

Controlled-release urea encapsulated by ethyl cellulose/butyl acrylate/vinyl acetate hybrid latex

Yue Li¹, Da Zhen², Shuijiao Liao^{1*}, Duanwei Zhu³, Xun Yang¹

¹College of Basic Sciences of Huazhong Agricultural University, Wuhan, China 430070

²Hubei University of Technology, College of Bioengineering, Wuhan, China 430068

³Centre for Microelement Research of Huazhong Agricultural University Laboratory of Plant Nutrition and Ecological Environment Research, , Wuhan, China 430070

*Corresponding author: e-mail: liaosj@mail.hzau.edu.cn

Fertilizer encapsulation through polymer membranes can reduce fertilizer losses and minimize environmental pollution. In this paper, an emulsion of ethyl cellulose (EC)/vinyl acetate (VAc)/butyl acrylate (BA) was successfully prepared by pre-emulsified semi-continuous seed emulsion polymerization. EC/BA/VAc films showed biodegradability. The influence of the EC content on the properties of EC/BA/VAc films was also investigated by DSC, a water absorbency analysis, etc. Controlled-release urea encapsulated by EC/BA/VAc latex was prepared in a film coating machine and conformed to the standards for slow-release fertilizers of the Committee of European Normalization. The release of urea from controlled-release urea encapsulated by EC/BA/VAc latex containing 0%, 5%, 10%, and 15% EC was 75.1%, 65.8%, 70.1% and 84.1%, respectively, after 42 days, and controlled-release urea encapsulated by EC/BA/VAc latex (5% EC) had the best controlled-release ability. Therefore, controlled-release urea encapsulated by EC/BA/VAc latex has many potential applications in agricultural industry.

Keywords: coated urea, ethyl cellulose/butyl acrylate/vinyl acetate, hybrid latex, emulsion polymerization, controlled-release ability.

INTRODUCTION

Fertilizer encapsulation through polymer membranes can reduce fertilizer losses and minimize environmental pollution. Polymer coating materials include bio-based coating materials and conventional synthetic polymers such as polyolefins, acrylic resins and glycerol ester^{1–3}. Compared with conventional synthetic polymers, bio-based coating materials have captured much research attention because of their relatively low cost, abundance, renewable and environmentally friendly properties. In recent years, modified natural polymers such as modified corn stover, starch, cellulose, castor and wheat straw have been used as controlled-release materials in fertilizer^{4–11}.

Biodegradable cellulose is an abundant and inexhaustible material. However, the application of cellulose is restricted because it is insoluble in most solvents. Ethyl cellulose (EC) is a cellulose derivative that is thermoplastic, nontoxic and stable and is soluble in organic solvents. EC has been used in pill coatings^{12–13} and fertilizer coatings due to its excellent film-forming abilities and hydrophobicity¹⁴. However, EC is often used with plasticizers and modified by copolymerization with different monomers such as caprolactone monoacrylate¹⁵ and polystyrene¹⁶ to reduce its fragility. Plasticizers can easily escape from EC fertilizer coating materials and are harmful to the environment. Thus, EC is mainly modified by copolymerization to reduce its fragility. Most copolymerizations are carried out in organic solvents such as methanol and acetone^{17–21}. A few copolymerizations are performed in water. For example, Chen et al.²² reported that ethyl cellulose (EC)/butyl acrylate (BA)/methyl methacrylate (MMA) hybrid latexes can be prepared by batch emulsion polymerization in water containing 6.6% toluene and 6.7% hexadecane by weight. In our previous study²³, we have only prepared EC/BA/VAc hybrid latex by pre-emulsified semi-continuous seed emulsion polymerization in water without any organic

solvent and evaluated the effects of the EC content on the monomer conversion, particle size, and viscosity of EC/BA/VAc emulsions. However, we did not prepare controlled-release film materials and coated fertilizer containing EC.

To date, controlled-release film materials and coated fertilizer containing EC have not yet been prepared through an environmentally friendly method without any organic solvents and plasticizers. In the present study, we produced EC/BA/VAc hybrid latex films with excellent film-forming ability, hydrophobicity, biodegradability and tenacity through an environmentally friendly method without any organic solvents and plasticizers, and we prepared a controlled-release polymer coated urea and study its slow-release ability.

EXPERIMENTAL

Materials, emulsion polymerization and emulsion characterization

The materials, emulsion polymerization and emulsion characterization tools employed in the present study were described in our previous study²³. Emulsion polymerization was performed in a three necked round-bottom flask. The general recipe was listed in the Table 1. Firstly, EC, BA and VAc were mixed, then added slowly into the water solution containing SDS and OP-10 under vigorous stirring. The mixture was ultrasonicated for

Table 1. Urea permeability of EC/BA/VAc films with different EC contents (emulsifier = 3 wt.%, BA/VAc = 3/7, PVA = 0.5 g)

EC%	0	5	10	15
Average thickness of the film [μm]	210	242	213	249
UP [mg L ⁻¹ m ⁻² h ⁻¹]	0.615	0.278	0.423	3.883

30 min to obtain pre-emulsion. The residual surfactant solution, PVA water solution and a certain amount of pre-emulsion were placed into the flask, the mixture was degassed under nitrogen gas for 20 min at room temperature, and subsequently raised to 75°C. The introduction of 30% potassium persulfate (KPS) water solution gave the starting time of the polymerization. The residual pre-emulsion and 40 wt% KPS was added into the flask during 5 h. Finally, 30 wt% KPS was added into the flask and the reaction mixture was kept at 85°C for 1 h to get the polymer emulsion. The polymer emulsion was filtered with 200 mesh copper mesh, the final concentration of organics in water emulsion was 19.98%–16.34% by gravimetric analysis. All reagents are chemical pure, supplied by Sinopharm Chemical Reagent Co., Ltd..

Film preparation and characterization

EC/BA/VAc film was prepared via a solution-casting method. The desired amount of EC/BA/VAc emulsion was cast in a Teflon mold at room temperature for one day and was dried in a vacuum oven at 50°C for 24 h. The film was analyzed by differential scanning calorimetry (DSC). An appropriate amount of sample was sealed in an aluminum pan. The DSC thermoscan of the film was then recorded under a dry nitrogen atmosphere at a heating rate of 10°C min⁻¹ from -50°C to 100°C using a DSC 200F3 apparatus (NETZSCH, Germany). Tensile testing was carried using a universal testing machine at room temperature (RGT-2, Rui Geer Instrument Co., Ltd., Shenzhen, China) according to Chinese National Standard GBT1040.3–2006²⁴. Scanning electron microscopy (SEM) was observed by an SEM (SU-8010, Hitachi, Japan) with an accelerating voltage of 20 kV. The water absorbency of the film was tested according to the method described in the literature²³.

Urea permeability of EC/BA/VAc film

The urea permeability of the films was measured using a permeability cup containing 50 mL of a solution of 7.5 mg/mL urea that was sealed by the selected film. The cup was placed upside down in a beaker containing 250 mL of water for 2 h, and the change in the urea concentration in the beaker was recorded. The urea permeability was

calculated according to the following formula: $UP = \frac{C}{tS}$, where UP is the urea permeability (mg L⁻¹ m⁻² h⁻¹), C is the urea concentration in the beaker, t is time (2 h) and S is the area of the permeable film, respectively⁶. Urea was measured using a spectrophotometric method²⁴. A solution (10.00 mL) containing 2% (w/v) *p*-dimethylaminobenzaldehyde in absolute ethanol and 3.00 mL of 1/3 (v/v) hydrochloric acid was added to 10.00 mL of a solution of urea. After 10 min, the absorbance of the solution was measured at 440 nm against a reagent blank with a spectrophotometer (Evolution 300, Thermo Nicolet Corporation). The concentration of the yellow-colored compound in the sample was determined by comparison with a calibration curve.

Preparation of coated urea

The urea coating was prepared by a BGB-3 high-efficiency film coating machine (Changzhou Zhiyang

Machinery Equipment Co., Ltd). Firstly, urea particles (average diameter 2 mm) were added into a coating pan (diameter 370 mm), then the blower heater were turned on and the coating pan rotated at 30 revolutions per minute (rpm), and an emulsion of EC/BA/VAc was sprayed onto the urea when the temperature reached 70°C. Urea continuously rotated in the coating pan and was gradually coated by sprayed emulsion and the total spraying time was 30 min. And then, the coated urea was dried in vacuum oven at 70°C for 24 hours to ensure the water is evaporated completely and stored in a desiccator. The obtained material contained 17% of polymer and 83% of urea.

Urea release in water

Urea release tests were performed in triplicate in a glass bottle sealed with a cap at 30°C. In total, 2 g of coated urea particles packed into a 200-mesh nylon net bag and 60 mL of distilled water was added to the glass bottle. All the solution in the glass bottle was removed to determine the amount of urea released from the coated material, and 60 mL of distilled water was added at set intervals (after 1 day, 3 days, 5 days, 7 days, 10 days, 14 days, 28 days, 42 days and 56 days). The urea content was measured using a spectrophotometric method²⁵.

All chemical analyses were replicated three times and the means were calculated.

RESULTS AND DISCUSSION

Properties of EC/BA/VAc latex films

Differential scanning calorimetry Analysis of EC/BA/VAc films

Fig. 1 shows the DSC curves of EC/BA/VAc films with different EC contents. The glass transition temperature (T_g) is the intersection of two tangents at the start of the corresponding endotherm in the the DSC curve. According to Fig. 1, the T_g of EC/BA/VAc films containing 0%, 5%, 10% and 15% EC was 29.9°C, 19°C, 11.7°C, and -3°C, respectively. These results suggested that hydrogen bonds and interactions between polar groups in the polymer were weakened due to the addition of EC,

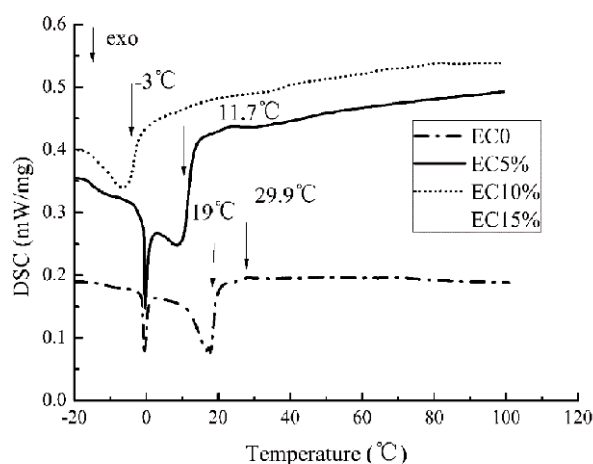


Figure 1. DSC curves of EC/BA/VAc films with different EC contents (emulsifier = 3 wt. %, BA/VAc = 3/7, PVA = 0.5 g)

which is similar to the results of previous studies²⁶⁻²⁷. Compared to Tg of pure EC, which is 120°C, Tg of EC/BA/VAc films was lower. As a result, EC/BA/VAc films produced in the present study had better flexibility than pure EC.

Mechanical analysis of EC/BA/VAc films

The elongation at break of the films was tested, and the results are listed in Fig. 2. The elongation at break of EC/BA/VAc films containing 0%, 5%, 10%, and 15% EC was 336.84%, 359.40%, 456.96% and 607.49%, respectively. Thus, the tensile properties of EC/BA/VAc films at room temperature were greater than that of BA/VAc films (0% EC). The observed change in the mechanical properties agreed with the DSC measurements and the results described in the literature²². The addition of EC may have weakened the hydrogen bonds and interactions between polar groups of the polymer.

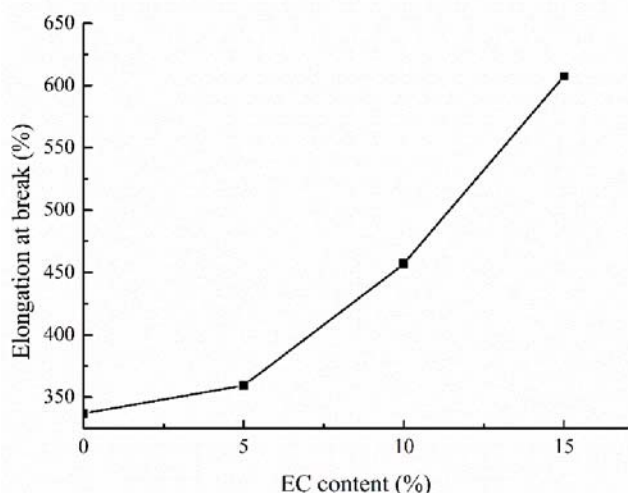


Figure 2. Mechanical properties of EC/BA/VAc films with different EC contents (emulsifier = 3 wt.%, BA/VAc = 3/7, PVA = 0.5 g)

Water absorption of EC/BA/VAc films

The water absorbency of EC/BA/VAc films with different amounts of EC is shown in Fig. 3. The water absorbency of BA/VAc film was 94%, and the water

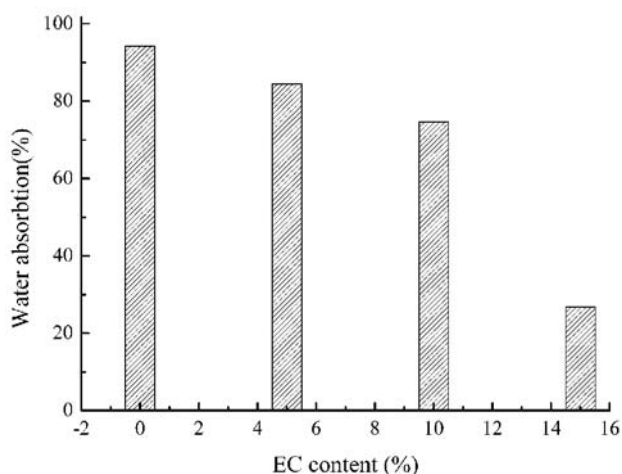


Figure 3. Water absorption of EC/BA/VAc film with different EC contents (emulsifier = 3 wt.%, BA/VAc = 3/7, PVA = 0.5 g)

absorbency of EC/BA/VAc film containing 5%, 10% and 15% EC was 86%, 72% and 27%, respectively. The BA/VAc film had the highest absorbency properties, and the water absorbency ability of the EC/BA/VAc film decreased with an increase in the EC content because the amount of strongly hydrophilic hydroxyl groups decreased in the EC/BA/VAc film when hydrophobic EC was grafted onto the polymer.

Urea permeability of EC/BA/VAc films

Table 2 shows the average thickness and urea permeability of EC/BA/VAc films with different EC contents. The urea permeability decreased from 0.615 mg L⁻¹ m⁻² h⁻¹ (0% EC) to 0.278 mg L⁻¹ m⁻² h⁻¹ (5% EC) because an increase in the EC content of EC/BA/VAc film lowered the hydrophilicity. The largest urea permeability of the EC/BA/VAc films (3.883 mg L⁻¹ m⁻² h⁻¹) was obtained when the EC content was 15% (Table 2) because the polydispersity index of the EC/BA/VAc emulsion (15% EC) was larger than that of the others¹⁶, which increased the film porosity.

The release rate of nutrients from slow-releasing fertilizers can be depicted with the following formula²⁸: $N = N_0 (1 - e^{-kt})$, where t is the time (h), N (%) is the nutrient release rate (t h), N₀ (%) is the maximum nutrient release rate and k is the nutrient release rate constant. Fig. 4 shows the cumulative permeability curve of the EC/BA/VAc film. The release of urea in the permeability cup was caused by osmotic pressure and decreased with a decrease in the urea concentration of the cup. The urea release rate in Fig. 4 was fitted with exponential function and can be illustrated as: $N = 0.7742 (1 - e^{-0.0472t})$ and the square of coefficient of correlation (R²) was 0.9939.

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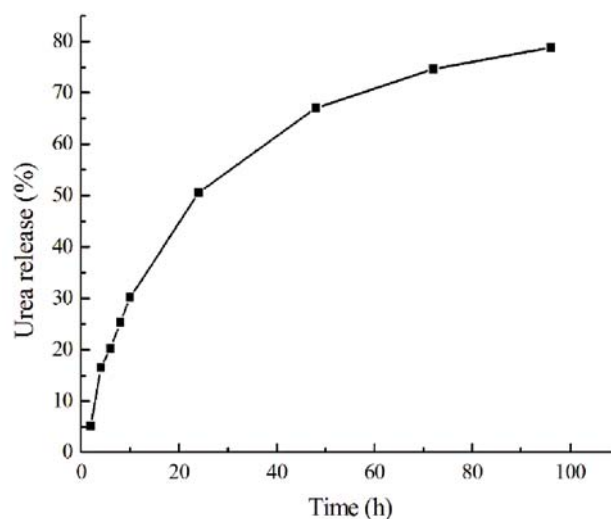


Figure 4. Cumulative permeability curve of EC/BA/VAc films (emulsifier = 3 wt.%, EC = 10, BA/VAc = 3/7, PVA = 0.5 g)

Biodegradation of EC/BA/VAc films

The EC/BA/VAc film was divided into small pieces, buried into soil containing 50% water, and stored for 90 days at 30°C. The films were observed by SEM, and many pits were detected on the original film surface (Fig. 5), which indicated that the film had begun to decompose. The film would completely decompose in soil, but this process might have taken more than 90 days; thus, the film can maintain internal substances such as fertilizer for a long period of time.

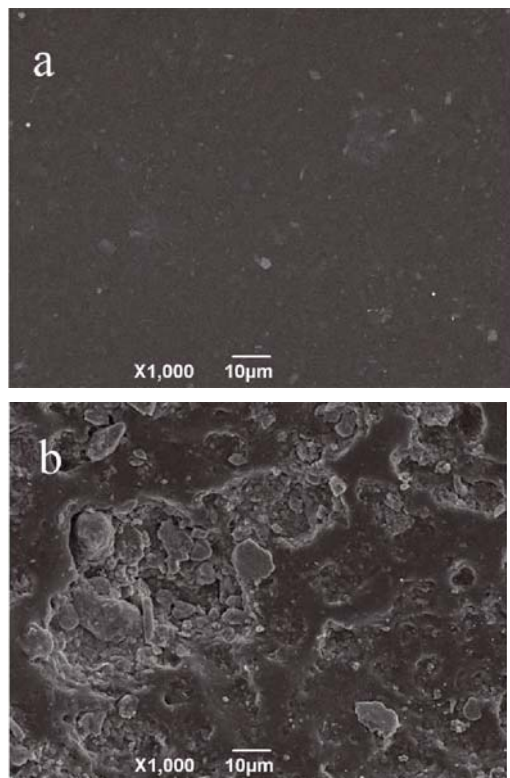


Figure 5. SEM micrographs of EC/BA/VAc films (emulsifier = 3 wt.%, EC = 10%, BA/VAc = 3/7, PVA = 0.5 g) before (a) and after (b) degradation

Urea release rate of coated fertilizer

The surface of urea particles coated with EC/BA/VAc latex was not as smooth as that of urea (Fig. 6). An “S”-shaped release curve was observed for the urea coated with EC/BA/VAc film which was similar with the literature⁹. As shown in Fig. 7, the release of urea after 42 days from urea coated with EC/BA/VAc film containing 0%, 5%, 10% and EC 15% was 75.1%, 65.8%, 70.1% and 84.1%, respectively. The urea content was less than 75 wt. % on the 28th day, which indicated that the slow-release properties of the film conformed to the standards for slow-release fertilizers set by the Committee of European Normalization (CEN)²⁹. Urea coated with EC/BA/VAc latex possessed excellent controlled-release properties, and urea coated with EC/BA/VAc latex (5% EC) had the best controlled-release ability (Fig. 7).

The release of urea from polymer-coated urea may be characterized with diffusion mechanism: water penetrates the coating through microscopic pores and increases the osmotic pressure within the coated core, thus stretching the coating. The stretching increases the micro-pores, enabling the release of nutrients through them. Control over nutrient release is achieved by varying the permeability of the coating material³⁰. The reason why the

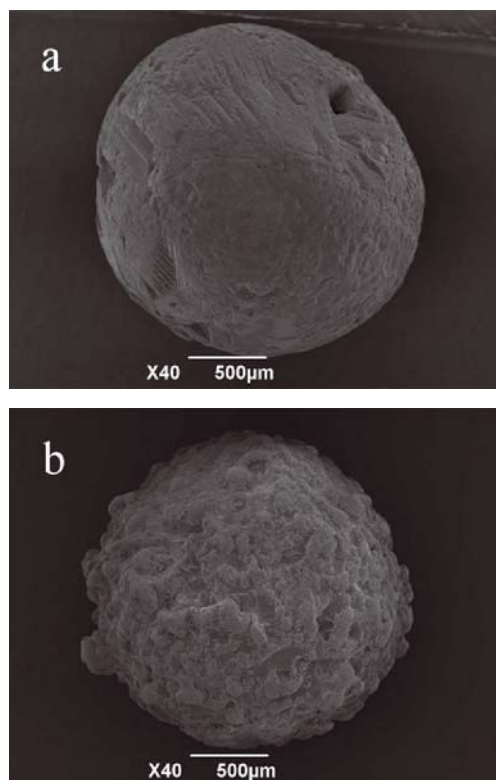


Figure 6. Scanning electron micrograph of urea (a) and urea coated with EC/BA/VAc latex (emulsifier = 3 wt.%, EC = 10%, BA/VAc = 3/7, PVA = 0.5 g) (b)

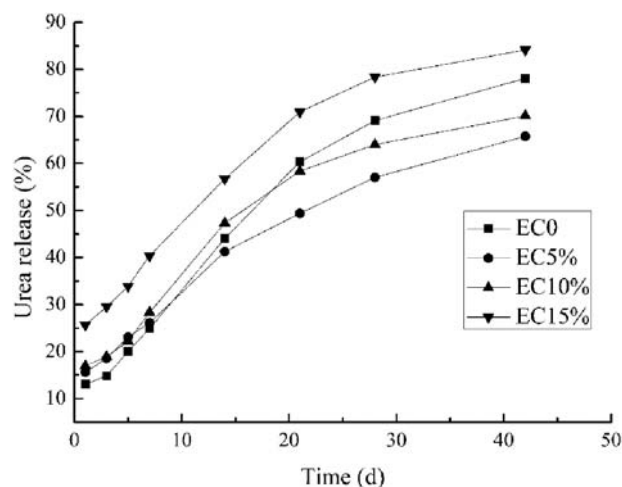


Figure 7. Release curves of urea from EC/BA/VAc-coated urea (BA/VAc = 3/7, PVA = 0.5 g, emulsifier content = 3%) with different EC contents

release of urea from the urea coated with EC/BA/VAc film containing 5% EC had the best slow-release ability maybe because the fertilizer coating material containing 5% EC had smallest urea permeability (Table 2).

CONCLUSIONS

EC/BA/VAc films for coated urea have been prepared from an EC/BA/VAc emulsion using a solution-casting method. The EC/BA/VAc films showed biodegradability. The EC/BA/VAc films with greater EC contents showed lower water absorbency properties and superior flexibility. Coated urea was prepared in a film coating machine, and urea coated with EC/BA/VAc latex possessed excellent controlled-release properties. The release of urea from coated EC/BA/VAc films containing 0%, 5%, 10%, and

15% EC was 75.1%, 65.8%, 70.1% and 84.1%, respectively, after 42 days, and urea coated with EC/BA/VAc latex (EC5%) showed the best controlled-release ability.

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