

Thermally Responsive Methylcellulose-based Gels and High Internal Phase Pickering Emulsion as Pesticide and Fertilizer Delivery Carriers for Forestry Management

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Methylcellulose (MC), as a simple cellulose derivative has unique merits, involving water solubility and inherent temperature-induced phase transitions, which have potential in sustainable pesticide delivery applications. Despite the discovery of MC's thermally responsive property in 1935, it attracted attention just a few years ago, owing to increasing demands for sustainable materials. However, the phase transition temperature of MC thermogel is relatively high, and factors on tuning its low critical solution temperature are also not clearly elucidated, which restricts its gelation and Pickering emulsion delivery material developments. This editorial discusses solutions in terms of tunable thermally induced phase transitions of MC, hydroxypropyl methyl cellulose, carboxyl methylcellulose, and their thermogels and high internal phase Pickering emulsions as potential pesticide- and fertilizer-delivery carrier materials to enrich diverse forestry management practices and contribute to sustainable agricultural ecosystems and unmanned aerial vehicles-based low-altitude economy.

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Methylcellulose and Its Derivatives-based Thermogel for Pesticide Delivery

Angle oak trees, which are a primary forestry species in U.S. southern Louisiana and Texas regions, are vulnerable to deterioration by the *Lymantria dispar*. A practical approach to address this problem is by spraying pesticides *via* unmanned aerial vehicles (UAV) periodically to protect the trees from deterioration. However, owing to the pesticide's fast evaporation, short-time retainment, and runoff during constant high temperature and frequent rainy seasons, more than 90% of pesticide chemicals are not utilized efficiently. These waste agrochemicals potentially cause environmental risks and pollute the Mississippi River. It is thus highly desirable to develop environmentally benign carrier materials in controlled-pesticide delivery.

Methylcellulose (MC) has an inherent thermal gelation property, such that it has potential to serve as a pesticide delivery carrier material in forestry management applications. Despite the fact that MC's thermal gelation and its low critical solution temperature (LCST) property had been discovered several decades ago (Heymann 1935), developing MC-based thermally responsive gelation delivery materials is just now getting attention, which can be attributed to societal demands for sustainability. The general working principle of MC thermogel for controlled pesticide delivery is attributed to its non-covalent hydrophobic interaction variations among polymer chains or volume shrinking of

its crosslinked gelation upon external thermal stimuli. Its stimuli-responsive controlled release properties are closely related to the LCST. However, the thermally induced phase transition temperature of MC thermogel is relatively high, with an LCST around 50 to 70 °C, which restricts its thermally controlled-pesticide delivery applications. It is thus a crucial research question on how to tune MC phase transition temperature and then push its thermal gelation down to approximate physiological temperature ranges at 20 to 40 °C. According to MC thermal gelation mechanism, the hydrophobic association of methyl substitution groups governs its gelation properties (Heymann 1935). Increasing methyl substitutions facilitates their hydrophobic association and results in decreased LCST values. The straightforward method is to tailor the degree of substitution (DS) of MC methyl groups, thereby achieving MC thermal gelation with reduced phase transition temperatures. Additionally, MC thermal gelation is primarily determined by the competition of hydroxyl-water and methyl-methyl interactions. Therefore, a promising approach to tune MC thermal gelation temperatures is *via* the dehydration effect by using polyelectrolytes, *e.g.*, blends of MC with xanthan gum owing to its dehydration effect of carboxylic acid groups.

When using MC gels as pesticide delivery carrier materials, another limitation is how to render it sufficiently adhesive so that it can be retained on tree branches and leaves and then achieve the objective of pesticide delivery efficiently. An effective approach is to increase multiple hydrogen bonding interactions through aldehyde-modified MC at C2-C3 bonds *via* the periodate oxidation for its adhesive strength enhancement with tree branches and leaves. Additionally, owing to weak methyl-methyl association interactions, MC thermal gelation usually has structural stability issues. Another practical challenge is about how to increase its thermal-gelation adaptability and stability under field testing conditions. The MC post-modifications *via* the crosslinker divinyl sulfone or citric acid and/or aldehyde-modified MC *via* diamine cross-linking make it possible to enhance structural stability and environmental adaptability under the prerequisite of maintaining the MC methyl group integrity. As further considerations on research extensions, the MC-based thermogel pesticide or fungicide delivery system has potential for widely agricultural practices on orange and apple trees and blueberry plants for yield enhancement and farmer income benefits in the States of California and Washington, along with New Jersey, U.S.

Hydroxypropyl methyl cellulose (HPMC), as a MC derivative, also has attracted attention as a pesticide delivery carrier material, owing to its inherent thermal gelation and excellent surface adhesive properties. Namely, the multiple hydroxyl groups of HPMC contribute to the hydrogen bonding interactions, thereby enhancing its gelation adhesives with tree leaves. Thanks to its surface functional groups, hydrogel beads of HPMC provide another optional form of sustainable pesticide delivery carrier materials. Such gels can be further developed by cross-linking with divinyl sulfone. The HPMC hydrogel beads are also probably able to control weed growth, thereby reducing its competition with tree roots in fertilizer and nutrition absorbance for sustainable forestry management. However, the exact mechanism of HPMC thermal gelation is not clearly understood currently. As HPMC includes both methyl and hydroxypropyl substitute moieties, the general explanation in academia of the HPMC thermogel mechanism involves combined phase separation similar to that of hydroxypropyl cellulose aqueous solution upon heating and hydrophobic associations like MC thermogel. Additionally, HPMC thermogel's gelation properties are directly governed by its bulky substitute moieties. For instance, a derivative of HPMC, hydroxypropyl methylcellulose acetate succinate, almost loses thermogel properties. As

advanced characterization techniques are developing, *e.g.*, in-situ liquid phase transmission electron microscopy and small angle neutron scattering, its chain conformation and thermogel mechanism, and governing factors along with pesticide delivery carrier material applications will be further understood.

As one more type of MC derivative, carboxyl methylcellulose (CMC) also can produce thermal gelation, while its inherent thermogel property is relatively weak, such that it can't work effectively with pesticide delivery applications. Grafting modifications are common approaches by using thermally responsive polymers, such as poly(*N*-isopropylacrylamide) (PNIPAM), but they usually involve complicated synthetic protocols. Thanks to the unique carboxyl groups in CMC, an emerging synthetic method known as decarboxylative radical polymerization can produce thermally responsive PNIPAM-grafting-CMC *via* a straightforward and less tricky protocol (Mendoza et al. 2022). According to this synthetic method, a series of temperature-, pH-, light- and CO₂-responsive vinyl-based monomers can be grafted on the CMC surface *via* the radical decarboxylation polymerization for further developing multiple-responsive CMC thermal gelation carrier materials in pesticide delivery. This emerging synthetic method is also applied for other cellulose fibers with carboxyl groups, *e.g.*, TEMPO-oxidized cellulose nanofibril and cellulose nanocrystal (CNC), which opens a new path for developing CNC intelligent pesticide delivery system for forestry practices along with sustainable agriculture applications. Additionally, post modifications on CMC surface functional groups can be further undertaken to enhance their gelation properties, namely, physical and chemical cross-linking of CMC, TEMPO-oxidized cellulose nanofibrils, or sulfate-derivatized nanocellulose *via* charge interactions and dimethyl diallyl ammonium chloride chemical crosslinking. Regarding tuning CMC gelation phase transition temperature, followed by the previous tuning MC phase transition practices, screening, and exploring CMC with broad ranges of DS and molecular weight needs to get attention for attaining its appropriate phase transition temperatures. These thermally responsive HPMC and CMC gelation are ideal pesticide delivery carriers in forestry practices, despite almost not getting much attention currently.

Methylcellulose-based High Internal Phase Pickering Emulsions for Pesticide and Fertilizer Delivery

Pickering emulsions refers to emulsions stabilized *via* micro- or nanoparticles. MC-based Pickering emulsion is another promising approach for controlled-pesticide delivery. However, it is a challenge to develop MC-based Pickering emulsions encapsulated with pesticides with long-term stability, although the neat MC displays amphiphilic properties. Pickering emulsions might be prepared by tuning MC amphiphilic property *via* the post-modification of aldehyde-MC with diverse amines in order to retain its MC-based Pickering emulsions with long-term stability. It is also a practical solution to further tune the MC DS and molecular weight, thereby achieving the controlling release of pesticides efficiently. Additionally, these MC-based emulsions can be further manufactured into oil powders *via* a spray drying process for diverse forest management practices. However, the conventional MC-based oil/water Pickering emulsion can only encapsulate limited volumes of pesticides. High internal phase Pickering emulsions (HIPEs), as another type of emulsions, can storage oil phase at a level of at least 74%. Therefore, HIPEs as an advanced delivery carrier can store high volumes of pesticides and develop MC-based high internal phase Pickering emulsions have the potential to attain controlled, sustained, and

long-term pesticide delivery, thereby dealing with biological deterioration on forestry management. In addition to the biological threat from *Lymantria dispar*, angle oak trees are susceptible to fire. Unfortunately, there has been almost no attention to developing multiple functional MC-based HIPE delivery system for both controlling delivery of pesticide and forestry fire protection. From a practical application perspective, it is possible to potentially reduce biological deterioration and fire risk on forestry by encapsulating intumescent phosphorus (P)- and nitrogen (N)-fire additives (e.g., urea and phytic acids) into the MC-based HIPEs. Additionally, MC-based HIPE foam materials by doping conductive fillers can be further developed into thermoelectric materials-based early warning fire alarm sensors to monitor forestry wildfire, aiming at reducing fire accidents. Interestingly, most intumescent-based fire additives involve P and N elements, which have potential as forest fertilizers. Delivered intumescent fire additives involving phosphorus and nitrogen elements through MC-based HIPE carriers appear likely to benefit tree growth and forestry ecosystems. Thus, developing diverse MC-based gelation, beads, HIPEs, and hydrogel carriers for potassium (K), N, and P fertilizer delivery is highly desirable. Additionally, NPK Fertilizers-encapsulated MC oil particles from MC-based emulsions can be further developed *via* two- or three-nozzle spray dryers. Most importantly, these spray-dried MC-based oil particles can be easily reversibly back to their original emulsions with solvent dilutions. These pesticides- and/or fertilizers-encapsulated MC-based oil powders are thus promising as novel controlled release particles for forestry and agricultural applications, owing to their storage and easy transportation. For example, MC-based oil particles with controlled release of NPK fertilizers have potential to enhance corn, soybean, and wheat yields and increase their local farmer incomes in the Agriculture-based States of Nebraska, Kentucky, Dakota, and Iowa, U.S. Additionally, it can be predicted that U.S. Federal- and State-Government supports, policies, and strategies on “fertilizer and pesticide delivery *via* biomaterials integrated with artificial intelligence- and UAV-based low-altitude economy” will be enacted next a few years. The concept of “low-altitude economy” refers to the emerging economy conducted in the airspace below 3,280 feet above the ground (Bowley 2025). As the rapid development of low-altitude economy, the UAV delivery services have potential as partial alternatives to laborers in diverse fields, *e.g.*, timely monitoring, management, and protection of forests and agricultural crops *via* UAV CT scanning and drone spraying of pesticide and fertilizers. As another example, drone delivery services from California and Florida local strawberry farms to customers among neighboring cities will come soon to tackle low shelf-life inherent limitations.

References Cited

- Bowley, T. (2025). “The “low-altitude” economy is taking off,” (<https://institute.bankofamerica.com/transformation/low-altitude-economy.html>)
- Heymann, E. (1935). “Studies on sol-gel transformations. I. The inverse sol-gel transformation of methylcellulose in water,” *Transactions of the Faraday Society* 31, 846-864. <https://doi.org/10.1039/tf9353100846>
- Mendoza, D. J., Ayurini, M., Browne, C., Raghuvanshi, V. S., Simon, G. P., Hooper, J. F., and Garnier, G. (2022). “Thermoresponsive poly(N-isopropylacrylamide) grafted from cellulose nanofibers *via* silver-promoted decarboxylative radical polymerization,” *Biomacromolecules* 23, 1610-1621. <https://doi.org/10.1021/acs.biomac.1c01444>