

Frontal Polymerization for the rapid obtainment of polymer composites

Original

Frontal Polymerization for the rapid obtainment of polymer composites / Malucelli, G., Mariani, A.. - In: ACS OMEGA. - ISSN 2470-1343. - ELETTRONICO. - 9:24(2024), pp. 25448-25456. [10.1021/acsomega.4c03017]

Availability:

This version is available at: 11583/2989329 since: 2024-06-24T11:33:16Z

Publisher:

ACS

Published

DOI:10.1021/acsomega.4c03017

Terms of use:

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright

(Article begins on next page)

Frontal Polymerization for the Rapid Obtainment of Polymer Composites

Giulio Malucelli* and Alberto Mariani*

Cite This: *ACS Omega* 2024, 9, 25448–25456

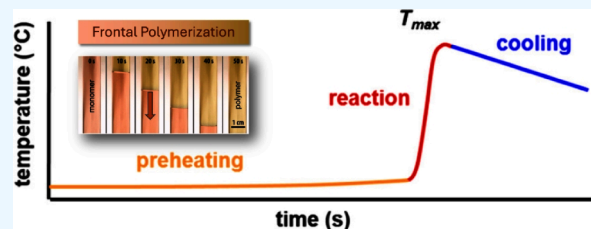
Read Online

ACCESS |

Metrics & More

Article Recommendations

ABSTRACT: Among the different polymerization techniques, frontal polymerization (FP) has gained high interest from the scientific community because of its peculiar characteristics: in particular, compared to classic polymerization reactions, FP allows for a better exploitation of the heat of polymerization involved, without requiring any external energy input apart from an initial photo or thermal ignition that triggers the reaction. The latter usually propagates in a few tenths of seconds or (at most) minutes through a hot self-sustaining polymerization front, giving rise to the formation of fully cured thermosetting networks or thermoplastic polymers. Furthermore, different polymerization mechanisms can be involved in FP reactions, comprising cationic or anionic, ring-opening metathesis, and free-radical polymerization, among others. Further, it is possible to run FP reactions in bulk, in solution, or even using solid monomers if they are melted at the temperature of the front, notwithstanding the possibility of using reactive systems containing fillers or fiber/fabric reinforcements. In this context, the use of FP is becoming very important also for the design and production of advanced (nano)composite materials, saving processing time and achieving the completeness of the curing reaction, even in the presence of high filler/reinforcement loadings. Therefore, this mini-review aims to provide the reader with the basics of FP and its main peculiarities, even in the context of preparing high-performing composites. In this respect, some recent case studies witnessing the potentialities of frontal polymerization for the design of advanced (nano)composite systems will be elucidated. Finally, some perspectives about possible future developments will be proposed.



1. INTRODUCTION

Thanks to their peculiarities that make them available for advanced industrial applications, polymeric composites are gaining a remarkably increasing interest from the scientific community and the industry. Indeed, their lightness, as well as high specific strength and stiffness, make them a reliable alternative to “standard” materials (i.e., metal alloys and ceramics) for the manufacturing of components for construction (such as structures and bridges), automotive (car bodyworks and bumpers), aviation (airplane parts), military (ships, boats, and aerospace parts), and even the biomedical sector.¹

Specifically referring to composites for structural applications (i.e., fiber-reinforced thermosetting polymer matrix composites), the existing autoclave-based manufacturing methods are surely time- and energy-consuming; further, the cost of these processes remarkably increases with increasing the size of the component to produce. To fix these issues, several out-of-autoclave manufacturing processes have been designed and suggested: they include thermal press curing and vacuum-assisted resin transfer molding, among others. To further improve both the thermosetting composite manufacturing processes and the quality of the obtained final materials, quite recently, Robertson and co-workers assessed FP as a very energy-efficient, reliable, and suitable technique for the

obtainment of out-of-autoclave and out-of-oven composite materials.²

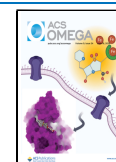
FP exploits a self-propagating exothermic reaction wave (i.e., the so-called localized polymerization front), which can convert liquid monomers to fully cured polymer networks, also in the presence of fillers or reinforcements, often incorporated at relatively high loadings. The exothermic front propagation is usually triggered by an external stimulus (commonly employing just a thermal or photo ignition in a very localized zone), hence saving energy compared with prolonged conventional autoclave- or oven-curing methods. Further, the completeness of the curing or polymerization reaction is achieved in a very short time, ranging from tenths of seconds to a few minutes, depending on the reactivity of the monomers and the adopted experimental conditions (composition of the system, presence of solvents, size of the reactor, etc.).^{3–6}

Received: March 29, 2024

Revised: May 24, 2024

Accepted: May 27, 2024

Published: June 4, 2024



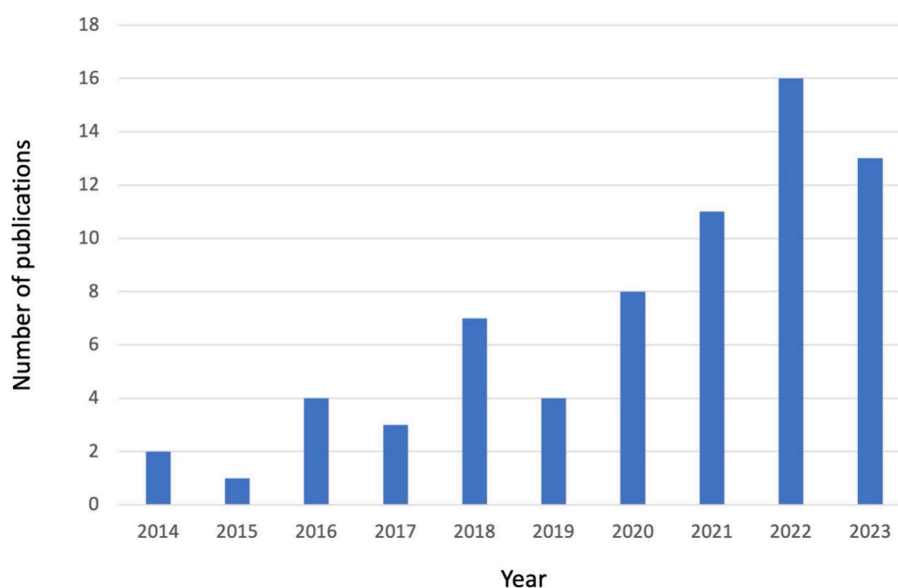


Figure 1. Number of publications (from 2014 to 2023) in peer-reviewed journals, dealing with “frontal polymerization and composites” (data collected from the Web of Science database, accessed on March 7, 2024).

The research interest in the preparation and characterization of polymer composites through frontal polymerization has remarkably grown in the last ten years, as witnessed by the increasing number of publications (articles, letters, and reviews) in peer-reviewed journals (Figure 1).

Therefore, the present work aims to summarize the very recent outcomes on the design, preparation, and characterization of polymeric composites obtained by frontal polymerization, providing the readers with a concise and clear overall picture of the big potential offered by this technique. To satisfy the possible interest of readers who are not familiar with FP, its basics will be briefly presented (more details are available in some comprehensive reviews^{3,4,6}). Then, some very recent case studies will be discussed on the use of frontal polymerization for the design of advanced composite systems, specifically dedicated to fiber-reinforced composites for structural applications and nanocomposites (mainly for functional purposes) containing different nanofillers. Finally, some perspectives on possible future developments of frontally polymerized composites will be proposed.

2. BASICS OF FP: FROM SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS (SHS) TO FRONTAL POLYMERIZATION

If a chemical reaction is sufficiently exothermic, a mixture of reactants can be ignited by a hot heat source. This is the fundamental prerequisite that characterizes SHS.

SHS is an alternative approach to traditional ceramic production methods, based on classic powder metallurgy processes, i.e., the sintering of chemically inert powders (ceramic components) at high temperatures, creating solid materials or objects.

In a general definition, SHS is a self-sustaining reaction process that produces practically valuable compounds and materials. In principle, any type of chemical reaction that is sufficiently exothermic may self-sustain and be used in the SHS process, including synthesis from elemental powders, solid compound reactions, thermite-type reactions, and combustion of porous solid reactive media in a gaseous oxidizer.⁷

Based on the use of high heat loads and their configuration, the automatic wave mode with local ignition has become popular since the 1950s. In this way, inorganic materials can be synthesized by self-heating layer by layer at high temperatures at the expense of internal energy. Numerous chemical reactions that are sufficiently exothermic to support a self-sustaining synthesis process have been found. Initially, it was suggested that they require an adiabatic temperature higher than 1800–2000 °C.⁸ More recently, adiabatic temperatures as low as 587 °C and 429 °C were reported for the synthesis of Bi₂Te₃ and Sb₂Te₃, respectively.⁹ The self-propagating wave mode is ensured by heat transfer from hot combustion products to cold reactants. The process is characterized by a well-defined combustion front that penetrates a reactive medium and converts it into final materials. Furthermore, the reaction rate is relatively high and depends on the velocities of the combustion waves, which typically vary between 0.1 and 10 cm/s. High heating rates (up to 10⁶ °C/s) and high-temperature gradients (up to 10⁷ °C/cm) at the reaction front result in extreme nonisothermal conditions during the product formation.

Frontal polymerization can be considered a sort of SHS process typically applied to organic polymer materials. FP has long been considered a macromolecular synthesis technique capable of giving rise to interesting phenomena of nonlinear dynamics, and its in-depth study was mostly reserved for physicists, mathematicians, and physical chemists who studied it by analogy with self-propagating high-temperature synthesis through SHS.^{10,11}

Indeed, in analogy with SHS, for the first decades, most of the research work was devoted to understanding the basic phenomena involved. In this respect, in the 1990s Pojman and his group published many papers focused on nondynamic phenomena involved in FP.^{3,6}

In frontal polymerization, a monomer that is generally liquid or in solution (but FPs are also reported on solid monomers) undergoes an ignition at a localized zone in the reactor due to the application of an external energy source (typically heat or light). If the monomer-to-polymer conversion reaction is sufficiently exothermic, the external energy source can be removed, as the heat that develops can polymerize the polymer layers adjacent to

those of the ignition. A hot polymerization front is then generated, which propagates along the entire reactor, transforming the monomer into polymer.

The temperatures and velocities of the curing fronts are typically much lower than those found in SHS, and vary between ca. 120 °C and 180 °C, and ca. 0.2 and 5 cm/min, respectively. More rarely, values outside these ranges have been recorded but still far from those that characterize most of the SHS synthesis of ceramic materials mentioned above.

Figure 2 shows the typical progress of frontal polymerization. Generally, it occurs in vertically arranged reactors, in which the

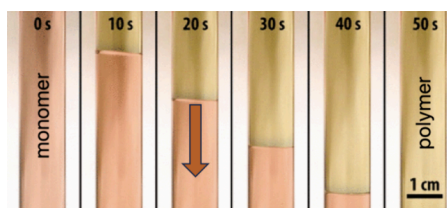


Figure 2. Time evolution of a descending polymerization front. Adapted from ref 3 under CC-BY-NC-ND 4.0 license.

ignition takes place by applying energy at a point located near the upper surface of the monomer. This way, the propagation of the front takes place downward (the solid polymer is formed on top of the liquid monomer). Although this may seem somewhat counterintuitive, this direction of propagation is often necessary to avoid the instabilities associated with convective motions, which may happen if the ignition occurs from the bottom.

Moreover, despite the exothermic requirements of the polymerization being respected, not all the descending fronts can be considered stable. In fact, if the polymer is liquid at the front temperature and/or is soluble in the underlying monomer, the front can be destroyed by fingering:¹² the hot polymer drips into the cold monomer, removing heat from the propagating front and triggering bulk polymerization within the monomer itself.

Moreover, since the velocity of the polymerization fronts is generally much lower than that typical of SHS, the amount of heat that develops per unit of time does not allow FP processes to be considered adiabatic, since the amount of heat dissipated toward the walls of the reactor or, as in the case of composites, toward the filler dispersed in the monomer is not negligible. This implies that there is a tendency to minimize the surface area and that the amount of inert filler cannot exceed certain values.

Figure 3 shows the temporal evolution of the temperature measured at a point on the reactor away from the ignition point. The preheating zone is that in which the front is far away and corresponds to the ambient one. The reaction zone is practically coincident with the propagating front; the higher the velocity of the reaction, the greater the slope of the curve. The maximum of

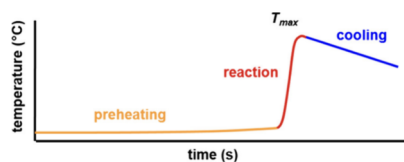


Figure 3. Temperature as a function of time measured at a point far from the ignition zone. Reprinted from ref 3 under CC-BY-NC-ND 4.0 license.

the curve represents the temperature of the front (T_{max}), followed by cooling.

In 1993, White and Kim proposed FP as an alternative technique for the in situ cure for the obtainment of thick composites. A progressive lay-up and in situ curing process to produce thick polymeric composite structures was proposed. The authors found that manufacturing cycle times were reduced by combining lay-up and curing. In addition, by tuning the reaction parameters, such as curing temperature, ambient temperatures, and material feed rate, polymer degradation due to sudden and local increases in temperature was avoided.¹³

It is important to highlight that both the presence of the filler and the progressive addition of material (which contribute to inhibiting undesired convective motions through better control of the viscosity of the polymerizing system) allowed the successful occurrence of an ascending polymerization front.^{6,14–16}

3. SOME RECENT CASE STUDIES

This section will present an up-to-date overview of the main research outcomes, specifically focusing on the very latest advances in the design of nanocomposites and fiber-reinforced polymer composites, providing the reader with a clear overview of the high potential offered by frontal polymerization and describing the reliability, effectiveness, and suitability of the obtained (nano)composite materials for the envisaged applications.

3.1. Nanocomposites Obtained through Frontal Polymerization: Recent Advances. More than 20 years ago the possibility of designing novel composite materials (both thermoplastic and thermosetting) was discovered and demonstrated, which embeds different types of nano-objects and exhibits high thermal, mechanical, and electric performances, thanks to the synergistic effects occurring between the continuous and dispersed phases.¹⁷

As far as frontal polymerization is concerned, the incorporation of nano-objects into a polymer matrix not only improves the properties of the resulting nanocomposites but also allows for the development of a stable polymerization front, hence making their synthesis easier. More specifically, the fast propagating front impedes the occurrence of reaggregation phenomena of the dispersed nanostructures, thus preserving their homogeneous distribution within the polymer matrix.¹⁸

The scientific literature reports several nice examples of the use of FP for obtaining high-performing nanocomposite materials: such nano-objects as carbon nanotubes, graphene, activated carbon, metal nanoparticles, nanoclay platelets, carbon dots, and quantum dots, among others, have successfully been incorporated in different frontally polymerized systems and the properties of the resulting materials thoroughly investigated, aiming to identify new potential application sectors.^{4,19}

Interestingly, Dean and co-workers exploited the incorporation of carbon black nanoparticles into dicyclopentadiene (DCPD) to enhance the conversion of UV radiation provided by a mercury vapor lamp into localized heat, suitable for propagating the photoactivated polymerization front.²⁰ At a very low loading (i.e., 1 wt %), the carbon black nanoparticles turned out to significantly lower the radiation energy required for triggering the polymerization reaction (by about 30%) and increase the temperature rise (by about 10%), as depicted in Figure 4. Applications in coatings, adhesives, and 3D-printed structures were envisaged.

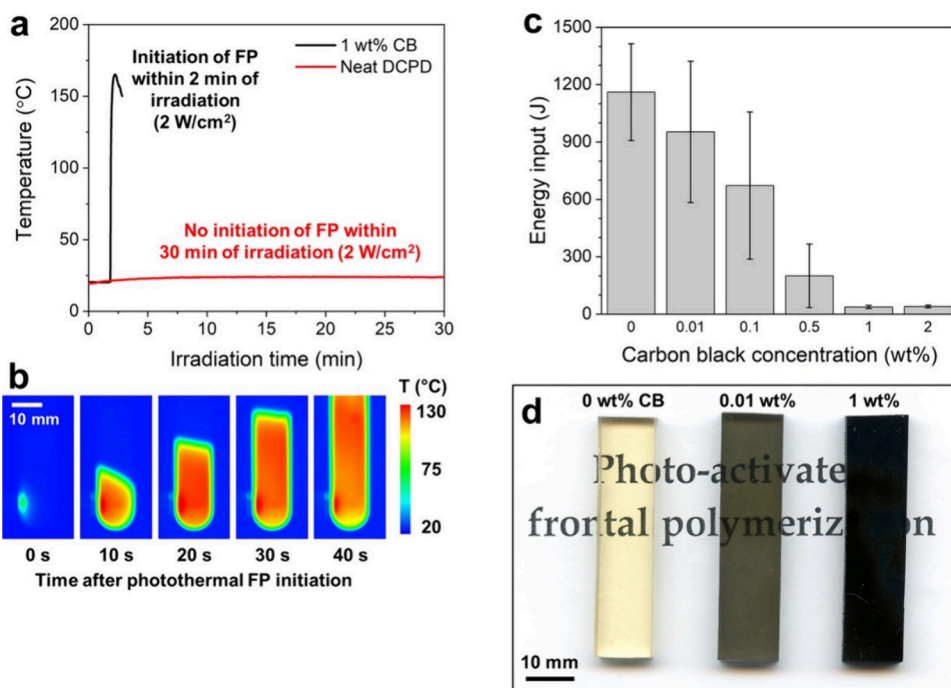


Figure 4. Photothermal FP initiation of DCPD resins containing different carbon black (CB) nanoparticle loadings. (a) Temperature profiles of resins under 2 W/cm^2 irradiation. (b) Thermal images of front propagation through a test tube containing DCPD at 1 wt % of CB. (c) Energy input (calculated as time to initiation \times radiation intensity \times spot size) required for FP initiation for resins with various CB concentrations. (d) Optical images of frontally polymerized nanocomposite samples with increasing CB loadings. Reprinted with permission from ref 20. Copyright 2020 American Chemical Society.

A similar approach was then utilized by Hu and co-workers, who exploited UV-photoinduced FP for preparing epoxy nanocomposites containing multiwalled carbon nanotubes (MWCNTs) at different loadings, ranging from 0.2 to 0.8 wt %. Before its incorporation into the resin, the nanofiller was further modified through a surface carboxylation reaction. The resulting frontally polymerized nanocomposites exhibited a remarkable increase in the front velocity (from 0.81 for unfilled epoxy to 3.04 cm/min for the nanocomposite containing carboxylated MWCNTs at 0.4 wt % loading), in the glass transition temperature (from 88°C to 146°C) and, very interestingly, in the impact strength (from 3.8 to about 28 MPa). All these findings suggested the potential use of the designed nanocomposites for fast repairing and deep curing applications.²¹

Another growing sector in which frontal polymerization emerged as an efficient method refers to stimuli-responsive nanocomposite hydrogels. Quite recently, Li and co-workers designed novel pH-responsive nanocomposite hydrogels based on acrylamide and choline chloride and containing N-doped carbon nanotubes at different loadings (namely, 0.2, 0.5, and 1 wt %). Both front velocity and T_{max} values increased with increasing the amount of carbon nanotubes; furthermore, the noncovalent interactions taking place between the nanofiller and the hydrogel network accounted for a significant increase in the compressive strength of the obtained hydrogels, from 19.8 to 59.9 kPa, respectively, for the unfilled hydrogel and the nanocomposite containing 1 wt % of filler. Further, the nanocomposite hydrogels exhibited pH-responsiveness in acidic media, envisaging their suitability for the design of efficient drug delivery systems.²²

In a further research effort, the same group exploited the frontal polymerization method for obtaining nanocomposite

hydrogels using a deep eutectic solvent made of urea, acrylamide, and choline chloride, in which ZnO nanoparticles were dispersed at different loadings (namely, 0.4, 0.8, and 1.2 wt %).²³ ZnO was also selected not only for its antibacterial features but also because it can suppress the generation of bubbles, hence stabilizing the propagating front during FP. The swelling ability of the synthesized hydrogels was found to increase with increasing the nanofiller loading, reaching about 12% for the system containing the highest ZnO loading. Furthermore, all the nanocomposite hydrogels showed photosensitive features that significantly increased with increasing the nanofiller content. Finally, thanks to the incorporation of ZnO nanoparticles, the hydrogels exhibited outstanding antibacterial properties: more specifically, 1.2 wt % ZnO accounted for an antibacterial rate against *E. coli* and *S. aureus* of about 88%.

Nanocellulose is a sustainable emerging material that has been considered for the design and preparation of advanced composites. In this context, Arellano-Cruz et al. designed and synthesized nanocomposite hydrogels based on copolymers of N-vinylcaprolactam and acrylic acid and containing 1 wt % of nanocellulose, exploiting the frontal polymerization technique. N,N'-Methylene-bis-acrylamide was employed as a cross-linker. The obtained nanocomposite hydrogels showed high thermal stability, due to the incorporation of the cellulose nanocrystals, as well as pH-responsiveness features that were not affected by the presence of the nanofiller.²⁴

The UV-ignited frontal polymerization assisted by a magnetic field was recently exploited for preparing epoxy nanocomposites containing graphene nanoplatelets (GNPs) mixed with Fe micropowder (final loading: 2 wt %), aiming at obtaining an anisotropic thermally conductive nanocomposite, thanks to the magnetic alignment of the nanofiller maintained during FP.²⁵ Figure 5 shows a schematic representation of the process,

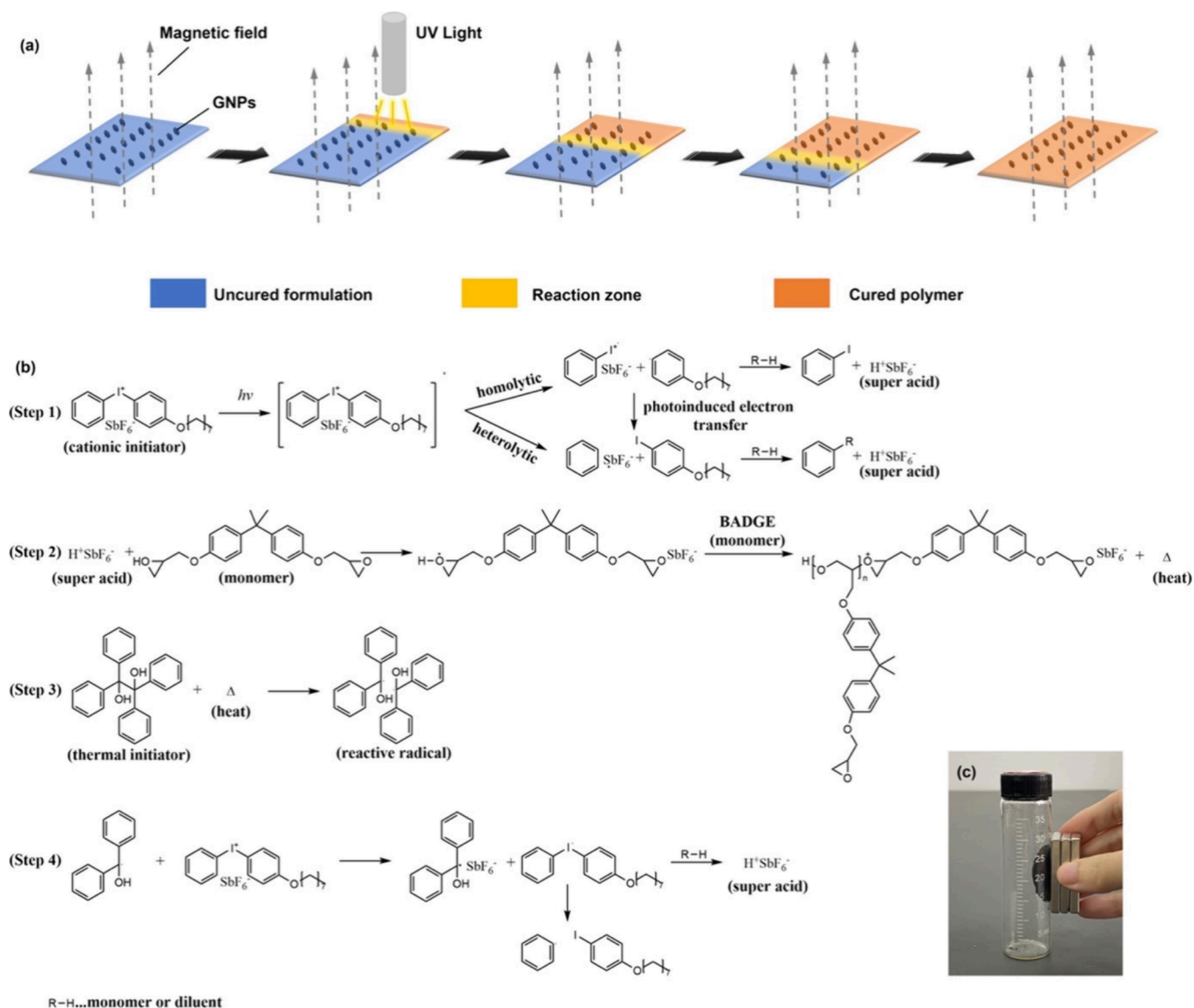


Figure 5. (a) Scheme of UV-initiated FP, assisted by a magnetic field. (b) Mechanism of RICFP using an iodonium salt as the photoinitiator. (c) Orientation effect of GNPs/Fe mixtures under the applied magnetic field. BADGE: Bisphenol A diglycidyl ether. Reprinted with permission from ref 25. Copyright 2022 Elsevier.

elucidating the mechanism of radical-induced cationic frontal polymerization (RICFP), and the orientation effect of GNPs/Fe mixtures under the applied magnetic field. Compared with the composites obtained through classic thermal curing, the UV-ignited frontal polymerization assisted by a magnetic field accounted for a significant increase (by about 61%) in the thermal conductivity along the thickness (and corresponding to the magnetic field direction) of the nanocomposites, hence highlighting the suitability of the designed materials for the rapid fabrication of high thermally conductive composites.

Another important sector, where FP recently has received interest, refers to the design, synthesis, and characterization of anisotropic nanocomposite foams with enhanced mechanical properties. In this context, Daguerre-Bradford and co-workers exploited the RICFP for preparing anisotropic epoxy foams in the presence of carbon nanotubes at 0.05 wt %; a foaming agent, namely Safoam RAZ-P from Reedy Chemical, was employed at 0.5 wt %. As a result of FP and the concurrent foaming process, an elongated cylindrical microporous structure was obtained:

the formed cylindrical pores showed a high orientation, following the direction of the open boundary. It is worth noticing that the mechanical behavior of foams was strictly related to the changes in boundary conditions, i.e., to the triggering of FP from the top or the bottom of the reaction test tubes. In particular, higher compressive moduli (+76%) and crushing stress values (+55%) were obtained by triggering the reaction from the top of the vessels, rather than from the bottom. Finally, the presence of carbon nanotubes resulted in decreased density, compressive properties, and anisotropy: this finding was ascribed to the higher irregular size and shape of the resulting pores, compared to the unfilled foams.²⁶

Recently, Kugabaeva and co-workers succeeded in obtaining magnetically active bimetallic nanoparticles (namely FeCo and FeNi) of a given composition and stabilized by an N-doped carbonized polymer matrix, which were simultaneously formed during the FP of suitable molecular precursors (namely cocrystallized acrylamide complexes of Fe(III)/Co(II) and Fe(III)/Ni(II) metal nitrates) and their successive controlled

thermolysis.²⁷ The overall process is schematized in Figure 6. The so-obtained magnetic nanoparticles were found to be

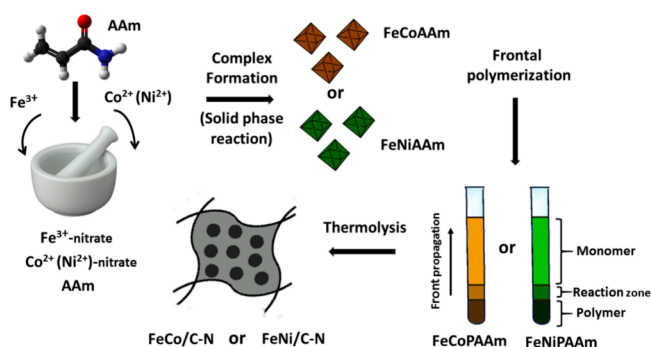


Figure 6. Scheme of the preparation of FeCo- and FeNi/N-doped carbon nanocomposites (C–N). AAm: acrylamide; FeCoAAm: FeCo acrylamide complex; FeNiAAm: FeNi acrylamide complex; FeCoPAAm: FeCo polyacrylamide complex; FeNiPAAm: FeNi polyacrylamide complex; FeCo/C–N: FeCo/N-doped carbon nanocomposite; FeNi/C–N: FeNi/N-doped carbon nanocomposite. Reprinted from ref 27 under CC-BY license.

resistant to oxidation and aggregation; further, the frontal polymerization technique allowed for effective control of the size of nanoparticles and, finally, of their magnetic features.

Very recently, Zhou and co-workers exploited the frontal ring-opening metathesis polymerization of DCPD and phenyl-functionalized polyhedral oligomeric silsesquioxane (POSS) cages, bearing three or four norbornene groups, to obtain low dielectric constant nanocomposites; the nanofiller loading was set at 5, 10, 20, and 40 wt %.²⁸ The incorporation of the nanofiller had a limited effect on the frontal polymerization velocity of the investigated systems; conversely, the dielectric constants were remarkably lowered and achieved their minimum values (around 2.1) at the highest nanofiller loading. Further, the nanocomposite containing 40 wt % of phenyl-functionalized-

POSS bearing four norbornene groups exhibited the lowest coefficient of thermal expansion (79.3 ppm/°C), the highest glass transition temperature (188 °C), and the highest elastic modulus (2.32 GPa) as well.

3.2. Fiber-Reinforced Composites Obtained through Frontal Polymerization: Recent Advances. The preparation of fiber-reinforced composite materials is usually performed by exploiting bulk polymerization processes of the resin in heated molds, autoclaves, or ovens, in which the manufactured component undergoes temperature and pressure cycles.

In a pioneering work, Robertson and co-workers demonstrated the feasibility of FP as an effective and reliable method to manufacture fiber-reinforced composites (particularly referring to carbon fiber-poly(dicyclopentadiene) composites) in shorter times than bulk polymerization, achieving very uniform curing of the resin through the sample's thickness and providing mechanical features that are comparable with those of its oven-cured counterpart.² This work was further supported and implemented by numerical simulations/modeling studies carried out by the same research group,^{29–31} also simulating FP-driven instabilities.³²

In a further research effort, Garg and co-workers demonstrated the possibility of rapidly fabricating vascular thermosets and carbon fiber-reinforced composites at room temperature through the frontal polymerization of DCPD, combining the polymerization of the latter with the acid-catalyzed depolymerization of a sacrificial polymer template (namely poly(propylene carbonate)). This way, both fabrication energy and time were lowered by 4 and 3 orders of magnitude, respectively, compared to conventional curing and vascularization processes carried out on samples of similar size in an oven.³³

Tran and co-workers exploited the RICFP to obtain epoxy composites filled with several types of fillers, such as glass microspheres, mica, graphite, aluminum, and short carbon fibers.³⁴ From an overall point of view, it was demonstrated that FP was effective even at very high filler loadings, despite a

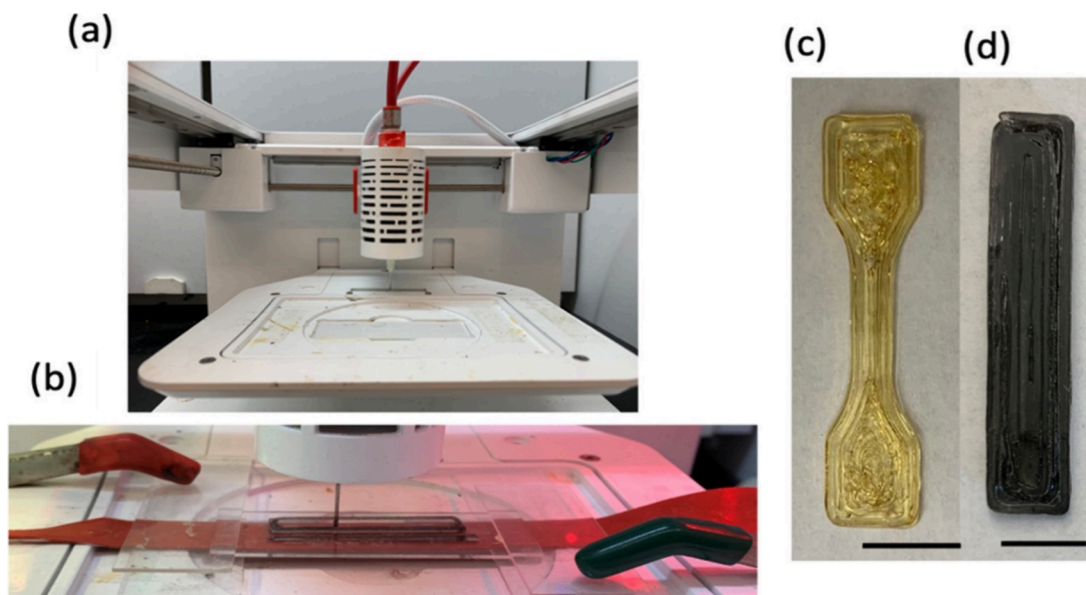


Figure 7. Extrusion-based printer setup and printing demonstration. (a) Printer setup. (b) Carbon fiber-reinforced composites printing demonstration. (c) A flexible heater (red belt beneath the glass substrate) was used to initialize the frontal polymerization; printed virgin poly(dicyclopentadiene) tensile bar. (d) As-printed carbon fiber-reinforced composites cuboid. Scale bar: 10 mm. Reprinted with permission from ref 35. Copyright 2021 Elsevier.

decrease in the front velocities with increasing the filler content. Furthermore, the tensile mechanical behavior of the frontally polymerized composites was comparable with that observed for counterparts subjected to thermal curing, notwithstanding that the former were manufactured with a lower energy intake and in a few minutes (rather than hours).

Zhang and co-workers demonstrated that it is possible to use FP for 3D-printing (Figure 7) discontinuous carbon fibers with different surface modifications (carboxyl-grafting, sizing, and norbornene-grafting) once dispersed in DCPD at 1, 3, and 5 wt % loading.³⁵ As assessed by tensile tests, the best-performing composites were those containing norbornene-grafted fibers at 3 wt %: in particular, both tensile strength and toughness increased by 170% and 15%, respectively, compared to those of 3D-printed unfilled DCPD resin.

To overcome the issues related to the presence of defects in carbon fiber-reinforced epoxy composites and the limitation related to the low fiber volume percent that can be employed in FP processes, Malik and co-workers recently proposed redox cationic frontal polymerization (RedCFP) as a novel FP method.³⁶ In particular, they investigated the role of stannous octoate (employed as the reducing agent) on the cationic FP of BADGE resin, even reinforced with carbon fiber biaxial noncrimp fabric (fiber volume exceeding 50 vol %), comparing the mechanical and thermal behavior with that of a standard anhydride-cured counterpart. The RedCFP allowed for manufacturing composites with glass transition temperatures beyond 100 °C and with limited defectiveness.

Staal and co-workers thoroughly investigated how to extensively control the local heat balance in RICFP processes, trying to minimize the heat uptake of fiber loadings, which limits the manufacturing of composites with fiber volume fractions usually employed in industrial processes.³⁷ In particular, they demonstrated that it was possible to properly control the heat generation by changing the concentration of the initiator; further, using highly insulating mold elements accounted for decreased heat losses, hence improving the propagating front characteristics. Finally, by tuning the cycloaliphatic resin composition, it was feasible to manufacture carbon fiber-reinforced composites with fiber volume fractions as high as 45.8%.

Then, the FP approach was extended to the manufacturing of continuous woven carbon fiber- and glass fiber-reinforced epoxy composites.³⁸ In particular, the in-plane and in-depth FP behaviors of the two types of composites were thoroughly studied: unlike the carbon fiber-reinforced composite, which exhibited a remarkable increase in both front velocity and front temperature compared to the unfilled resin, the glass fiber-reinforced system showed a small increase in the front temperature and a lowering in the front velocity. Three main parameters (exothermicity of the reaction, specific heat capacity, and thermal conductivity of the fibers) were found to affect the in-plane frontal polymerization behavior; conversely, the in-depth FP behavior of the investigated composites was strictly related to both the porosity and the thermal conductivity of the used fabrics.

Very recently, RICFP was combined with 3D printing to obtain nanocomposites made of a mixture of BADGE, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexanecarboxylate, and tri(ethylene glycol) divinyl ether, embedding carbon nanofibers and fumed silica.³⁹ To demonstrate extrusion-based additive manufacturing, a desktop 3D printer was modified to control resin extrusion and deposition, employing a digital syringe

dispenser and triggering FP either by using a soldering iron or two UV spotlights. The formulations containing 4 wt % of both carbon nanofibers and fumed silica allowed for free-standing printing, as they exhibited the right rheological behavior for consistent extrusion through the 3D printer nozzle, avoiding sagging of the extruded material at the nozzle tip.

4. CONCLUSIONS AND PERSPECTIVES

As outlined in this mini-review, FP is a convenient technique of macromolecular synthesis that has now become sufficiently mature to be exploited for practical applications, namely in the preparation of composites and nanocomposites. However, the addition of a filler to the reactive monomer mixture may sometimes be problematic but also lead to undeniable advantages.

In fact, in the case of nanocomposite systems, the nanofiller could have a density so different from that of the liquid monomer that it leads to rapid sedimentation and therefore to a nonhomogeneous final material. On the other hand, in these cases, if the thickness of the monomer layer is not excessive, the high speed of the polymerization front that characterizes FP may be able to ensure that curing takes place much faster than the sedimentation process itself, thus limiting the above-mentioned problem or avoiding any reaggregation processes, sometimes found in traditional processes, which are characterized by much slower kinetics.³

Additive manufacturing represents a further, perhaps obvious, use of the FP technique, as already demonstrated over 30 years ago by White and Kim.¹³ A further practical problem, which is encountered especially in the preparation of micro- or macrocomposites (e.g., in the presence of fibers or by using putties), where the amount of inert material is high, is the large amount of heat dissipated. In these cases, the temperature reached by the curing fronts may be too low to allow the reaction to self-sustain, thus resulting in quenching. Whenever possible, the alternative may be the use of reactive fillers that, instead of absorbing heat by subtracting it from that necessary for the propagation of the front, provide it thanks to appropriate exothermic chemical or physical transformations. In this context, composite systems or organic–inorganic hybrids were successfully prepared by exploiting the exothermicity of the frontal polymerization of an organic monomer (hexanediol diacrylate) and a simultaneous frontal geopolymerization (which led to the formation of a ceramic material embedded in the organic polymer).³

Our final recommendation is to refine this latter approach, in particular by combining the frontal polymerization of organic monomers with the SHS synthesis of ceramic materials, whose ignition and adiabatic temperatures are low enough to be compatible with the thermal stability of the final polymer composite material, which would thus be generated in a single step, in a short time and with great economic and energy savings.

■ AUTHOR INFORMATION

Corresponding Authors

Giulio Malucelli – *Politecnico di Torino, Department of Applied Science and Technology, 15121 Alessandria, Italy;*

✉ orcid.org/0000-0002-0459-7698;

Email: giulio.malucelli@polito.it

Alberto Mariani – *University of Sassari, Department of Chemical, Physical, Mathematical, and Natural Sciences, 07100 Sassari, Italy;*

✉ orcid.org/0000-0001-8973-4542;

Email: mariani@uniss.it

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acsomega.4c03017>

Funding

The authors thank the European Union—NextGenerationEU (National Sustainable Mobility Center CN00000023, Italian Ministry of University and Research Decree no. 1033-17/06/2022, Spoke 11—Innovative Materials & Lightweighting). The opinions expressed are those of the authors only and should not be considered as representative of the European Union or the European Commission's official position. Neither the European Union nor the European Commission can be held responsible for them. A.M. thanks the University of Sassari (2023–2024 FAR UNISS).

Notes

The authors declare no competing financial interest.

Biographies

Giulio Malucelli is a professor of materials science and technology at Politecnico di Torino, Italy. He graduated in Chemical Engineering at Politecnico di Torino and holds a Ph.D. in Chemistry (from the University of Genova, Italy). He is mainly engaged in investigating structure–property–processing relationships in polymers and polymeric micro- and nanocomposites. He has received several grants from both national and European projects.

Alberto Mariani is full professor of Polymer and Industrial Chemistry at the University of Sassari, Italy. He received his master degree in Chemistry in 1988 and his Ph.D. in Chemical Sciences in 1992 at the University of Sassari. His main research fields are frontal polymerization and, more generally, the synthesis of polymer materials, in particular those characterized by interesting structural or functional properties. His research has been supported by National and European funds.

REFERENCES

- (1) Hsissou, R.; Seghiri, R.; Benzekri, Z.; Hilali, M.; Rafik, M.; Elharfi, A. Polymer composite materials: A comprehensive review. *Compos. Struct.* **2021**, *262*, 113640.
- (2) Robertson, I.; Yourdkhani, M.; Centellas, P.; Aw, J.; Ivanoff, D.; Goli, E.; Lloyd, E.; Dean, L.; Sottos, N.; Geubelle, P.; Moore, J.; White, S. Rapid energy-efficient manufacturing of polymers and composites via frontal polymerization. *Nature* **2018**, *557*, 223–227.
- (3) Suslick, B. A.; Hemmer, J.; Groce, B. R.; Stawiasz, K. J.; Geubelle, P. H.; Malucelli, G.; Mariani, A.; Moore, J. S.; Pojman, J. A.; Sottos, N. R. Frontal Polymerizations: From Chemical Perspectives to Macroscopic Properties and Applications. *Chem. Rev.* **2023**, *123* (6), 3237–3298.
- (4) Li, Q.; Shen, H.-X.; Liu, C.; Wang, C.-F.; Zhu, L.; Chen, S. Advances in frontal polymerization strategy: From fundamentals to applications. *Prog. Polym. Sci.* **2022**, *127*, 101514.
- (5) Chechilo, N. M.; Khvilivitskii, R. J.; Enikolopyan, N. S. On the Phenomenon of Polymerization Reaction Spreading. *Dokl. Akad. Nauk SSSR* **1972**, *204*, 1180–1181.
- (6) Pojman, J. A. Frontal Polymerization: in *Polymer Science: A Comprehensive Reference*; Matyjaszewski, K.; Möller, M., Eds.; Elsevier BV: Amsterdam, 2012; pp 957–980.
- (7) Levashov, E. A.; Mukasyan, A. S.; Rogachev, A. S.; Shtansky, D. V. Self-propagating high-temperature synthesis of advanced materials and coatings. *Int. Mater. Rev.* **2017**, *62* (4), 203–239.
- (8) Holt, J. B.; Dunmead, S. D. Self-Heating Synthesis of Materials. *Annu. Rev. Mater. Sci.* **1991**, *21* (1), 305–334.
- (9) Su, X.; Fu, F.; Yan, Y.; Zheng, G.; Liang, T.; Zhang, Q.; Cheng, X.; Yang, D.; Chi, H.; Tang, X.; Zhang, Q.; Uher, C. Self-propagating high-temperature synthesis for compound thermoelectrics and new criterion for combustion processing. *Nat. Commun.* **2014**, *5*, 4908.
- (10) Pojman, J.; Fortenberry, D.; Ilyashenko, V. Frontal Polymerization as an Analog of SHS. *Int. J. Self-Propag. High-Temp. Synth.* **1997**, *6*, 355–376.
- (11) Jeszenszky, A.; Szabo, S.; Nagy, I. P. Comparative Review on SHS Thermodynamics Applied for Frontal Polymerization of Acrylamide and Triethylene Glycol Dimethacrylate. *Polym. J.* **2006**, *38*, 364–368.
- (12) Mariani, A.; Malucelli, G. Polymer Hydrogels and Frontal Polymerization: A Winning Coupling. *Polymers* **2023**, *15*, 4242.
- (13) White, S. R.; Kim, C. A Simultaneous Lay-Up and in situ Cure Process for Thick Composites. *J. Reinf. Plast. Comp.* **1993**, *12*, 520–535.
- (14) Pojman, J. A. Cure-on-Demand Composites by Frontal Polymerization: in *Encyclopedia of Materials: Plastics and Polymers*; Hashmi, M. S. J., Ed.; Elsevier: 2022; pp 85–100.
- (15) Gary, D. P.; Bynum, S.; Thompson, B. D.; Groce, B. R.; Sagona, A.; Hoffman, I. M.; Morejon-Garcia, C.; Weber, C.; Pojman, J. A. Thermal Transport and Chemical Effects of Fillers on Free-Radical Frontal Polymerization. *J. Polym. Sci.* **2020**, *58*, 2267–2277.
- (16) Groce, B. R.; Lane, E. E.; Gary, D. P.; Ngo, D. T.; Ngo, D. T.; Shaon, F.; Belgodere, J. A.; Pojman, J. A. Kinetic and Chemical Effects of Clays and Other Fillers in the Preparation of Epoxy-Vinyl Ether Composites Using Radical-Induced Cationic Frontal Polymerization. *ACS Appl. Mater. Interfaces* **2023**, *15*, 19403–19413.
- (17) Keledi, G.; Hári, J.; Pukánszky, B. Polymer nanocomposites: structure, interaction, and functionality. *Nanoscale* **2012**, *4*, 1919–1938.
- (18) Davtyan, S. P.; Tonoyan, A. O. The frontal polymerization method in high technology applications. *Rev. J. Chem.* **2019**, *9*, 71–94.
- (19) Zhang, N. X.; Liu, C.; He, Z. L.; Li, Q.; Chen, S. One-Pot Synthesis of Robust Fluorescent Nanocomposite Gel via Frontal Polymerization. *Macromol. Rapid Commun.* **2023**, *44*, 2200832.
- (20) Dean, L. M.; Ravindra, A.; Guo, A. X.; Yourdkhani, M.; Sottos, N. R. Photothermal Initiation of Frontal Polymerization Using Carbon Nanoparticles. *ACS Appl. Polym. Mater.* **2020**, *2*, 4690–4696.
- (21) Hu, G.; Fu, W.; Ma, Y.; Zhou, J.; Liang, H.; Kang, X.; Qi, X. Rapid Preparation of MWCNTs/Epoxy Resin Nanocomposites by Photo-induced Frontal Polymerization. *Materials* **2020**, *13*, 5838.
- (22) Li, B.; Liu, J.; Fu, D.; Li, Y.; Xu, X.; Cheng, M. Rapid preparation of PAM/N-CNT nanocomposite hydrogels by DEM frontal polymerization and its performance study. *RSC Adv.* **2021**, *11*, 35268.
- (23) Li, B.; Zhou, M.; Cheng, M.; Liu, J.; Xu, X.; Xie, X. Rapid preparation of ZnO nanocomposite hydrogels by frontal polymerization of a ternary DES and performance study. *RSC Adv.* **2022**, *12*, 12871.
- (24) Arellano-Cruz, D. C.; Illescas, J.; Martínez-Gallegos, S.; del Carmen Díaz-Nava, M. Synthesis and characterization of nanocomposites with nanocellulose obtained through frontal polymerization and study of their properties. *MRS Adv.* **2021**, *6*, 947–951.
- (25) Wu, Q. UV-activated frontal polymerization for preparation of magnetically oriented graphene nanoplatelets/epoxy composites. *Mater. Lett.* **2022**, *321*, 132370.
- (26) Daguerra-Bradford, J. A.; Lepcio, P.; Camarda, D. S.; Lesser, A. J.; Cristadoro, A. M.; Linnenbrink, M.; Schütte, M. High performance foams and their nanocomposites generated via liquid state frontal polymerization. *J. Polym. Sci.* **2023**, *1*–13.
- (27) Kugabaeva, G. D.; Kydraliev, K. A.; Bondarenko, L. S.; Baimuratova, R. K.; Karpenkov, D. Y.; Golovkova, E. A.; Degtyarenko, P. N.; Golubeva, N. D.; Uflyand, I. E.; Dzhardimalieva, G. I. Polymer-Assisted Synthesis, Structure and Magnetic Properties of Bimetallic FeCo- and FeNi/N-Doped Carbon Nanocomposites. *Magnetochemistry* **2023**, *9*, 213.
- (28) Zhou, D.-L.; Wang, J.; Bai, H.; Han, D.; Fu, Q. High-Performance low-k Poly(dicyclopentadiene)-POSS nanocomposites achieved by frontal polymerization. *Chem. Eng. J.* **2024**, *485*, 150140.
- (29) Vyas, S.; Goli, E.; Zhang, X.; Geubelle, P. Manufacturing of unidirectional glass-fiber-reinforced composites via frontal polymerization: A numerical study. *Compos. Sci. Technol.* **2019**, *184*, 107832.
- (30) Goli, E.; Parikh, N.; Yourdkhani, M.; Hibbard, N.; Moore, J.; Sottos, N.; Geubelle, P. Frontal polymerization of unidirectional

carbon-fiber-reinforced composites. *Compos. - A: Appl. Sci. Manuf.* **2020**, *130*, 105689.

(31) Vyas, S.; Goli, E.; Zhang, X.; Geubelle, P. H. Frontal vs. bulk polymerization of fiber-reinforced polymer-matrix composites. *Compos. Sci. Technol.* **2020**, *198*, 108303.

(32) Goli, E.; Peterson, S. R.; Geubelle, P. H. Instabilities driven by frontal polymerization in thermosetting polymers and composites. *Compos. Part B-Eng.* **2020**, *199*, 108306.

(33) Garg, M.; Aw, J. E.; Zhang, X.; Centellas, P. J.; Dean, L. M.; Lloyd, E. M.; Robertson, I. D.; Liu, Y.; Yourdkhani, M.; Moore, J. S.; Geubelle, P. H.; Sottos, N. R. Rapid synchronized fabrication of vascularized thermosets and composites. *Nat. Commun.* **2021**, *12*, 2836.

(34) Tran, A. D.; Koch, T.; Knaack, P.; Liska, R. Radical induced cationic frontal polymerization for preparation of epoxy composites. *Compos. - A: Appl. Sci. Manuf.* **2020**, *132*, 105855.

(35) Zhang, Z.; Liu, R.; Li, W.; Liu, Y.; Pei, Z.; Qiu, J.; Wang, S. Frontal polymerization-assisted 3D printing of short carbon fibers/dicyclopentadiene composites. *J. Manuf. Process.* **2021**, *71*, 753–762.

(36) Malik, M. S.; Wolfahrt, M.; Schlögl, S. Redox cationic frontal polymerization: a new strategy towards fast and efficient curing of defect-free fiber reinforced polymer composites. *RSC Adv.* **2023**, *13*, 28993–29003.

(37) Staal, J.; Smit, E.; Caglar, B.; Michaud, V. Thermal management in radical induced cationic frontal polymerisation for optimized processing of fibre reinforced polymers. *Compos. Sci. Technol.* **2023**, *237*, 110009.

(38) Luo, T.; Fu, K.; Zhu, H.; Chen, Y.; Yang, B.; Li, Y. In-plane and in-depth frontal polymerization behaviors of continuous fiber-reinforced epoxy composites. *Polym. Compos.* **2024**, *45*, 3604–3616.

(39) Groce, B. R.; Aucoin, A. V.; Ullah, M. A.; DiCesare, J.; Wingfield, C.; Sardin, J.; Harris, J. T.; Nguyen, J. C.; Raley, P.; Stanley, S. S.; Palardy, G.; Pojman, J. A. Free-Standing 3d Printing of Epoxy-Vinyl Ether Structures Using Radical-Induced Cationic Frontal Polymerization. *ACS Appl. Polym. Mater.* **2024**, *6*, 572–582.