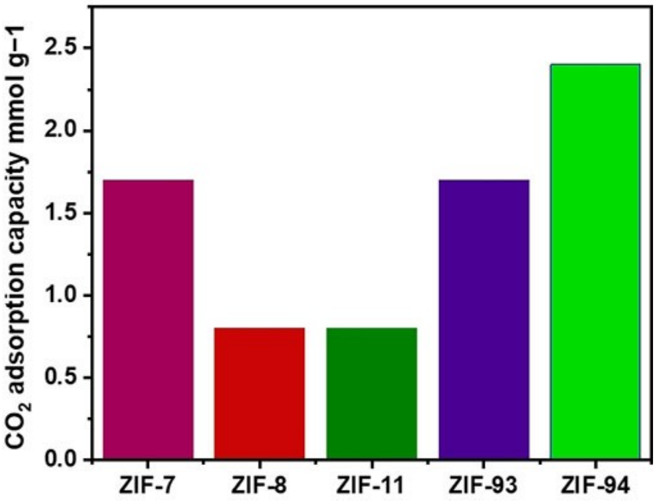

Figure 5. CO_2 adsorption capacity of different selected ZIFs at 100 kPa operating pressure and 25 °C, data were taken from.[57]

ZIF based MMM materials as a first stone to ensure their sustainable application.[4]

Another type of porous organic crystalline materials, having highly ordered and periodic network structure[60] and drawing tremendous attention in molecular sieving, are COFs.[61] COFs can be easily exfoliated into nanosheets due to the weak interlamellar interaction forces between their layers, that enable them for selective and ultrafast molecular sieving.[62,63] Moreover, COFs are extremely compatible with polymers in MMM since they feature the advantages of their pure organic nature, superior specific surface area, high thermal and chemical stabilities, and ordered and tunable porous network structures.[64,65] Due to such properties of COF particles, their inclusion in MMMs was found useful for multipurpose applications.[61,64–66] Zhang et al. reported a COF based MMM (of cross-linked poly(ethylene oxide) matrix) towards gas separation, wherein the fabricated MMM overperformed the pristine polymer membrane with a remarkable CO_2 permeability of 804 Barrer and notable CO_2/N_2, CO_2/CH_4, and CO_2/H_2 selectivities of 61, 20 and 15, respectively.[67] The resulting MMM also exceeded so-called Robeson upper bound limit reported for polymer membranes.[6]

Finally, another important issue here deals with the stability of MMMs in terms of aging[68,69] and plasticization,[70] where the filler (e.g. MOF)-polymer interactions may restrict the re-conformation of the polymer chains (maintaining them in their initial positions) enhancing the membrane stability.

5. One Pot Fabrication (Same Solvent for Filler Synthesis and MMM Casting)

MOFs are typically crystalline materials, whose structure and other special properties can be altered during their post synthesis handling. An interesting approach to keep the original properties of the MOFs, ensuring their better affinity and performance in MMMs, consist of their crystallization in the polymer suspension (i.e., in situ synthesis) prepared to cast the MMM. In line to that, Seoane et al. showed a unique one-pot methodology for MMM fabrication where the carboxylate-type MOF MIL-68 was synthesized in the polysulfone (PSF) cast solution in THF (the solvent for both the MOF synthesis and the MMM casting).[71] Besides being a clear simplification, such approach reduced crystal separation and drying steps and allowed the fabrication of MMMs with superior gas separation performance as compared to the pure PSF membranes for both CO_2/N_2 and CO_2/CH_4 gas mixtures.[71] Moreover, Chen et al. later demonstrated the in-situ synthesis of ZIF67-PA12 nanocomposite powders where a uniform distribution of ZIF-67 crystals on the PA12 polymeric surface was observed.[72] Marti et al. reported MMMs fabricated with both traditional and in-situ synthesized UiO-66 (in Matrimid® polyimide polymer matrix) where both membranes were found equivalent, which justified legacy of the in-situ approach.[67] Additionally, Maleh and Raisi carried out the in-situ synthesis of ZIF-8 in Pebax® 2533, then compared with conventional ZIF-8 in MMM for gas separation performance.[73] Wherein, prior filler based MMM showed a 28% increment in CO_2 permeability (from 57.5 Barrer to 73.2 Barrer), and CO_2/N_2 and CO_2/CH_4 selectivity improvements by 250% (from 23.4–82) and 208% (from 10.6–32.6), respectively. Moreover, Zhao et al. reported a new approach for gas sensor by fabricating a MOF based MMM through an in-situ self-assembly approach of MOF in the polymer matrix solution. The resulted gas sensor MMM was found successful with visual detection limit of 3.2 ppb of HCl(g) within 1 min of response time.[74]

6. In Situ Polymerization of the Membrane Selective Material

MMMs prepared following the conventional approaches face several challenges such as continuous and defect free membranes for high filler loading due to high viscosity, poor compatibility between filler and polymer, uncontrolled membrane thickness and non-uniform dispersion of fillers. Such drawbacks can be solved by polymerization of percolating monomers (sometimes with the help of an initiator) through inter-MOF interstices, thanks to in situ polymerization. Li et al. have reported the preparation of MMMs by an in-situ polymerization procedure where they have used ZIF-8 as a model MOF.[75] Wherein, acrylate monomers glycidyl methacrylate and butyl methacrylate were selected since they are readily polymerizable in aqueous solution. The MMM fabrication was performed following two stages: firstly, MOF particles were deposited on a porous substrate through filtration, then monomers and initiator solution was percolated onto the MOF layer. Variation of MOF concentration plays a vital role on the achievement of an optimum selective layer thickness which significantly determines the separation performance of the membranes. The optimized membrane (42 wt% ZIF-8 loading) was found satisfactory for Congo Red dye nanofiltration with a maximum rejection of 97% and water permeability of $1.12\ L\,m^{-2}\,h^{-1}\,bar^{-1}$.[75]

It is interesting to note that a clear precedent to this approach is the preparation of thin film nanocomposite (TFN) membranes by interfacial polymerization (IP) with nanoporous fillers, first carried out with zeolites[76] and then with MOFs for nanofiltration[77] and also gas separation[78] (see Figure 6). In particular, Sorribas et al. reported the synthesis of TFN membranes for organic solvent nanofiltration, which were fabricated dispersing selective MOFs in the polyamide (PA) layer placed on top of the cross-linked polyimide support via in situ IP.[77] With this technique the filler nanoparticles are totally embedded in the PA membrane, whose formation is affected by the presence of the filler until the point that it favors the synthesis of thicker PA films.[78] Interestingly, other authors have hypothesized that the acid generated during the interfacial polymerization reaction may degrade the MOF (ZIF-8) structure releasing Zn^{2+} cations that, as Lewis acid catalysts, influence the PA membrane formation from its monomers.[79]

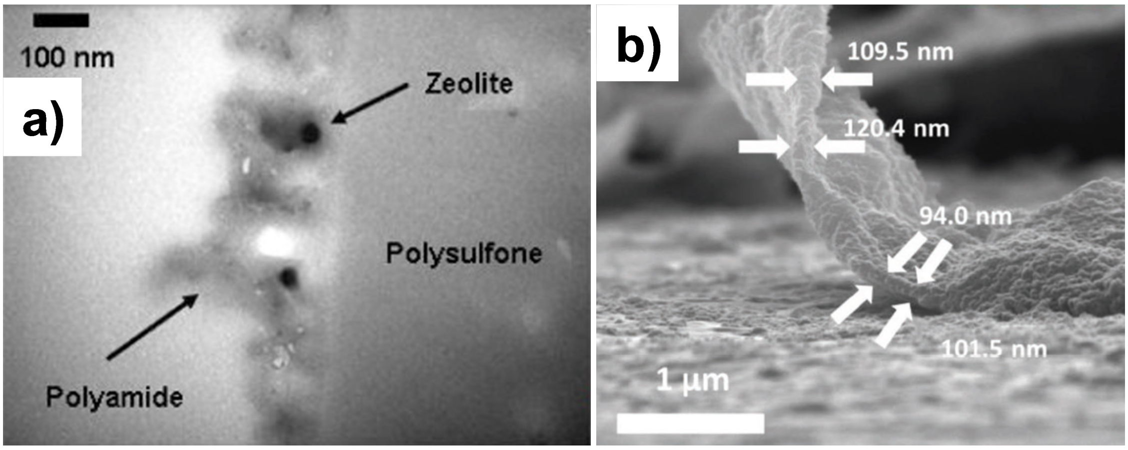

Figure 6. (a) Transmission electronic microscopy image showing cross section of PA film with zeolite A nanoparticles. Reproduced with permission from,[76] Copyright © 2007 Elsevier B.V. All rights reserved. (b) Scanning electronic microscopy image of TFN membrane with ZIF-8 nanoparticles detached from the polyimide support; the arrows show the thickness of the PA layer, reproduced with permission from,[78] Copyright © 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. All rights reserved.

7. Polymer Side-Chain Modification

In addition to the modification of filler surface, it is also possible to modify polymer side chain with new functional groups which will provide favorable sites for fillers to be incorporated with good filler-polymer interaction. In line to that, Jiang et al. reported that MMMs can be prepared by modification of polysiloxane side chain with thiol (−SH) functional group, which enabled the self-assembly of methacrylamide decorated UiO-66-HN-Met in the polymer matrix.[80] The authors used the resulted membrane as a platform to support gold nanoparticle to fabricate a highly efficient continuous through-flow composite membrane reactor for Knoevenagel condensation of 4-nitrobenzaldehyde with malononitrile and 4-nitrophenol reduction at ambient condition.[80] Moreover, Zhang et al. demonstrated that the presence of hierarchical triptycene units in polyamide matrix allowed well dispersion of ZIF-90 filler without agglomeration.[81] The authors claimed that the conjunction between organic ligands in ZIF-90 and triptycene units was responsible for the good filler-polymer interaction achieved. Additionally, the study of the literature suggests that such polymer side-chain modifications can also directly influence the gas separation performance of the obtained MMMs. The existence of polar groups having intensive affinity towards CO_2 in the membrane produce a better separation performance dealing with CO_2/N_2 or CO_2/CH_4 gas mixtures. Accordingly, poly(ether-block-amide) (PEBA) copolymers (which contain polyether polar functional groups[57]) are interesting for CO_2 separation application since they offer high permeation for quadrupole CO_2 molecules without sacrificing mechanical stability and selectivity.[3] Recently, Lee et al. have proposed energy efficient and plasticization resistant MMM for the separation of the propylene/propane mixture with C_3H_6 permeability of 6.3 Barrer and C_3H_6/C_3H_8 selectivity of 23.7.[82] They cross-linked polyimide (6FDA-DAM) with ethylenediamine to increase the polymer matrix compatibility with MOF (UiO-66 and UiO-66-NH_2).[82]

8. Modification of Filler

To increase the compatibility between fillers and polymers, often dispersing particles are modified with functional groups, which increases filler interaction within the matrix phase. Accordingly, Zornoza et al. reported that the modification of MIL-53(Al) with amino functional group (i.e. NH_2-MIL-53(Al))increased its compatibility in PSF based MMMs, which eliminates chances of internal defects in the membranes.[83] The modification was done through the use of an amino-functionalized ligand during the synthesis of the MOF. As a result, such membranes were found effective for CO_2/CH_4 separation with a selectivity of ca. 48. Feizani et al. uncovered the effect of the -NH_2 functionalization on MIL-53(Al), founding that a NH_2-MIL-53(Al) containing MMM surpassed the MIL-53(Al) based MMM in terms of CO_2/CH_4 mixture separation performance.[84] Along their work, the authors confirmed an increased interaction between the MOF crystals and the polymer matrix. Similarly, Wang et al. used Zr-MOFs NH_2-UiO-66 and UiO-66 in polyimide to fabricate MMMs, where they found that NH_2-UiO-66 based membrane showed a better separation for both CO_2/N_2 and CO_2/CH_4 mixtures. They further claimed that the MMM containing NH_2-UiO-66 overcame the Robeson upper bound 1991 but failed to exceed that of 2008.[85] In another research, Xin et al. reported that the modification of MIL-101(Cr) with sulfonic functional group increased its compatibility with sulfonated polyetheretherketone polymer matrix.[86] The MMM having the modified MOF overperformed that of the non-modified MOF based MMM in terms of both CO_2 permeability and CO_2/CH_4 selectivity. Eventually, the resulted MMM having the sulfonated version of the MOF overcame the Robeson upper bound.

In addition to the persisting approaches for fabrication of MMMs, there are still possibility to enhance their performance thanks to the approach of post-synthesis modification (PSM) of filler. Such modification can be performed by solvent assisted ligand exchange (SALE) which was first reported by Karagiaridi et al. for catalysis application.[87] Sanchez-Lainez et al. monitored the continuous exchanging of ZIF-8 with benzimidazole to obtain a variety of hybrid ZIF-8/ZIF-7 core-shell structures.[88] The resulted hybrid structure was dispersed in PBI polymer matrix to fabricate a MMM with remarkable H_2/CO_2 separation over pristine PBI with H_2 permeability of 1921 Barrer and H_2/CO_2 selectivity of 11.8.[88] Delving deeper into the same idea, Yu et al. reported that SALE can be applied to synthesize hybrid MOF structures wherein they synthesized 13 different complex MOF architectures with application as precursors for carbons for electrochemical storage of sodium.[89] Recently, Perez-Miana et al. modified by SALE ZIF-8 with 2-undecylimidazolate (see Figure 7) and incorporated it, making the MOF more hydrophobic for better compatibility with polymer, to fabricate polymer PIM-1 based MMMs which were applied to separate a mixture of CO_2/N_2 where an improved separation performance was observed. In fact, the gas separation performance of the 10 wt% modified ZIF-8 MMM overcame the Robeson upper bound 2008.[90] Moreover, Cseri et al. applied the PSM method covalently grafting UiO-66, UiO-67 and UiO-68 nanoparticles with poly(N-isopropylacrylamide).[91] The resulting structure confirmed good interfacial properties which mitigated interfacial pinholes in MMM towards nanofiltration applications.[91] Recently, Wang et al. have reported surface modification by covalently bonding of Schiff based network (SNW-1) with polyvinylamine (PVAm) which was noted as SNW–P.[92] MMM based on PVAm showed better dispersion of modified filler (SNW–P) compared to unmodified SNW-1, which suggest PSM as an efficient approach to overcome filler-polymer incompatibility.[92]

However, while functionalizing MOFs by either approach, care should be taken to ensure their porosity is not drastically altered when a bulkier linker is applied, so that the remaining porosity is able to play the expected filler role of allowing selective diffusion and solution. Finally, in addition to the amendment of functional groups on fresh MOFs, it is possible to modify accessible MOFs on the surface of MMMs as well. In line to that, Denny and Cohen unveiled the possibility of in-situ PSM of MOFs on the surface of MMMs with different functional groups to increase the affinity between the MOF and polymer matrix, helping to avoid micro-voids in their interface.[93] These authors functionalized (towards UiO-66-NH_2) 33% of the surface accessible in MOF UiO-66 particles on the fabricated MMMs made of polymer polyvinylidene fluoride (PVDF) by immersing the membrane in 2-amino-1,4-benzenedicarboxilic acid at 55 °C for 24 h. Such PSM could be increased up to 75% by treating UiO-66-NH_2 MMMs with acetic anhydride at 55 °C for 24 h.[93]

Additionally, a new computational approach has been showcased to increase filler/polymer interaction at their interface which termed as engineered interfacial interlocking structures.[94] Such structures are obtained due to the persistence of defects at MOF surface which creates interfacial pocket wherein part of the polymer chain backbone is interlocked. Consequently, the MOF-polymer adhesion increased in such engineered interlocked structures which facilitates accelerated transport of CO_2, N_2 and CH_4 gases.[94] Finally, Table 2 includes a summary of the seven strategies dealing with together with key examples of filler-polymer pairs reported as MMMs.

9. Conclusions

This work outlines the possible approaches to increase the compatibility between fillers and polymers to prepare defect free MMMs and TFN membranes so that the produced membranes could take advance of all the special features that nanoporous fillers have: chemical composition, sieving ability, porosity and pore size, crystallinity, particle size, hybrid character, etc. This work is expected to support readers with the importance of adaptation of both fillers and polymers in line of producing effective membranes, with promising separation performance. The effect of the modification of the filler internal and/or external surface without dramatically compromising its coherent properties of solubility and diffusivity can be considered as the most important general strategy to minimize the filler agglomeration and improve the separation performance of the corresponding membrane.

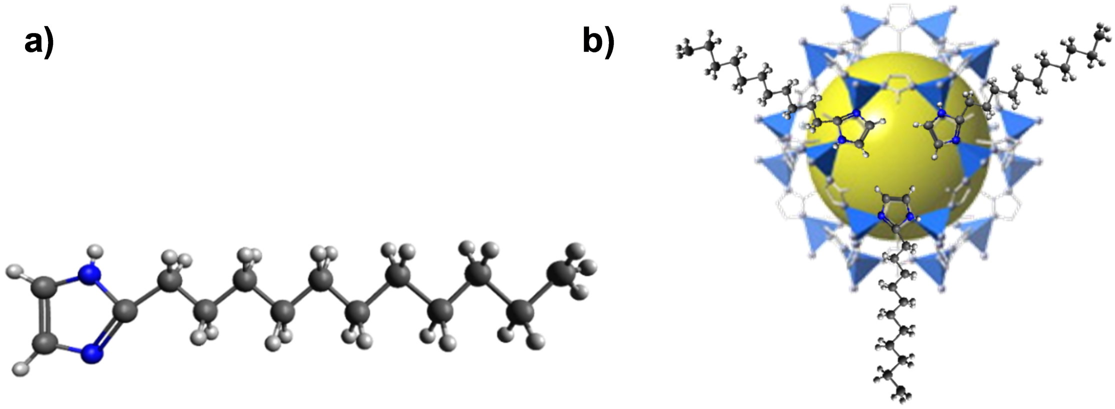

Figure 7. (a) 2-Undecylimidazole (umIm) molecule and (b) structure of ZIF-8-umIm upon ligand exchange from ZIF-8, reproduced with permission, reproduced with permission from,[90] © 2024 Copyright Clearance Center, Inc. All rights reserved.

Table 2. Summary of the strategies and filler-matrix pairs being reported in MMMs.

Strategy	Examples of filler-polymer pairs
Increase of external surface area of filler	MCM-41 and polysulfone (PSF)[29]
	MgO NPs and polyimide (PI)[31]
	Layered AlPO and PI[16]
Priming	ZIF-8 and PIM-1[44]
	Iron oxide NPs and H_2SO_4 crosslinked chitosan[46]
	TiO_2 and PVC[47]
Use of intrinsic compatible filler	ZIF-94 and PI 6FDA-DAM[58]
	MIL-178 and Pebax® 3533[59]
	ZIF-94 and Pebax® 1657[4]
	COF and cross-linked poly(ethylene oxide)[67]
One pot fabrication (same solvent for synthesis and MMM casting)	MIL-68 and PSF[71]
	ZIF67 and polyamide (PA)[72]
	UiO-66 and PI[67]
	ZIF-8 and Pebax® 2533[73]
In situ polymerization of the membrane selective material	Zeolite and PA[76]
	ZIF-8, MIL-53(Al), NH_2-MIL-53(Al) and MIL-101(Cr) and PA[77]
	ZIF-8 and PI[78]
Polymer side-chain modification	Thiol-modified polysiloxane and methacrylamide decorated UiO-66-HN-Met[80]
	ZIF-90 and hierarchical triptycene modified PA[81]
Post-synthetic modification of filler	NH_2-MIL-53(Al) and PSF[83]
	NH_2-UiO-66 and PI[85]
	-SO_3H functionalized MIL-101(Cr) and sulfonated polyetheretherketone[86]
	ZIF-8 modified with 2-undecylimidazolate and PIM-1[90]

The experimental strategies described here can be completed with semiempirical approaches followed to compare fillers and polymers as those based on Hansen solubility parameters,[7,95] which could be useful to select the best solvents and most suitable filler-polymer pairs. Also, molecular simulations can be invoked to screen MOFs (typically from the adsorption-diffusivity point of view but not from that related to the filler-polymer interaction) as membrane components for gas purification[96] or to represent and molecularly understand the filler-polymer interaction in a given MMM.[97]

Finally, after the study of the main approaches to enhance the filler-polymer interaction in composite membranes, the following recommendations are given. First, use of nanoporous fillers with a nature inclined towards the chemistry of the polymer (i.e. organic-inorganic or organic fillers better than inorganic ones). Second, increase the filler external surface area to enhance the interaction with the polymer. Third, if the latter is done through the reduction of particle size, agglomeration can become an issue and thus the best result may not be achieved with the lowest particle size.[98] Last but not least, rationalization using simulation tools, optimizing the filler loading and studying the reliability and reproducibility of the results, when possible, should be considered.

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Conflict of Interests

The authors declare no conflict of interest.

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