Smart Microcapsules containing Enzymes for Laundry Applications

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ABSTRACT SUMMARY
Enzyme containing microcapsules (EMC) with desirable controlled release properties were prepared by a spray drying technique for application in laundry detergents. Functionalised polymers were developed to prepare EMC with ionic strength triggered release properties. Ionic strength changes during the laundry process result in the efficient and controlled release of the enzyme payload.

INTRODUCTION
Enzymes are desirable for use (as single or mixtures) in laundry detergents offering a variety of cleaning and stain removal benefits. However, achieving full enzyme performance in the wash relies on keeping the enzyme stable in the detergent. This is especially challenging in Heavy Duty Liquid detergent (HDL) due to enzyme interactions with the other detergent ingredients. Enzyme instability in HDL is typically driven by surfactant and chelant induced unfolding, and proteolysis. A solution to deliver a high level of enzyme stability for prolonged periods in the HDL is to protect the enzymes via microencapsulation ¹. The key challenges to deliver a viable EMC for use in a HDL with limited triggered release mechanisms (pH, and temperature are not viable levers) is the need to deliver both a high level of enzyme stability in the HDL with fast full release of the enzyme, within a few minutes of the wash process. In addition a process of making EMC must preserve enzyme activity, be safe for use and handling, and be economically viable. There are few reports describing enzyme encapsulation for liquid laundry applications ²-⁸ and none that successfully address the technical challenges set out. The present work describes EMC prepared from cellullosic polymers which fulfil the requirements.

EXPERIMENTAL METHODS
Cellulose acetate phthalate (CAP) and an Alpha-Amylase (Natalase 200L®) were procured from GM Chemie Pvt Ltd, India and Procter & Gamble respectively. CAP was modified and then used to prepare the microcapsules containing Amylase enzyme by a spray drying technique as described earlier ⁹,¹⁰. A HDL, nil enzymes of Procter & Gamble was used to study the residual enzyme activity measured via stability and leakage in the HDL upon aging and the enzyme release from the EMC upon dilution. The water source used to dilute the HDL was formulated from de-ionized water with the addition of various salts to resemble municipal water used in the United States (US tap water).

Enzyme Assay: Quantitative determination of the Alpha-Amylase was performed following a standard method using Infinity Reagent ™. Serial concentrations of Natalase 200L® solutions were prepared to calibrate and quantify the enzyme.

EMC stability in HDL: A known amount of the EMC (g) was added to a known amount of HDL (mL) and incubated at 35°C, for specific periods of time (days) at a static condition. Upon aging, the EMC were filtered from the HDL and analyzed for residual active enzyme (AE) content to obtain the amount of enzyme that has leaked from the EMC (expressed as a % of the initial, time = 0 days).

Release of enzyme from EMC post incubation in HDL: A known amount of the EMC (g) was added to a known amount of HDL (mL) and incubated at 35°C for a specific period in an oven at a static condition. The HDL containing the EMC sample was diluted using US tap water, using an overhead stirrer. Aliquots were removed after 5 and 10 minutes and analyzed using the Amylase assay.

RESULTS AND DISCUSSION
Microencapsulation of actives such as enzymes using polymeric materials is well known. However, the use of such materials to achieve highly stable microcapsules (with ideally no leakage of the active) in a liquid detergent, with fast full release upon dilution in the wash (<5-10 minutes, upon ~200 fold dilution) is a very difficult technical challenge. The EMC polymer architecture should offer suitable hydrophobicity to avoid enzyme leakage during storage, while offering suitable swelling/dissolution properties to drive fast full release of the enzyme upon a decrease in ionic strength (HDL dilution during the wash), the available trigger for HDL.

Modification of CAP with an alkaline reagent produced a CAP-salt form, creating a triggered responsive CAP polymer to ionic strength. This behavior is governed by the following equation¹¹.


\[ \Pi_{\text{ion}} = RT \sum (c_i - c_i') \]

Where
\[ \Pi_{\text{ion}} = \text{ion swelling osmotic pressure} \]
\[ R = \text{General gas constant, } T = \text{Abs Temp} \]
\[ c_i \text{ and } c_i' = \text{concentration of ions inside and outside of gel (polymer).} \]

Amylase EMC of 2-10 micron, were prepared using modified CAP (Fig 1), designed for use in HDL.

Fig 1: SEM photograph of the Amylase Microcapsules

Fig 2: Leakage of Amylase enzyme from the microcapsules stored in HDL as a function of time

Fig 3: Release of Amylase enzyme from aged microcapsules in US water with differing ionic strengths

The EMC were incubated in HDL at 35ºC and the enzyme leakage was measured as a function of time (from 0 to 70 days, see Fig 2). The EMC show a very low level (~1%) of enzyme leakage at day 0 attributed to surface enzyme release from the EMC. Further measurements indicate excellent stability of the EMC in the HDL. Even after 70 days incubation, the enzyme leakage does not increase further versus the day 0 measurement. To understand the response of the EMC to ionic strength, aged EMC were added to US tap water spiked with different concentrations of ionic strength and the release properties were measured (Fig 3). Enzyme measurements demonstrate that the release of AE decrease with the increase in ionic strength. This set of experiments confirm that the EMC exhibit ionic strength triggered release behaviour and also that under typical wash conditions (ionic strengths of <0.005M) the enzyme will be effectively released (>80%). These EMC can be used to encapsulate a variety of other enzymes. HDL containing such EMC deliver the intended full wash performance.

CONCLUSION
Enzyme containing microcapsules that are architecturally designed using ionic strength triggered release polymers, such as CAP, are strong candidates for use in liquid detergents. These microcapsules have been successfully designed to be stable in high ionic strength liquid detergents and yet dissolve readily releasing the enzyme when the ionic strength is lowered like that in a typical washing process. When protected in the polymeric capsules the enzyme is not de-activated through the spray dry processing or in the HDL, delivering excellent enzyme performance in the wash.

REFERENCES
4. Van De Scheur et al, WO 00/36067, (1993)