Agriculture: Polymers in Crop Production
Mulch and Fertilizer

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Abstract
It is known that to a great extent plant growth is determined by microclimates of the growing media. Under field condition such favorable microclimate can be created artificially by means of mulching including various plastic covering. Plastic mulch controls the dynamics of incoming and outgoing radiation and thus changes the soil thermal properties and conserves soil moisture by checking evapotranspiration losses. Several synthetic and natural polymers such as polyethylene (PE), poly(vinyl chloride), polybutylene, copolymers of ethylene with vinyl acetate, polyesters, starch, cellulose, and chitosan are being used to develop plastic mulch of varied properties. Synthetic polymers more specifically PE is being used extensively for mulching purpose. Off late in view of environmental concerns and problems related to disposal, various degradable plastics like oxo-degradable, biodegradable plastics are developed for crop mulching. To increase fertilizer use efficiency and reduce losses through leaching, run off, and volatilization, polymer-based controlled-release fertilizer formulations are developed. These fertilizer formulations ensure release of nutrients at very slow rate over prolong period of time to avoid losses of nutrients and optimum availability of nutrient around the rhizospheric zone. Different synthetic or natural polymers were reported to develop controlled-release fertilizer formulation either by encapsulating the core water soluble fertilizer or by chemically attachment to the functional groups of polymeric chain. The release of nutrients from these polymeric formulations occurs through membrane diffusion or hydrolysis and other degradation process.

Keywords: Agriculture; Controlled release; Fertilizer; Mulch; Polymer.

INTRODUCTION
Global fruit and vegetable production has increased remarkably over the last few decades. In 2011, more than 1 billion tonnes of vegetables and 640 million tonnes of fruits were produced throughout the world.[1] The increase in cereal and oilseed crops has been significant as well. Besides the use of high yielding crop varieties and chemical fertilizers, improve production practices also played an important role in increasing the global food production. Agricultural, particularly horticultural, crop production has been renewed by the use of synthetic polymers (plastic) in forms of mulch, drainage, drip irrigation system, and plant nutrient carriers. Mulching and plant nutrient carries are one of the major sectors among different use of polymers in agriculture. In the late 1950s, for creating artificial climate to benefit plant growth plastic mulch films (which are polyethylene [PE], polyvinyl chloride [PVC], and ethylene vinyl-acetate (EVA) polymer) were first used in university researches. The success of these research trials leads to
wide adaptation of plastic mulch by commercial growers in vegetable and fruit production since the 1960s.[1,2] Due to the extensive use of plastic in agriculture a new term was coined, i.e., Plasticulture which is defined as “the use of plastic in agriculture,” which includes, but is not limited to plastic mulch films to control weed, loss of nutrient and moisture, and regulate soil thermal property; drip irrigation tape for efficient utilization of irrigation water; and structural support in low and high tunnels cultivation.[3] So initially the use of polymers were restricted in the field as mulch and irrigation tape or in the greenhouse and protected cultivation due to lower cost and excellent physical properties such as transmittance, permeability, and plasticity. It was estimated that per year the world consumption of plastics in agriculture is nearly 6.5 million tonnes.[4] With the boom in the use of synthetic polymers in agriculture, an associated major concern has risen in terms of efficient handling and disposal of used polymers due to its persistency through environmentally safe ways. To address the degradability issue while being effective, reactive functional polymers are being investigated and developed through the advancement of polymer research recently. These polymeric films with controlled degradable nature have the advantages of complete degradation into soil soon after crop harvest thus reducing the cost of handling and environmental pollution. Besides the use of polymers in agricultural structures, the wide use of novel polymers is reported in developing agrochemical delivery system. Novel synthetic polymers have widely used to develop nutrient formulations with the advantage of efficient and adequate nutrient supply to support optimum plant growth, reduced pollution, etc. In recent decade, smart polymers have been developed and used to achieve smart nutrient delivery systems where optimum delivery of nutrient is integrated with soil moisture management around the rhizosphere. This entry deals with the key aspects of polymer use in agriculture highlighting types of polymers in the field of mulch and nutrient/fertilizer delivery system.

**POLYMER IN AGRICULTURAL MULCH**

Mulch is a protective covering around the crop plants with aims of improving plant growths, crop productivity, and pest control. The specific objective of mulching is to create a microclimate around the rhizospheric zone which is favorable to plant growth with respect to temperature distribution and soil moisture retention.[5,6] Light-textured soil, especially during prolonged dry period, has an adverse effect on plant growth by quick loss of water through evapotranspiration. In such a situation, mulch ensures adequate moisture supply to the plant by acting as a protective barrier for such moisture loss. In cold climatic region or in winter it acts as a thermal insulation for the plant roots. The soil temperature under plastic mulch depends on the thermal properties (reflectivity, absorptivity, or transmittance) of a particular material to incoming solar radiation.[6] The other benefits of mulch include reduction of weed population,[9,10] insect control,[11,12] preservation of surface soil structure,[13,14] increased plant growth though CO₂ retention under film,[15] reduction of soil compaction,[16] and minimizing erosion and loss of nutrients through leaching and run off.[17,18] Different types of mulching materials were reported ranging from crop residues,[6,9] saw dusts,[20] papers,[21,22] and plastics.[15,23] The use of plastic mulch in agriculture is generally recommended for high-value row crops. Use of plastic mulch has the advantages of being light weight, easy handling, and better coverage compared to natural mulch.[24] For the control of soilborne insect pests and nematodes either by the application of volatile insecticides and nematicides or by physical means such as soil solarization requires proper coverage of surface by polymer mulch.[25,26] The polymers used for mulching purpose are of different types.

**Mulch based on Synthetic Polymers**

The most widely use synthetic polymer for mulching purpose is PE. It was first prepared as sheet film by British scientists in 1938,[27] PE was first used in green house as replacement of glass and later on it was used in crop mulching due to its light weight, greater coverage area per volume then natural mulch i.e., crop residues,[4,28] PE is widely used due to its easy processibility, flexibility, high chemical resistance, and odor and toxicity free nature.[29] The PE mulch sheet includes low-density PE (LDPE) (0.92–0.93 g/cm³), most commonly used PE mulch sheet, linear low-density PE (LLDPE), with high puncture resistance and mechanical stretch properties, and high-density PE (0.94–0.96 g/cm³) (HDPE), with highly reliable moisture and vapor barriers properties.[30] The width of a typical PE mulch sheet used in the United States ranged from 0.0152 to 0.0508 mm.[31] PE sheets such as LDPE and HDPE are available in different colors and finishes as per the requirement of the quality of soil and type of crop. PVC is the second most widely used film material after PE. PVC is prepared from reacting acetylene with hydrochloric acid in presence of high temperature and pressure. Pure PVC is a very rigid plastic material, and to increase its flexibility plasticizers (dioctyl phthalate, tricresyl phosphate, etc.) are added. Copolymer of polyethylene vinyl acetate (PEVA) is also being used to prepare mulch film. EVA has more elastic property than PE and improves the heat retention properties. The chemical structure of synthetic polymers is given in Fig. 1.

**Transparent Film Mulching**

The objective of transparent film mulching is the quick heating of the soil and conservation of the soil moisture. The transparent PE sheet absorbs little solar radiation and transmits most (85% –90%) of the incoming radiation.
(shorter wavelength) but resists the heat loss (higher wavelength radiation) from the soil, thus increases the soil temperature under the sheet. The relative transmission of the sheets depends on the thickness and the degree of opacity of the PE. The loss of soil moisture through evapotranspiration is also restricted and collected at the underside of the sheet. The water droplets at the underside of the sheet, transparent to the incoming short-wave radiation, are opaque to the radiating long-wave infrared radiation, and thus contribute to the restriction of heat loss from the soil in the form of infrared radiation. The use of the transparent sheet increases the soil temperature depending on the season, soil type, moisture content, and sunshine level, and they are more effective in trapping heat than black or smoke grey film. It was reported that soil temperature under transparent PE mulch is higher to the tune of 6°C in the 5 cm soil depth compared to the bare soil. The increase of soil temperature and enclosed environment also led to enhanced activity of volatile fumigant. Use of transparent sheet does not control weed effectively. Different color mulch is more effective in trapping heat than black or smoke grey film. Different color mulch is also for weed control. Black film mulch blocks the solar radiation, it effectively controls weed population. Thus, the use of black mulch reduces the chance of damage of crop roots by mechanical weed control measures. Besides PE, other plastics used in black film mulch are PVC, polybutylene, PEVA, etc. Black mulches are being used most popularly in strawberry and pine apple cultivation for the control of humidity and suppression of weed growth.

**Fig. 1** Chemical structure of synthetic polymers (I–VI) used as agriculture mulch film

**Poly(ethylene) (PE)**

**Poly(butylene)**

**Poly(vinylchloride)**

**Poly(ethylene-co-vinyl acetate)**

**Black Film Mulching**

Black film mulch is opaque to incoming solar radiation and acts like black body absorber (UV, visible, and infrared) and radiator (infrared). The absorbed energy is lost to atmosphere through infrared radiation or thermal convection. The black mulch also increases the soil temperature by transferring heat to the soil. A good amount of heat can be transferred to soil by physical contact between soil and sheet as the thermal conductivity of soil is relatively higher than air. During daytime, through black mulch, the soil temperature can be increased to the tune of 2°C–3°C compared to bare soil. Because the black mulch blocks the solar radiation, it effectively controls weed population. Thus, the use of black mulch reduces the chance of damage of crop roots by mechanical weed control measures. Besides PE, other plastics used in black film mulch are PVC, polybutylene, PEVA, etc. Black mulches are being used most popularly in strawberry and pine apple cultivation for the control of humidity and suppression of weed growth.

**Colored and Infrared Transmitting Film Mulch**

Infrared transmitting (IRT) film mulch is discovered recently in polymeric mulch technology and selectively transmits a section of electromagnetic spectrum. These polymeric sheets absorb PAR (photosynthetically active radiation) and transmit infrared radiation. Because of the PAR activity they can control weeds and at the same time it can enhance the soil temperature to some extent, thus providing a solution between transparent and black film mulch. The color of these mulches can be blue-green or brown. These mulches can increase the soil temperature to transparent mulch but without the accompanying weed problem. Different color mulch is effective for different crops. Red color mulch gives best results in tomato while blue color mulch produces best result for peppers by reflecting photosynthetic active wavelengths. Silver mulch is reported to control whitefly, whereas yellow-brown plastic mulch is reported to delay the incidence of yellow leaf curl.

**Advantages of Plastic Mulch**

**Improved Plant Growth and Yield**

Plastic mulches have been used for increasing crop production through modifying soil microclimate, increasing water use efficiency (WUE), and decreasing pest and...

Besides agricultural crops, plastic mulching is widely recommended for tree nurseries. Effect of black PE mulch on the survival of Douglas-fir seedlings was studied, and it was found that after 7 and 18 weeks of planting, 94% and 47% of the mulched seedlings was survived as compared to 91% and 33% for unmulched seedlings, respectively. Effect of black PE mulch as an alternative to mechanical cultivation in establishing plantations of hybrid poplars was studied and lower mortality and greater shoot growth was found in the mulched trees during periods of average rainfall or limited drought. Perforated black plastic mulch was reported to significantly increase the height and stem diameter growth of loblolly pine (*Pinus taeda* L.) and yellow poplar (*Liriodendron tulipifera* L.), and these enhanced growth effect was attributed to reduced evapotranspiration loss from surface soil and competing vegetation. Similarly, black plastic mulch was reported to enhance growth and survival of pine plantation, *Betula verrucosa*, *sugar maple*, *Green ash* (*Fraxinus pennsylvanica* Marsh), etc.
Table 1  Impact of plastic mulch on yield compared to bare ground

<table>
<thead>
<tr>
<th>Crop</th>
<th>Plastic mulch description</th>
<th>Effect on yield compared to bare ground</th>
<th>Location</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tomato</td>
<td>Black</td>
<td>Positive</td>
<td>The United States</td>
<td>[40]</td>
</tr>
<tr>
<td></td>
<td>Black, gray, red, and silver</td>
<td>Positive</td>
<td>The United States</td>
<td>[41]</td>
</tr>
<tr>
<td></td>
<td>White</td>
<td>NSD</td>
<td></td>
<td>[41]</td>
</tr>
<tr>
<td></td>
<td>Silver, black, white/black, black/white</td>
<td>Positive</td>
<td>Jordan</td>
<td>[42]</td>
</tr>
<tr>
<td>Watermelon</td>
<td>Colored</td>
<td>Positive</td>
<td>The United States</td>
<td>[43]</td>
</tr>
<tr>
<td></td>
<td>Black, white transparent</td>
<td>Positive</td>
<td>Mexico</td>
<td>[44]</td>
</tr>
<tr>
<td>Cocoyam</td>
<td>Black and white transparent</td>
<td>Positive</td>
<td>Nigeria</td>
<td>[45]</td>
</tr>
<tr>
<td>Strawberry</td>
<td>Black degradable plastic</td>
<td>Positive</td>
<td>Sweden</td>
<td>[46]</td>
</tr>
<tr>
<td></td>
<td>Transparent, blue, red, yellow, brown, green, black</td>
<td>Positive</td>
<td>The United States</td>
<td>[47]</td>
</tr>
<tr>
<td>Muskmelon</td>
<td>Black embossed</td>
<td>Positive</td>
<td>The United States</td>
<td>[48]</td>
</tr>
<tr>
<td></td>
<td>Black</td>
<td>Positive</td>
<td>Mexico</td>
<td>[49]</td>
</tr>
<tr>
<td></td>
<td>Transparent and wave length selective IRT 76</td>
<td>Positive</td>
<td>The United States</td>
<td>[50]</td>
</tr>
<tr>
<td>Yellow crookneck squash</td>
<td>Silver reflective</td>
<td>Positive</td>
<td>The United States</td>
<td>[51]</td>
</tr>
<tr>
<td>Wheat</td>
<td>Transparent</td>
<td>Positive</td>
<td>India</td>
<td>[52]</td>
</tr>
<tr>
<td></td>
<td>Black mulch</td>
<td>NSD</td>
<td></td>
<td>[52]</td>
</tr>
<tr>
<td></td>
<td>Plastic film</td>
<td>Positive</td>
<td>China</td>
<td>[53]</td>
</tr>
<tr>
<td></td>
<td>Plastic film</td>
<td>Positive</td>
<td>China</td>
<td>[54]</td>
</tr>
<tr>
<td></td>
<td>White transparent high density</td>
<td>Positive</td>
<td>China</td>
<td>[55]</td>
</tr>
<tr>
<td></td>
<td>NR</td>
<td>Positive</td>
<td>China</td>
<td>[56]</td>
</tr>
<tr>
<td></td>
<td>NR</td>
<td>Positive</td>
<td>China</td>
<td>[57]</td>
</tr>
<tr>
<td>Broccoli</td>
<td>Black, blue, gray, silver, and white</td>
<td>Variable</td>
<td>The United States</td>
<td>[58]</td>
</tr>
<tr>
<td>Bell pepper</td>
<td>Black, white, and silver</td>
<td>Variable</td>
<td>The United States</td>
<td>[59]</td>
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<td>Cotton</td>
<td>White transparent</td>
<td>Positive</td>
<td>China</td>
<td>[60]</td>
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<td>Douglas-Fir Seedling</td>
<td>Black, white, and paper</td>
<td>NSD</td>
<td>The United States</td>
<td>[61]</td>
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<td>Ground nut</td>
<td>Black</td>
<td>NSD</td>
<td>India</td>
<td>[62]</td>
</tr>
<tr>
<td></td>
<td>Transparent</td>
<td>Positive</td>
<td>Vietnam</td>
<td>[63]</td>
</tr>
<tr>
<td>Cucumber</td>
<td>Black</td>
<td>Variable</td>
<td>Mexico</td>
<td>[64]</td>
</tr>
<tr>
<td></td>
<td>Brown, blue, black, white, silver, and red</td>
<td>Positive</td>
<td>Mexico</td>
<td>[65]</td>
</tr>
<tr>
<td>Potato</td>
<td>White on black, silver on black and aluminum on black</td>
<td>Positive</td>
<td>Mexico</td>
<td>[66]</td>
</tr>
<tr>
<td></td>
<td>Black film</td>
<td>Positive</td>
<td>China</td>
<td>[67]</td>
</tr>
<tr>
<td></td>
<td>Transparent</td>
<td>Positive</td>
<td>China</td>
<td>[68]</td>
</tr>
<tr>
<td></td>
<td>NR</td>
<td>NSD</td>
<td>China</td>
<td>[69]</td>
</tr>
<tr>
<td>Sweet corn</td>
<td>Black</td>
<td>Positive</td>
<td>Canada</td>
<td>[70]</td>
</tr>
<tr>
<td>Rice</td>
<td>Plastic film</td>
<td>Variable</td>
<td>China</td>
<td>[71]</td>
</tr>
<tr>
<td>Maize</td>
<td>Black</td>
<td>Variable</td>
<td>Nigeria</td>
<td>[72]</td>
</tr>
<tr>
<td></td>
<td>NR</td>
<td>Positive</td>
<td>China</td>
<td>[73]</td>
</tr>
<tr>
<td></td>
<td>Plastic film</td>
<td>Variable</td>
<td>China</td>
<td>[74]</td>
</tr>
</tbody>
</table>

(Continued)
Soil Thermal Property

Plastic mulch influenced the soil thermal properties by modifying the radiation budget (absorptivity vs. reflectivity) and water loss from the soil surfaces (Table 2). The color of the plastic mulch largely controls the reflective properties and its impact on soil microclimate. The major plastic used in mulching crop is a black translucent/opaque type made from LDPE. Black-colored plastic mulch acts as a black body and absorbs most of the incoming ultraviolet, visible, and infrared wavelengths and radiates back the thermal energy in thermal radiation or long-wave infrared radiation.[90] Thus, black plastic mulch releases back most of the absorb energy in through radiation and forced convection. Contrary to black plastic mulch, transparent mulch transmits 85%–90% incident radiation depending on the properties.[91] So, soil can receive short-wave incoming solar radiation passing through the transparent plastic but cannot release them back to the atmosphere. Soil releases the long-wave radiation which cannot pass through the clear plastic mulch. Thus, clear plastic mulches are mainly used in temperate climate or during the winter season to give favorable soil temperature for early emergence and establishment of summer crops. On the other hand, the black plastic mulch is used in tropics for maintaining favorable soil temperature without drastic diurnal change in surface soil temperature (Fig. 3). Opposite trend was also reported i.e., black plastic mulch had the greatest soil root zone temperature compared to transparent or white plastic mulch.[90] It was found that better heat transfer between the plastic and soil (i.e., Black mulch) was a more effective heating mechanism than the transmission of short-wave radiation (i.e., clear mulch) in particular experimental condition.

Soil Moisture

Mulching soil surfaces also alter the soil water regime through modifying evaporative loss and soil thermal regime. Mulching can conserve soil moisture and increase the WUE in several crops (Table 2). The WUE under mulching condition depends on other management issues such as irrigation method, and soil and crop properties. Among different studies, most of the author had reported the positive impact of increasing soil water content under mulch compared to the bare soil. The mechanism behind increasing the soil moisture through mulching is attributed to the fact that plastic mulches are highly impervious to the water vapor.[92] Thus, even under high evaporative demand of the atmosphere, mulched soil can retain most of the soil moisture by not losing it where plastic mulch act simply as physical barrier.

Weed and Pest Control

Plastic mulch has also been recognized for controlling the weeds and pest. Black mulch inhibits the weed seed germination growth by simply prohibiting the sunlight to reach them. Contrary, transparent mulch could possibly allow the growth of the weed and thus require added weed management.

Soil Fumigation and Solarization

Plastic mulch being impervious to the gaseous movement acts as an excellent barrier for the fumigants and solarization process.

Reduced Fertilizer Leaching

The impervious mulch allows excess water to run off the field without taking away the fertilizer from root zone. Thus, plastic mulch helps in keeping the nutrient in plant root zone for efficient utilization of nutrient.

Disadvantages of Plastic Mulch

Removal and Disposal

The major problem with the use of plastic mulch is its removal and disposal from agricultural field at the end of the crop season. Plastic mulch is generally being disposed
of by burning, buried in soil, or landfill, but these have been restricted due to growing concern of environmental impact.

Higher Initial Cost

The higher initial cost for laying out the mulch and formation of raised bed in the field is another constrain for wide adaptation of the mulching technique in low-value crop production system. The high-value horticultural crops such as tomato, watermelon, and strawberry are mostly grown with mulch.

### Mulch Based on Degradable and Natural Polymers

Synthetic nonbiodegradable polymeric film such as PE, PVC, EVA, and polybutylene are widely used as agricultural mulch because of their excellent mechanical properties and low cost. However, synthetic polymer film causes problems like removal and disposal during harvesting and other cultivation practices. They lead to environmental pollution after their use due to their nonbiodegradable nature. Farmers usually incorporate used films into the

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**Table 2** Impact of plastic mulches on soil temperature, water content, and WUE at different places

<table>
<thead>
<tr>
<th>Location</th>
<th>Latitude</th>
<th>Description of mulch</th>
<th>Impact on soil temperature</th>
<th>Impact on soil water content</th>
<th>Impact on WUE</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>The United States</td>
<td>NR</td>
<td>Black</td>
<td>Increased</td>
<td>NR</td>
<td>NR</td>
<td>[90]</td>
</tr>
<tr>
<td>Nigeria</td>
<td>06°52’ N</td>
<td>Black and white transparent</td>
<td>Increased</td>
<td>Increased</td>
<td>NR</td>
<td>[45]</td>
</tr>
<tr>
<td>India</td>
<td>77°9’ N</td>
<td>Transparent white</td>
<td>Increased</td>
<td>Increased</td>
<td>Increased</td>
<td>[52]</td>
</tr>
<tr>
<td>The United States</td>
<td>123°17’ N</td>
<td>Black and white transparent</td>
<td>NSD</td>
<td>Increased</td>
<td>Increased</td>
<td>[61]</td>
</tr>
<tr>
<td>India</td>
<td>21°31’ N</td>
<td>Black</td>
<td>Increased</td>
<td>NR</td>
<td>NR</td>
<td>[62]</td>
</tr>
<tr>
<td>China</td>
<td>35°8’ N</td>
<td>Plastic film</td>
<td>Increased</td>
<td>Increased</td>
<td>NR</td>
<td>[53]</td>
</tr>
<tr>
<td>The United States</td>
<td>NR</td>
<td>Black and transparent</td>
<td>Increased</td>
<td>NR</td>
<td>NR</td>
<td>[47]</td>
</tr>
<tr>
<td>China</td>
<td>35°57’ N</td>
<td>Plastic film</td>
<td>NR</td>
<td>Increased</td>
<td>Increased</td>
<td>[54]</td>
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<td>China</td>
<td>36°02’ N</td>
<td>Plastic film</td>
<td>Increased</td>
<td>Increased</td>
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<td>[74]</td>
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<tr>
<td>Nigeria</td>
<td>NR</td>
<td>Black and white transparent</td>
<td>Increased</td>
<td>Increased</td>
<td>NR</td>
<td>[72]</td>
</tr>
<tr>
<td>China</td>
<td>35°33’ N</td>
<td>Black</td>
<td>NR</td>
<td>NSD</td>
<td>Increased</td>
<td>[67]</td>
</tr>
<tr>
<td>Vietnam</td>
<td>20°39’ N</td>
<td>Transparent</td>
<td>Increased</td>
<td>Increased</td>
<td>NR</td>
<td>[63]</td>
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<tr>
<td>Canada</td>
<td>45°37’ N</td>
<td>Black</td>
<td>Increased</td>
<td>Increased</td>
<td>NR</td>
<td>[79]</td>
</tr>
<tr>
<td>China</td>
<td>37°53’ N,39°36’ N, 38°05’ N</td>
<td>NR</td>
<td>Increased</td>
<td>Increased</td>
<td>NR</td>
<td>[69]</td>
</tr>
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<td>China</td>
<td>35°33’ N</td>
<td>Transparent</td>
<td>Increased</td>
<td>Increased</td>
<td>Increased</td>
<td>[68]</td>
</tr>
<tr>
<td>The United States</td>
<td>NR</td>
<td>Black and blue</td>
<td>Increased</td>
<td>NR</td>
<td>NR</td>
<td>[58]</td>
</tr>
</tbody>
</table>

NSD, no significant differences.
soil leading to soil pollution or they burn the used plastic films, causing harmful air pollution.\textsuperscript{[91–95]} To solve these problems, there is a growing awareness to develop biodegradable or photodegradable film with short service lifetime. In recent decades, biopolymeric mulch film based on starch, cellulose, lignin, fruit by-products, soy protein, pectin, chitosan, etc. were reported. They were specially designed to have properties just like synthetic polymers with the added advantage of complete biodegradation in short time into water and carbon dioxide, thus reducing harmful effects of the use of synthetic polymers in environment. A large number of biopolymeric films with or without light-sensitizing additives have been designed for controlled biodegradation by microorganism and photodegradation.

Degradable plastics for mulch application can be classified into three classes: biobased polymers (starch, cellulose, chitosan, other polysaccharides, bacterial polyesters, and polypeptides), degradable synthetic polymers (polymers such as Poly(lactic acid) [PLA], polycaprolactone, polyamides, polyurethanes, and polyanhydrides) and poorly degradable synthetic polymers containing oxidizable moieties and/or oxidation agents as additives or as monomeric constituents. Chemical structure of biopolymers and degradable synthetic polymers used in agriculture mulch is provided in Fig. 4. Starch is one of the most available low-cost, natural biodegradable materials. But, the use of starch as plastic like material is limited because starch lacks essential properties like moldability and thermoplasticity.\textsuperscript{[96]} Therefore, starch has been reported to be modified to induce these essential properties. Hydrolysis of starch followed by functionalization with glycol has been reported to incite moldable and thermoplastic properties.\textsuperscript{[97]} Melted modified starch was also reported to be blended with other biodegradable polymers to be used as a functional polymer.\textsuperscript{[98]} Starch–PVA film, containing 60%–65% starch, 16% PVA, 16%–22% glycerol and 1%–3% formaldehyde, was reported to show water insoluble and flexible properties when coated with PVC and toluene diisocyanate–castor oil prepolymers.\textsuperscript{[99]} These starch–PVA blend films have controlled biodegradable properties. After controlled period, these starch–PVA films quickly deteriorate into small particles and mixed with soil. Starch was reported to be incorporated into PE chains by taking compatilizer, that is, poly(ethylene)-co-acrylic acid.\textsuperscript{[100]} Starch was also reported to be used as a filler in PVC films. Biodegradable mulch material was prepared by blending starch-based polymer with high-performance polyester polymers (e.g., polyhydroxybutyrate, PHB or polylactic acid, PLA). Osage orange wood was combined with PLA to form polymeric film for mulch application.\textsuperscript{[101]} The developed mulch film completely biodegrades through a single crop growing season. Natural fibers collected from ramie and cotton were combined with starch to generate mulch film for agricultural purpose.\textsuperscript{[102]} Biodegradable cellulose film was reported to be used in bell pepper cultivation as a mulching material. It was found that nitrate leaching through soil was reduced and the yield was enhanced but less significantly compared with the PE black mulch.\textsuperscript{[103]} Ecoflex\textsuperscript{\textregistered} is a biodegradable agricultural mulch manufactured by BASF, and it consists of synthetic copolymer of polybutylene adipate terephthalate (PBAT), PBAT possesses high flexibility, good impact strength, and good melt processability just like LDPE.\textsuperscript{[104]} PBAT easily forms composites with natural polymers (including starch, cellulose, other polysaccharides, PLA, and polyhydroxyalkanoate [PHA]) and contribute flexibility and hydrophobicity to the blend.\textsuperscript{[105]} Other commercially available biodegradable agricultural mulches are listed in Table 3.

PE was reported to be mixed with oxo-degradable additives to produce low-cost oxo-degradable PE film which was used as agricultural mulch.\textsuperscript{[106,107]} But degradation of these oxo-degradable PEs does not occur in soil and require exposure to light and air for long time.\textsuperscript{[108]} Combination of PE with metal salts of dialkyl dithiocarbamates (Iron, cobalt, nickel, etc.) was reported to produce photodegradable polymeric mulch film.\textsuperscript{[109]} The photodegradation of these polymeric films can be tuned by adjusting the ratio of the metal salts. Paper film has been considered as an alternative to plastic film; however, paper film suffers from very rapid degradation and is easily broken down after exposure to soil, rain, and wind. To enhance the performance of paper film as mulch, paper was coated with PE, polyester, and wax.\textsuperscript{[110–112]} Polymerized vegetable oil resins-coated paper was reported with increased strength and reduced biodegradation.\textsuperscript{[111]}

Fig. 4  Radiative balance of incoming and outgoing radiation in case of (A) black or opaque mulch and (B) transparent mulch
### Limitation of Biodegradable Mulch

To overcome the problem of disposal of plastic mulch and address the environmental concern, biodegradable mulches are being developed and used for the past few decades (Table 3). Additionally, biodegradable mulches have advantages over plastic mulch as they degrade in-situ and influence the soil quality. But, most of biodegradable mulch did not have any added advantages in terms of crop production over plastic mulch (Table 4). In some cases, supplementary weeding is also needed as the biodegradable mulch started degrading during the growing season. With these limitations, biodegradable mulch is still far from wide adaptation for crop production.

### FERTILIZER FORMULATIONS BASED ON POLYMER

It is well established that the use of fertilizers is necessary for crop growth and they are one of the most important agrochemical products. They are applied in soil for adequate supply of nutrients to plants and improve their growing. Till now 17 essential plant nutrients have been discovered and can be classified into macro- and micronutrients. Macronutrients are those nutrients which are required in substantial amount, more than that of iron (Fe), by the plant. They are C, H, O, N, P, K, Ca, Mg, and S, and O constitute more than 90% of plant biomass and are supplied to plant through carbon dioxide and water. The remaining six essential macro nutrients can be broadly classified into primary nutrients (N, P, and K) with high plant requirement and secondary nutrients (Ca, Mg, and S) with moderate plant requirement. As N, P, and K are required in large amount, their deficiency in plants are wide spread and can be corrected only through application of commercial fertilizers. Micronutrients (Fe, Mn, Cu, Ni, B, Mo, and Cl), though required by plant in very small amount, also reported to show widespread deficiency in recent decade due to intensive crop cultivation with high yielding varieties. Deficiency of these micronutrients is also recommended to be corrected by the application of micronutrient fertilizers. Most of these fertilizers either macro or micro are water-soluble inorganic salts (\(\text{NH}_4\text{SO}_4\), \((\text{NH}_4)\text{HPO}_4\), \(\text{Ca(H}_2\text{PO}_4\))\(_2\), \(\text{KCl}\), \(\text{FeSO}_4\cdot7\text{H}_2\text{O}\), \(\text{ZnSO}_4\cdot7\text{H}_2\text{O}\), \(\text{Na}_2\text{B}_4\text{O}_7\cdot10\text{H}_2\text{O}\), etc.) and they are taken up by plants in their ionic forms. Urea is the most famous nitrogen fertilizer which is present in organic form, but in soil it goes through transformation process (ammonification, \(\text{R-NH}_2 \rightarrow \text{NH}_3^+\), nitrification, \(\text{NH}_3^+ \rightarrow \text{NO}_3^-\)) by microbial enzymes to yield soluble ions to be taken up plants. These ammonium and nitrate ions (\(\text{NH}_3^+\) & \(\text{NO}_3^-\)), though readily absorbed by plant through roots, are also prone

<table>
<thead>
<tr>
<th><strong>Table 3</strong> Commercially available polymers and polymer blends employed in biodegradable agricultural mulches</th>
<th><strong>Product</strong></th>
<th><strong>Polymer</strong></th>
<th><strong>Manufacturer</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Biocycle®</td>
<td>Sucrose/PHA blend</td>
<td>PHB Industrial (Brazil)</td>
<td></td>
</tr>
<tr>
<td>Bio-Flex</td>
<td>PLA/copolyester blend</td>
<td>FKUR, Willich (Germany)</td>
<td></td>
</tr>
<tr>
<td>Biomax TPS</td>
<td>Starch + thermoplastic starch</td>
<td>DuPont (The United States)</td>
<td></td>
</tr>
<tr>
<td>Biomax L</td>
<td>PHA</td>
<td>Biomer (Germany)</td>
<td></td>
</tr>
<tr>
<td>Bionolle</td>
<td>PBS</td>
<td>Showa High Polymer (Japan)</td>
<td></td>
</tr>
<tr>
<td>Biopar</td>
<td>Starch co-polyester</td>
<td>Biop (Germany)</td>
<td></td>
</tr>
<tr>
<td>Biosafe™</td>
<td>PBAT/starch blend; PBS; PBSA</td>
<td>Xinfu Pharmaceutical Co (China)</td>
<td></td>
</tr>
<tr>
<td>Eastar Bio™</td>
<td>PBAT/starch blend</td>
<td>Novamont (Italy)</td>
<td></td>
</tr>
<tr>
<td>Eco-Flex®</td>
<td>PBAT/starch blend</td>
<td>BASF (Germany)</td>
<td></td>
</tr>
<tr>
<td>Ecovio</td>
<td>Ecovio</td>
<td>BASF (Germany)</td>
<td></td>
</tr>
<tr>
<td>EnPol</td>
<td>PBS</td>
<td>IRE Chemical (Korea)</td>
<td></td>
</tr>
<tr>
<td>Envio</td>
<td>Ecoflex (PBAT) + PLA + starch blend</td>
<td>BASF (Germany)</td>
<td></td>
</tr>
<tr>
<td>GreenBio</td>
<td>PHA</td>
<td>Tianjin GreenBio Materials (China)</td>
<td></td>
</tr>
<tr>
<td>Ingeo®</td>
<td>Starch + PLA; PBS + PLA</td>
<td>NatureWorks (The United States)</td>
<td></td>
</tr>
<tr>
<td>Mater-Bi®</td>
<td>PCL + starch blend</td>
<td>Novamont (Italy)</td>
<td></td>
</tr>
<tr>
<td>Mirel®</td>
<td>PHA</td>
<td>Metabolix (The United States)</td>
<td></td>
</tr>
<tr>
<td>Paragon</td>
<td>Starch + thermoplastic starch</td>
<td>Avebe (The Netherlands)</td>
<td></td>
</tr>
<tr>
<td>ReNew</td>
<td>Polyhydroxy alkanoate (PHA)</td>
<td>Danimer Scientific (The United States)</td>
<td></td>
</tr>
<tr>
<td>Skygreen®</td>
<td>Terephthalic acid co-polyester</td>
<td>SK Chemicals (Korea)</td>
<td></td>
</tr>
<tr>
<td>WeedGuard Plus</td>
<td>Cellulosic</td>
<td>Sunshine Paper Co. (The United States)</td>
<td></td>
</tr>
</tbody>
</table>

**Source:** Information of this table is collected from Refs. [199–201]. Italized entries are products that are almost entirely biobased: PBAT, polybutylene adipate terephthalate; PHA, polyhydroxyalkanoate; PLA, polylactic acid; PCL, poly(oxyoctylene adipate); PBS, polybutylene succinate; PBSA, PBS-co-adipic acid.

Lifetime-controlled biodegradable film was prepared by bridging PVA chains with functionalized polycaprolactone crosslinking. The resulting PVA-Poly lactone film is water resistant and amenable to biodegradation only when in contact with soil by microbes. It was observed that the degradation of biodegradable plastic mulch was faster and more than the paper mulch and the oxo-degradable polymer mulch under the above mentioned soil condition. The above mentioned soil degradation of oxo-degradable polymer mulch highly depends on the location and crop season.
Agriculture: Polymers in Crop Production Mulch and Fertilizer

Table 4  Biodegradable mulches’ degradability, efficiency to control weed, and impact on yield and quality of crops compared to the plastic (PE) mulch

<table>
<thead>
<tr>
<th>Crop</th>
<th>Location</th>
<th>Mulching material</th>
<th>Influence on yield and quality</th>
<th>Degradation status</th>
<th>Weed Control</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strawberry</td>
<td>Brazil</td>
<td>Eco-Flex</td>
<td>NSD</td>
<td>Tensile strength, elongation at break, and grammage and water sorption were reduced after 8 weeks</td>
<td>Effective</td>
<td>[116]</td>
</tr>
<tr>
<td></td>
<td>Portugal</td>
<td>Mateer-Bi</td>
<td>NSD</td>
<td>Relatively low degradation</td>
<td>—</td>
<td>[117]</td>
</tr>
<tr>
<td></td>
<td>The United States</td>
<td>Paper</td>
<td>NSD</td>
<td>Transparent mulch degrade quickly than black mulch</td>
<td>The black mulch effectively controls weeds</td>
<td>[118]</td>
</tr>
<tr>
<td>Tomato</td>
<td>The United States</td>
<td>Mateer-Bi</td>
<td>NSD</td>
<td>—</td>
<td>Effective</td>
<td>[119]</td>
</tr>
<tr>
<td></td>
<td>Spain</td>
<td>Eco-Flex</td>
<td>White mulch produced less yield, whereas black mulch maintain the same level of yield</td>
<td>White mulch degraded very fast (95%) compared to black mulch</td>
<td>Black mulch was more efficient in controlling weed than white mulch</td>
<td>[120]</td>
</tr>
<tr>
<td></td>
<td>Spain</td>
<td>Biodegradable material</td>
<td>NSD</td>
<td>Degraded timely</td>
<td>—</td>
<td>[121]</td>
</tr>
<tr>
<td></td>
<td>Spain</td>
<td>Mater-Bi</td>
<td>NSD</td>
<td>—</td>
<td>Inefficient than plastic mulch</td>
<td>[122]</td>
</tr>
<tr>
<td></td>
<td>Spain</td>
<td>Mater-Bi</td>
<td>NSD</td>
<td>Degraded after 3 months of crop harvest season</td>
<td>—</td>
<td>[123]</td>
</tr>
<tr>
<td>Muskmelon</td>
<td>Portugal</td>
<td>Mater-Bi</td>
<td>NSD</td>
<td>Biodegradation is very slow</td>
<td>—</td>
<td>[124]</td>
</tr>
<tr>
<td>Sweet corn</td>
<td>Canada</td>
<td>Mater-Bi</td>
<td>NSD</td>
<td>Broke down well at the beginning of the growing season</td>
<td>Supplemental weed is needed</td>
<td>[125]</td>
</tr>
<tr>
<td>Zucchini</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Cantaloupe</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Pepper</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Eggplant</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Watermelon</td>
<td>The United States</td>
<td>Plastigone PE</td>
<td>NSD</td>
<td>Early splitting and cracking occur</td>
<td>—</td>
<td>[126]</td>
</tr>
<tr>
<td></td>
<td>Italy</td>
<td>Mater-Bi</td>
<td>Yield and quality were improved</td>
<td>—</td>
<td>—</td>
<td>[127]</td>
</tr>
<tr>
<td></td>
<td>The United States</td>
<td>Paper</td>
<td>NSD</td>
<td>—</td>
<td></td>
<td>[128]</td>
</tr>
<tr>
<td>Paper</td>
<td>Australia</td>
<td>Mater-Bi</td>
<td>NSD</td>
<td>—</td>
<td>—</td>
<td>[129]</td>
</tr>
<tr>
<td>Grapevine</td>
<td>France</td>
<td>Mater-Bi</td>
<td>NSD</td>
<td>Degraded timely</td>
<td>—</td>
<td>[130]</td>
</tr>
</tbody>
</table>

To losses through leaching and volatilization. Similarly after dissolution not all the orthophosphate ions (H$_2$PO$_4^-$, HPO$_4^{2-}$ & PO$_4^{3-}$) become available to plant, a big fraction get fixed by free Al and Fe species in acidic soils and by free Ca$^{2+}$ ions in alkaline soils. This loss of nutrients is generally compensated by the farmers by applying overdose of fertilizers. But overuse can cause environmental problems such as increase of nitrate or phosphate concentration in the groundwater, contribution to the formation of acid rain, ozone layer depletion due to release of nitrous oxides by denitrification, etc. By reducing these nutrient losses in the field, it is possible to reduce rate of application, increase the use efficiency of fertilizers, and avoid pollution of the environment. [132] These inevitable losses of nutrients in the environment can be checked by adopting the concept of slow- or controlled-release fertilizer formulations. Through controlled-release fertilizer formulations an optimum concentration of nutrients in the soil can be maintained by tuning the factors which controls the rate and duration of nutrient release from the formulations. There are many advantages of controlled-release fertilizer formulations over conventional fertilizer. [133] They are as
follows: (1) reduction in the number of nutrient applications especially in long-term crops, (2) reduction in the application cost, (3) optimum availability of nutrients to plant, (4) reduction of nutrient loss through leaching under heavy rainfall condition or irrigation water, soil fixation, microbial degradation, volatilization, etc., (5) reduction in environmental hazard caused by fertilizer application, for example, ground water contamination and ozone depletion. Slow or controlled release of nutrient can be achieved by providing polymeric coatings on the fertilizers or using polymeric matrix as carrier of fertilizers/nutrients.

**Different Approaches of Polymer-Based Fertilizers Production**

Polymer-coated fertilizer formulations consist of water-soluble fertilizer core surrounded by a polymeric barrier that prevents the rapid release of nutrient into the environment. Previously, rate-controlling membrane made of sulfur and coal tar was used to develop coated urea granules. But these sulfur-coated urea had the disadvantages of crack development during logistics. So later on, several synthetic polymers and resins were tried to develop coating materials. The release of nutrients from these polymeric membranes coating followed the diffusion mechanism leading to slow release. The second category of fertilizer formulation includes uncoated fertilizers where nutrient are uniformly distributed in the polymer as monolithic matrix and release of nutrient occurs due to either chemical reaction or polymeric relaxation. An example of second category fertilizer formulation is polyurea. Polyurea was reported to be produced by reacting urea with formaldehyde and acetaldehyde. In 1924, BASF patented urea-formaldehyde polyurea product as slow-release nitrogen fertilizer. Polyurea was also reported to be developed by reacting urea with chlorinated polyacrylic acid. Isocyanates were also reported to react with urea to produce polyurea. The release of nitrogen from polyurea matrix occurs through chemicals reaction in soil and as like coated fertilizer does not depend on the chemical nature of coating and thickness. Polyurea has similar advantages of coated fertilizer formulations.

As early as in the 1960s, the concept of controlled release was tried and practiced in the fertilizer field. Different synthetic and biopolymers including PE, polystyrene, ethylene–propylene copolymer, EVA copolymer, natural rubber, and starch have been tried for the development of controlled-release fertilizer formulations. Here the zinc fertilizers were distributed in a polymer matrix and extruded. LDPE was also used to encapsulate urea prills, and it was reported that LDPE coating improved the crushing strength, abrasion resistance, impact resistance, chemical compatibility with superphosphate, and reduced the caking tendency. PE wax was used as a matrix to prepare formulation monoammonium phosphate, diammonium phosphate, single superphosphate and other N, P, and K fertilizers. The dissolution time of this fertilizer formulation was found to be doubled due to the use of PE wax. Polyolefin-coated urea fertilizer was developed in Japan. The coating is primarily a blend of polyolefin type resin, EVA copolymer, and polyvinylidene chloride as major components.

**Polystyrene** Recycled polystyrene foam was used to prepare polymer-coated urea (PCU) and large tablet polymer-coated urea. The developed coated urea formulations were low cost in nature and showed slow-release properties of nitrogen. Polystyrene was mixed with starch and the mixture was used to coat urea. Polycaprolactone was mixed to provide the biodegradable nature of polymer coating and to generate porosity. Soil release study showed that the coated urea released around 18%–28% of nutrient till the 10th day. Similarly, bioblend was prepared by mixing polystyrene with starch for polymeric coating of urea granules. Double coating slow-release formulation of urea was prepared by inner coating with polystyrene. As polystyrene provides hydrophobicity to the coating material, it’s content influenced the nitrogen release behavior.

**Polycrylates** Effect of different crosslinkers (Divinylbenzene/N,N′-methylenebisacrylamide /tetraethylenglycol diacrylate or pentaerythritol triacrylate) on acrylamide-coated urea was tested and it was found that the copolymer of acrylamide and tetraethylenglycol diacrylate showed best extended release properties. Commercial NPK granular fertilizer (6–20–30) was coated with polycrylonitrile (PAN) using phase inversion technique. The PAN produced porous membrane around the granules and the density of porosity determined the release rate of nutrients from the formulation. Urea granules were reported to be coated with urea formaldehyde followed by a second layer coating of crosslinked poly(acrylic acid)/organo-attapulgite through inverse suspension polymerization. The developed urea formulation had N content 28.3% and absorbed 80 times in tap water. Interest on research on clay polymer composites has rapidly been increasing due to their potential for many uses in agriculture and other industrial purposes. Chemical surface functionality and surface structure of clays and nanoclays play an important role in many technological application fields are being successfully utilized in controlled-release systems as modifying agents. Clay-polymer nano composites represent a new class of material alternative to conventional filled
polymers. In this new class of material, nano-sized clay (at least one dimension) are dispersed in a polymer matrix offering tremendous improvement in performance properties of the polymer. The first reports on clay–organic polymer nanocomposites date back to the early 1960s when the polymerization of various monomers intercalated in smectites started being studied.[158] Urea was entrapped in crosslinked poly(acrylic acid-acrylamide)/bentonite superabsorbent composites to develop slow-release nitrogen fertilizer.[159] The developed superabsorbent based fertilizer formulation showed high water absorbency (700 g g⁻¹) and extended nitrogen release characteristics up to 30 days. Poly(ethylene glycol) (PEG)-modified crosslinked acrylic acid matrix was used to encapsulate KH₂PO₄ and developed formulation showed slow-release characteristics.[160] Slow-release urea hydrogel was prepared by the free radical solution polymerization of hydrophilic monomers (acrylic acid and acrylamide) alone or in combination, that is, in the presence of urea solution and crosslinker molecule, N,N-methylene-bis-acrylamide.[161] Multilayered coated NPK fertilizer formulation was prepared by inverse suspension polymerization of NPK granules, coated with PVA and glutaraldehyde crosslinked chitosan, in various molar ratios of acrylamide and acrylic acid monomers in presence of persulfate initiator and TEMED (N,N′,N″,N″-tetramethylethylenediamine) and MBA (N,N′-methylebisacrylamide) crosslinker.[162] The release of N, P, and K nutrient was extended to 30 days in water, and the mechanism was found to be the pseudo-Fickian diffusion mechanism.

**Others** EVA along with PE was reported to develop controlled-release urea fertilizer.[163] The ratio of EVA to PE affects the release of nutrients from the formulations. Higher amount of EVA in the coating matrix resulted in higher release rate. EVA was used to coat iron microcapsule formulations with enhanced WUE. The release of iron from the formulation was retarded by the application of EVA coat.[164]

**Biopolymers**

**Poly(Lactic acid)** PLA and its copolymer, poly(lactic acid-co-ethylene terephthalate), were used to coat urea granules by spraying technique.[165] Besides spraying, atomisation technique was also used to prepare microsized PLA-coated urea.[166] PLA was blended with soy protein isolates and plasticized with triacetin to develop controlled-release NPK fertilizer formulation.[167] During melting of soy protein isolates, it formed highly ordered porous matrix in which PLA was found in dispersed phase along with NPK fertilizer. The release of NPK salts from these PLA matrices was studied by measuring conductivity of elution medium, and it was found that the release neither followed diffusion mechanism nor combined mechanism of diffusion and polymer relaxation. Slow-release bioplastic fertilizer composites were prepared by blending PLA, NPK fertilizer, and empty fruit bunch fiber.[168] Use of PLA and fiber in these composite fertilizer formulations enhanced the biodegradation property of the same.

**Cellulose** Cellulose acetate followed by poly(acrylic acid-co-acrylamide)/vermiculite superabsorbent composite were used to develop double-layer coating on fertilizer granules.[169] Because of the polymer coating with superabsorbent properties, the developed fertilizer granules showed slow-release character along with excellent water retention capacity. Cellulose acetate was also reported to be used as a coating material in urea through phase inversion technique.[170] Double-layer coating on urea by using ethyl cellulose and crosslinked poly(acrylic acid-co-acrylamide) was reported to improve release and water retention properties. Similarly, methyl cellulose was reported to develop hydrogel matrix along with polyacrylamide/Ca-montmorillonite and used for the development of slow-release urea formulation.[171] Carboxymethyl cellulose-grafted crosslinked polyacrylamide/zeolite hydrogel composites were reported to develop slow-release formulation of zinc micronutrient.[172] Without Zn²⁺ (ZnSO₄) impregnation, the hydrogel composites showed high water absorbcency to the tune of 600–700 g/g xerogel. The mathematical model analysis of the developed hydrogel composites showed that the mechanism of water absorption followed anomalous transport (combination of diffusion and polymer relaxation), whereas the water release phenomena followed purely Fickian diffusion. Impregnation of ZnSO₄ in the hydrogel matrix was done in situ during free radical polymerization, and the resulting zinc hydrogel formulation showed lower water absorbcency which was due to the charge screening effect of the free carboxylates groups by the divalent cations (Zn²⁺). Carboxymethyl cellulose-grafted crosslinked polyacrylamide hydrogel was also reported to develop slow-release formulation of boron micronutrient by in situ impregnation of borax during radical polymerization.[173] The developed boron formulations showed low water absorbcency to the tune of 30–60 g/g xerogel, which was due to the ability of borate anions, produced in situ during synthesis, to form crosslinking bond with cellulosic chains of carboxymethyl cellulose. The developed boron hydrogel formulations had high boron loading efficiency and had the capacity to release boron for an extended period of time.

**Starch** Starch was reported to blend with urea along with a stabilizer to develop the controlled-release urea formulation.[174] Starch was reported to add biodegradable nature in to polysulfone coating of NPK fertilizer and it was found that the increase content of starch led to the higher release rate of nutrients.[175] Slow-release urea fertilizer was produced by membrane encapsulation in starch-g-poly-L-lactide through in situ graft copolymerization.[176]
The introduction of hydrophobic poly-L-lactide reduced the swellability of starch, leading to the slow release of urea for an extended period of time (from several hours to 1 day). Starch–PVA blend film was reported for water-soluble granular fertilizers. \[175\] Introduction of formaldehyde in the starch–PVA film decreased the film nutrient ions permeability by inter- and intramolecular crosslinking of –OH bond of starch and PVA. Starch-g-poly(vinyl acetate) was reported as a biodegradable carrier material and used for encapsulating urea fertilizer. \[176\] Borate cross-linked urea modified tapioca starch was reported as a controlled delivery device of urea. \[177\] The hydrophobicity of the developed starch–borate–urea system was enhanced by incorporating lignin leading to further extended release of urea and stability of the polymeric system in water. Poly-vinyl alcohol modified starch was used to coat urea granule, and the thickness of coating determined the diffusion coefficient of urea release. \[178\] Starch-grafted poly(acrylic acid-acrylamide) was produced by the reverse suspension free radical polymerization and used to coat nitrogen and phosphorous fertilizer. \[179\] Upon application, 32% of these starch-grafted hydrogel-coated fertilizer formulation degraded after 55 days and about 60% of the nutrient was released by 30th day. Biodegradable polyurethane foam was prepared by reacting diisocyanate with Acacia mearnsi bark and corn starch in the presence of adipic acid diester of PEG-400. \[180\] This solid foam was used to encapsulate ammonium sulfate ((NH₄)₂SO₄) with slow release properties.

**Chitosan** Chitosan was used to prepare inner coating of NPK fertilizer granule followed by coating of poly(acrylic acid-co-acrylamide) through inverse suspension polymerization. \[181\] The water absorptivity of developed coated NPK fertilizer granule was found to be 70 times in tap water and released less than 15% of nutrient on the third day and about 75% of loaded nutrient on the 30th day. The inner chitosan layer on the coated fertilizer formulations extended the release of nutrient by slowly degrading by the act of microorganism. Chitosan nanoparticles were produced by polymerizing methacrylic acid to encapsulate NPK fertilizer. \[182\] The stability of colloidal suspension of chitosan nanoparticles was higher with addition of nitrogen and potassium compared to phosphorous. It was reported that higher anionic charge of calcium phosphate led to reduced stability of chitosan nanoparticles. Genipin-crosslinked chitosan microsphere was developed to encapsulate urea with high entrapment efficiency (78.5%–99%). \[183\] Higher amount of genipin crosslinker and chitosan reduced the rate of release of nitrogen from the microsphere, whereas high loading of urea led to enhanced release rate. Controlled-release formulation of co-granulated ammonium zinc phosphate and urea was prepared by inner coating with cellulose acetate butyrate followed by outer coating with carboxymethyl chitosan-g-poly(acrylic acid)/attapulgite superabsorbent composite. \[184\] The developed bilayer coating on mixed fertilizer showed reduced nitrogen leaching and runoff, and at the same time improved the soil moisture retention capacity and pH. Chitosan was used to bind kaolinite urea mixture to develop controlled-release formulation of urea. \[185\] The water release study showed that the urea-kaolinite granule with 7.5% chitosan binder released 59.27% of the total nitrogen on the 30th day.

**Lignin** An US patent in the early 1960s describes a lignin matrix for delivery of fertilizer. \[186\] Subsequently, many patents were reported where lignin was used as the base matrix for coating fertilizer and slow delivery of nutrients. \[187,188\] Commercially available pine lignin, obtained by Kraft process, was used to coat pelleted urea. \[189,190\] During the coating process lime oil and natural, dimerized, and esterified gum rosin was used as an adhesive. The coated urea pellet showed enhanced crushing strength compared to the uncoated urea pellet. Performance of ammoxidized lignin, as slow release nitrogen fertilizer, was compared with conventional urea in sorghum crop and it was found that though performance of conventional urea was better during initial plant growth period, due to higher solubility, ammoxidized lignin showed better performance during second plant growth stage due to slow release of nitrogen from the lignin matrix. \[190\] Lignin in combination with ethyl cellulose was used CR formulation of urea granules. \[191\] The lignin-ethyl cellulose coated granules were prepared in Wurster-type fluidized-bed equipment with high encapsulation efficiency (95.12%–97.18%). The use of ethyl cellulose was done to bring more hydrophobicity in the coating system and higher ethyl cellulose in the coating showed higher Tₘ value (the time taken for 50% of the urea to be released into water). Chelation of lignin, Kraft black liquor, with calcium acetate was used to develop slow-release urea formulation. \[192\] In comparison to acid precipitated lignin, calcium-chelated lignin showed more hydrophobicity and formulation based on it retained 58% urea after 24 h incubation study.

**Others** Controlled-release fertilizer formulation was prepared by using attapulgite clay as matrix followed by inner coating with guar gum and outer coating with guar gum-g-poly(itaconic acid-co-acrylamide)/humic acid superabsorbent polymer. \[193\] The developed fertilizer formulation had the advantages of reduction of nutrient losses through leaching and run off, improved soil moisture, and regulation of soil pH. pH responsive controlled-release fertilizer formulation was prepared by coating polydopamine-g-poly(acrylic acid) through atom transfer radical polymerization of acrylic acid. \[194\] The reaction was initiated through an mussel-inspired chemistry. Biobased polyurethane coating was done on urea prills to develop PCU. \[195\] The release of nitrogen from the developed PCU was further extended by developing interpenetrating network with epoxy resin. PHB alone or in combination with
ethyl cellulose was used to coat urea.[196] Thickness of coating determine the dissolution time of coated formulations, and urea granules sprayed with 5% w/v PHB and 5% w/v CTAB solution showed complete dissolution in 1 h in distilled water compared to uncoated urea (<1 min). Beside coated granule, PHB was also used to form film and pellet formulation of urea.[197] In situ free radical polymerization of sodium alginate, acrylic acid, acrylamide in the presence of montmorillonite, and fertilizer compound was used to develop slow-release superabsorbent nanocomposites encapsulated NPK fertilizer.[198] The presence of exfoliated montmorillonite structure in superabsorbent systems led to more reduction of nutrient release rate from the fertilizer.

CONCLUSIONS

The use of plastic mulch in agriculture has increased dramatically in recent decade due to its ability to provide optimum microclimatic condition for crop growth by maintaining soil temperature, moisture, and other pest-controlling benefits. PE film has popularly being used as plastic mulch since the 1950s because of its low cost, processibility, flexibility, and high chemical resistance nature. However, in view of disposal and environmental problems caused by the use of nondegradable synthetic plastic mulch, different controlled degradable plastic mulch was developed. These include oxo-degradable plastic mulch where different oxidizable moieties and/or oxidation agents as additives are added into poorly degradable plastic such as PE and PVC and biodegradable plastic mulch such as PLA, polycaprolactone, and polyamides. More recently biodegradable plastic films are prepared from composite polymers by using biopolymers such as starch, cellulose and chitosan. These composite polymer films have mechanical properties just like synthetic polymers with added advantage of complete biodegradation when the crop is harvested. Thus, the use of these biodegradable films reduces the harmful effect of synthetic polymer in the environment. Similarly like mulch, there are extensive uses of polymers in fertilizer delivery system. Water-soluble fertilizers are coated or dispersed in polymeric matrix or reacted with functional groups of polymeric chain to develop controlled-release fertilizer formulations. Over the conventional fertilizers, these formulations have the advantages of reduced dosage, less frequent application, reduction of nutrient loss by leaching, run off, volatilization, etc. Several synthetic polymers such as PE, polystyrene, and polycrylates are being used to develop controlled-release fertilizer formulations. Recently, more emphasis is being given to develop hydrogel/superabsorbent fertilizer formulations with an aim to achieve integrated water and nutrient management strategies. Several biopolymer (starch, cellulose, chitosan, etc.) grafted polycrylates and their clay composites are reported to encapsulate water-soluble fertilizers. These superabsorbent fertilizer formulations not only show good slow-release property, but also have excellent soil moisture preservation capacity, which could effectively improve the utilization of fertilizers and water resources simultaneously. Thus, these can be also used in dry areas to improve soil condition.

REFERENCES


