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Influence of handling and storage conditions on morphological and mechanical properties of polymer-coated particles: characterization and modeling

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ABSTRACT

Polymer-coated particles have been produced by top-spray fluid bed coater and both morphology and resistance to attrition have been analysed using Scanning Electron Microscope, SEM and Repeated Impact Tester, RIT respectively. Coating thickness, coated particle storage conditions and physical aging effects have been assessed. The coating thickness is found to be extremely relevant in raising the resistance to attrition. Thicker the coating and more resistant is the coated particles against attrition. This improvement is found to be more and more relevant while impact energy is increasing. The storage temperature is not influencing the morphology whereas is strongly affecting the resistance to attrition. Coated particles stored at −18 °C were found to be more resistant to attrition than ones stored at room conditions. Such differences, negligible at low energies (low numbers of impacts) increase as soon as the number of impacts and thus the energy rise. The coated particles, stored at ambient conditions, were subsequently aged in vacuum oven and the effect of aging steps was evaluated in terms of resistance to attrition. In aged coated particles were found a wasting in resistance to attrition directly proportional to the aging time. Moreover, the aging process was found to affect the breakage mechanism experienced by the coated particles during impact tests. The common attrition mechanism was found to be layer fatigue. Using the equation proposed by Tavares and King (2002) [48] as starting point, a new equation has been developed in order to fit to the resistance to attrition data. The equation takes into account the number of impacts, the velocity of the impacts, the coating thickness, the coefficient of restitution, e, of the coated particles and the mass specific fracture energy, $E_{f,m}$. This equation has been successfully applied for different coating materials and different coating thicknesses.

1. Introduction

Nowadays many particulate products are coated to give the product specific functionalities. Examples of these products are agglomerates, granules, tablets, pellets and crystals in the chemical, pharmaceutical and food industry. Possible reasons for applying coatings are [1]:

- Shelf life enhancement and prolongation
- To improve processability and physical properties such as solubility, dispersibility, hygroscopicity, and flowability, or to modify the density [2,3] and prevent segregation
- To achieve controlled, sustained, delayed and/or targeted drug delivery release properties [4,5]
- Safe and convenient handling of toxic materials
- To mask undesirable flavours or odours of the product [6]
- To enhance the overall quality of food enzymes and ingredients [7–10]
- To stabilize ingredients during processing (e.g. heat, pressure, and moisture)
- To improve aesthetic-like colour and the appearance of the company logo
- To avoid caking during storage and facilitate dosage and mixing of the products
- To increase strength of the product to prevent dust formation
- To separate core unstable ingredients from their environment and prevent degradation reactions (e.g. moisture, acid, oxygen, high temperatures, light or other food ingredients) [11,12].

Nowadays more and more effort is devoted to develop measuring systems which allow us to perform tests on coated particles which is a representative measure of coating shell resistance-strength. Most of these systems use either single or multi impact events.

Impact testing has been also used to describe crushing behavior of single catalyst particle failure of solid single particles or agglomerates [13,14], particle fragmentation [15,16], influence of structural characteristic of the compounds on their breakage resistance [17], resistance to attrition of salts crystals [18,19] or polymeric compounds [20].

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Such apparatus can be distinguished [21] in drop weight apparatus, air-gun apparatus, ejecting rotor device, shaking box testers and conducting particle impact testers.

A fundamental analysis of the coating material properties is required to ensure that the coated particles can withstand the mechanical stresses they are subjected to during production, transportation and handling. A coating shell with low mechanical strength may break during transport, leading to a change in the properties of the product. Storage conditions can also play an important role in preserving the properties of the coated particles. There is a large diversity of climates (temperatures and humidity) that coated particles can be exposed to. A systematic study on the relation between storage conditions and coating properties is therefore required. It can be concluded that current knowledge on the measurement of the mechanical properties of and the impact of storage conditions on particle-coating properties is limited.

Currently, the technology for preserving/enhancing the mechanical strength of coated particles mainly relies on experience. In fact, only little fundamental understanding of granule strength and breakage has been obtained. In literature there are contradicting results about the relationship between moisture content and strength of particles and agglomerates [22]. Moreover, there are no fundamental predictions for breakage behavior and resistance to attrition available in relation to storage conditions and moisture content. The design and manufacture of coating shell require the analysis of coating material properties in order to ensure that the coated particles are able to sustain the mechanical stresses which are subject to during production, transportation and handling. Another critical problem that may occur with film-coated products is a change in physical and mechanical properties over time and is generally associated with wrong storage conditions and aging. The majority of the polymers used in coating applications are amorphous and are not at thermodynamic equilibrium at temperature below their glass transition temperature. During time, amorphous polymers undergo a slow transformation toward a thermodynamic equilibrium [23,24]. Such physical aging makes the polymer to be stiffer, more brittle, but much less ductile and viscoelastic as storage modulus increase whereas loss modulus tends to decrease [25]. When temperature is below the glass transition temperature of the polymer, the free volume of the polymer will slowly relax toward a lower free energy state over time determining a structural reorganization of the polymer chains [26] which significantly impacts the long-term stability and mechanical properties. Over time, changes in the polymer due to physical aging will have profound effects on the viscoelastic compliance of the material, hence affecting its long-term durability [27–29]. Thus, the ability to predict material performance correlating intrinsic properties, such as resistance to attrition with environmental storage and aging conditions, would greatly enhance the efficiency of design and development of coated particles. It has also demonstrated that storage conditions may play an important role in changing the controlled release profile of the coated particles [30,31]. For polymer-coated particles subjected to long-term exposure at elevated temperatures rather than extreme humidity conditions the viscoelastic nature of the polymer coating will contribute to macroscopic changes in composite stiffness, strength and fatigue life.

The objective of this paper is to study the effect of coating thickness, storage temperature and aging time on the resistance to attrition of reference coated pellets. Three distinct polymer coating agents were selected namely, two grades of HydroxyPropyl Methyl-Cellulose, HPMC and one grade of Polyvinyl Alcohol, PVA. Sodium Benzoate, Purox® has been chosen as core material. The particles are coated by means of top-spray fluidized bed coater. Per each coating agent three different amounts of coating solution have been sprayed and leading to three different thicknesses. Half batch has been stored at room temperature and remaining half batch in the freezer (−18 °C) immediately at the end of the coating process. The coated particles have been subsequently aged for a certain temperature and times. The resistance to attrition is measured by Repeated Impact Tester and the end-test coating shell's morphology has been evaluated as a function of coating thickness first, storage temperature and aging time secondly. A novel equation to model the resistance to attrition behavior of aged particles is proposed and successfully used to fit the experimental data.

1.1. Repeated impact testing

Beekman et al. [32] designed a device for measuring the resistance of particles to attrition under repeated impacts (Fig. 1). The technique was further developed by Pitchumani et al. [33].

The RIT accelerates particles towards the target and permits repeated impacts. There are two impacts for each turn of the flywheel. The particles are contained within the particle chamber and undergo impacts in unidirectional movement [33]. The impacts are mainly against the inner surfaces of the top and bottom wall of the chamber. Attrition is therefore dominating the mechanical stresses exerted onto the particles. Beekman [47] described three attrition sub mechanisms which are peeling, erosion and layer fatigue. The peeling mechanism, which we refer to as surface rounding, is characterized by initial removal of the corners, sharp edges and outer layer of the particle. Once this layer is removed the attrition rate decreases. Peeling is often followed by erosion, which is characterized by the linear decay of mass during attrition testing. The fatigue mechanism is the result of the accumulation of small damages, micro-cracks and plastic deformation, without any visible effect on the particle at low energy until a collapsing point occurs. If layer fatigue is a dominant mechanism, initially no attrition is observed. The principles of the mechanisms and the typical shape of the graphs are described in Fig. 1b.The impact velocity between particles and the chamber is equal to the maximal chamber velocity, which can be calculated by Eq. (1):

$$v_p = 2\pi fA \tag{1}$$

where f is the oscillation frequency of the flywheel and A is the amplitude of the motion of the chamber which is constant and equal to the radius of the flywheel. Stating preset and constant value of frequency f and only top–bottom collision particles–chamber, the number of impacts (N) can be calculated using Eq. (2):

$$N = 2ft \tag{2}$$

where t is the total duration of the experiment and f is the frequency of the flywheel. After each RIT experiment, the particles are sieved using a proper mesh to remove the dust and debris created by the impacts from the original particles. The particles were weighted before and after the RIT to determine the remaining mass (m_m) using Eq. (3):

$$m_{rm} = \frac{m}{m_0} \tag{3}$$

where m is the mass of intact particles after the RIT experiment and m_0 is the initial particle mass. The measurement error in the balance is in the order of 0.07% [34]. In purely elastic particles the kinetic energy is totally transferred to the particle at the instant of impact and is then totally transformed into kinetic energy again. With “viscoelastic” particles, the kinetic energy is still totally transferred to the particle at the instance of impact but only a fraction is transformed back into kinetic energy. The fraction of energy which is not transformed back into kinetic energy is transforming in “stored strain energy” which consists of local plastic deformation and micro-cracks accumulation. The dissipation energy by heating is always neglected.