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Effect of the plasticizer on permeability, mechanical resistance and thermal behaviour of composite coating films

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ABSTRACT

Thin layer deposit of a composite material on solid particle surfaces used in the food industry aims to ensure the protection of food powder against aggressive environments such as a moist atmosphere. The layer, having a thickness of a few fractions of millimetre, must have certain physico-chemical properties: it must be compatible with the product, it must be impermeable to water and oxygen, it must have good mechanical strength and good adhesion to the surface of the coated powder. Furthermore the layer must fulfil the regulatory requirements for food ingredients. Film properties like continuity, permeability, and mechanical resistance depend on the choice of the excipients included in the formulation and the operating conditions which can modify the constraints generated at the interface film-powder. As a consequence, the scientific issue consists of combining the local phenomena happening at a microscopic level on the surface of the particle with the processing technology and the process parameters. In a first step, the attention is focussed on the film and its formulation. For this step, films are prepared separately and they are dried under very smooth conditions. Test samples are taken from the formed composite films and contain hydroxypropyl methylcellulose as matrix (67% of dried material), micronised stearic acid as hydrophobic filler (20% of dried material) and a plasticizer (13% of dried material). The film formation procedure and the test method are described in detail. The effect of the type of plasticizer (different grades of PEG) on mechanical, thermal and permeability properties of the coating film is studied. The results show that PEG with higher molecular rate provides a better plasticizing effect for the film but increases the water vapour permeability of the film.

1. Introduction

The coating process consists of making a deposit on the support (powder) of a solid layer with a few micrometres of thickness and whose permeability properties against water vapour transfer or oxygen ensure its protection. Depositing this film is done by spraying a liquid suspension on moving solid particles and by drying the coated powder with hot air flow. Coating processes are complex. They are constituted by the following consecutive elementary steps: mixing, spraying of the coating agent, wetting, coating of the surface and drying. The properties of the coated product are based on different parameters which are divided into four groups, namely: support properties, coating agent properties, coating machine technology and process parameters. The interactions between these different groups of parameters generate the complexity of the process. The properties of the coating agent (type, concentration, viscosity, surface tension liquid–vapour, wetting solid–liquid) impact directly the particle size, particle size distribution, liquid distribution on the particle surface, film adhesion, drying speed and dry film properties (continuity, mechanical resistance, permeability). Thus, formulation steps of the coating agent are key parameters. The coating agent is made of film forming compounds (polysaccharides), which is the main component of the film network, associated with hydrophobic compounds (lipids) and with plasticizers to improve the mechanical properties of the film. These compounds are in an aqueous suspension. Among polysccharides, hydroxypropylmethylcellulose (HPMC) is one of the most widely used components in the food industry [6,7]. Indeed, according to [13], this compound has very good elasticity and film forming properties thanks to its long carbon chain structure. Moreover, HPMC is soluble in a wide range of solvents including water and ethanol. To reduce water diffusion through coating films, the most used components are long-chain fatty acids because of their high melting temperature and hydrophobicity [8,9,11]. In the work of [2], stearic acid (SA) is used as hydrophobic filler in modified cellulose based formulation. According to the work of [10], it is possible to formulate stearic acid and HPMC based coatings with equivalent or lower water vapour permeability than polyethylene films. Yet, an increase of the mass fraction of the stearic acid over 30% weakens the film in terms of crack appearance. It is necessary to specify that film forming agents are water soluble whereas hydrophobic fillers are insoluble. Thus, formulation conditions of the coating agent impact the stability, the particle size and the particle size distribution of hydrophobic filler and modify the film properties [14]. In addition to film forming and hydrophobic compounds, the third component generally used is a plasticizer

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aimed at reducing the film stiffness by weakening intermolecular forces and improving the molecular chain mobility [12,16]. One of the most used plasticizers for pharmaceutical particle coating is polyethylene glycol (PEG) in hydrocolloid based formulation like gelatine [4] or methylcellulose films (Turhan et al., 2001). The influence of PEG and its grade on permeability and mechanical film properties in the ternary system HPMC/SA/PEG has not yet been studied systematically. Thus, the objective of this work is to study the influence of different grades of PEG (200, 600, 1500, 4000, and 6000) used as plasticizer in composite HPMC based formulations, in which a hydrophobic filler has been dispersed. Measured properties are water vapour permeability, mechanical and thermal properties. This work presents an original method used to investigate films' plastic properties by working with interactions between formulation compounds through thermal properties of our coating films. Indeed, as in the works of [17], these interactions are usually measured with spectroscopy methods; we have decided to use DSC experiments to assess these interactions between film components.

2. Materials and methods

The works of [18] show that the stearic acid mass fraction increases until 20% inducing a significant reduction of gellan film water vapour permeability. Over this value, a high SA ratio (25%) makes the film more brittle with crack appearance. So, the coating agents are formulated with an aqueous suspension of HPMC, stearic acid and plasticizer PEG by keeping the mass fraction of the stearic acid in the dried film constant at 20% to completely avoid crack possibilities due to high SA ratio. Table 1 presents the mass fraction of the different compounds used in the coating agent.

2.1. Materials

The hydroxypropyl methylcellulose (HPMC) used is food grade Methocel E19. This compound has a viscosity of 19 cp in an aqueous solution at 2% (w/w) and 25 °C. The commercial SA used is actually a blend of stearic and palmitic acid (respectively 44% and 56% of mass fraction). It comes in the form of a white cohesive powder which has a melting temperature of 55 °C. The different grades of PEG used are: 200, 600, 1500, 4000 and 6000. These grades are functions of molecular weight. Grades 200 and 600 are viscous liquid at ambient temperatures whereas grades 1500, 4000 and 6000 are white powders. Table 2 presents the melting temperature and aspect of the compounds used at the ambient temperature. In order to assess the influence of the PEG grade on the properties of the coating agent, we have decided to separately test coating layers from the coated particle by working on thin films realized from colloid suspensions. The next paragraph presents the casting protocol of composite films.

2.2. Preparation and casting of composite films

2.2.1. Preparation of the suspension

Aqueous polymeric solutions (pure HPMC or HPMC and PEG) have been formulated by dispersing HPMC and PEG in deionised water at 80 °C under agitation for 20 min followed by rest imposed on the solution at 25 °C for 1 h to avoid all residual foam. Composite suspensions have been formulated by dispersing stearic acid in a solution of HPMC and PEG at 80 °C under agitation. Then stearic acid has been crystallized by cooling the suspension to ambient temperature. Suspensions have been finally degassed at 50 mbar for 1 h. Particle size distributions have been measured with a Master Sizer (MALVERN). Visual observation and particle size distribution measurements of the rested suspension show that the coating agent is stable until film drying. Moreover, with formulation parameters and compounds used, PEG grade does not have any significant influence on the particle size distribution (Fig. 1). The same type of particle size distribution has been observed for other grades of PEG (600, 1500 and 4000).

Table 1
Mass fraction of the different compounds in the formulation.

	HPMC E19	SA	PEG	Water
Without plasticixer	7.2%	1.8%	–	91%
With plasticixer	6%	1.8%	1.2%	91%

Table 2
Properties of used compounds.

Compound	Melting T °C	Melting enthalpy (J/g)	Aspect	Origin
HPMC E19	–	–	Fine powder	Dow chemical company
Stearic acid	55	193.8	Fine powder	MERK
PEG 200	−65	–	Fluid	Fisher scientific
PEG 600	22	128.8	Viscous fluid	
PEG 1500	43–46	173.7	Large crystal	
PEG 4000	54–58	199.6	Large glitter	
PEG 6000	56–63	204.8	Fines glitter	

2.2.2. Preparation of films

Aqueous formulations have been spread to form a 500 μm thick film on a glass plate thanks to a manual hand coater and a 500 μm fixed gate (TLC Plate Coater, hand operated, CAMAG, Muttenz, Switzerland). Films have been then dried for 24 h at 40 °C in an oven. Dry films have the following composition:

- Films without PEG: 80% HPMC, 20% stearic acid.
- Films with PEG: 67% HPMC, 20% stearic acid, 13% PEG.

Film thicknesses have been measured with a vernier calliper (±1 μm). Six measurements have been done for each sample and the average has been calculated.

2.3. Mechanical properties

Films have been cut into rectangular samples (width: 20 mm, working length: 80 mm) with an average thickness of 60 μm (±10 μm). Samples have been stocked for 24 h at 40 °C in the dried atmosphere of an oven in order to avoid any mechanical property modifications due to the presence of water in the film. Tensile tests have been realized in dried atmosphere, with a static tensile test machine from Instron (Instron Instrument Ltd.). Strain speed applied during tests was 1 mm/min until complete break of the test sample. Tensile strength (TS) and elongation at break (EB) have been measured during the

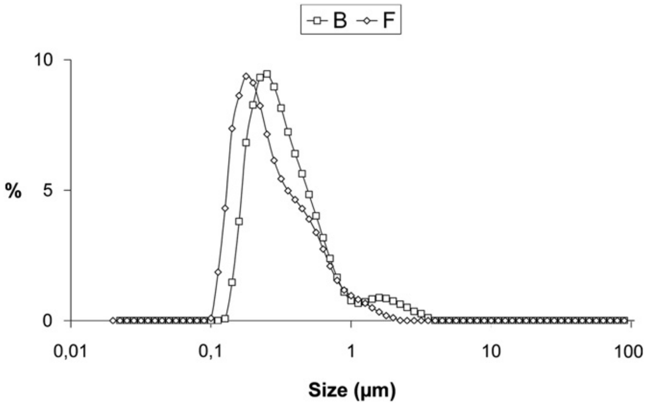

Fig. 1. Particle size distribution of stearic acid in the formulation. B: HPMC + SA + PEG200; F: HPMC + SA + PEG6000.