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Deposition and retention of differently shaped micro-particles on textiles during laundry processing.

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ABSTRACT

Particulate additives such as perfume microcapsules are present in detergent formulations to add fragrance to the washed garments. The key challenge is controlling the deposition and retention of such particulates onto textile surfaces, as a large proportion are simply washed down the drain during washing. In this study, the influence of particle shape on the mechanical entrapment of particulates within different fabrics is assessed using a laboratory mixer, which mimics the tumbling action of a washing machine. Using a combination of image analysis and mass balance it is found that with rough, irregular particles, the retention level across all fabric types studied is increased by a factor of up to 3 times when compared to smooth, spherical ones (typically used in industry). The retention rate is also found to be dependent on the tumbling duration, tumbler speed as well as on the fabric characteristics especially when a combination are used.

KEYWORDS: Particle deposition; Particle retention; Particle shape; Fabrics; Laundry; Microplastics.

INTRODUCTION

The deposition of particulate additives onto fabrics is of great interest for the home and personal care industry. These particulates are designed to improve and add certain functional benefits to textiles, which in turn provide desirable characteristics to the washed clothes, such as colour, whiteness, smell, softness, and antibacterial properties.[1-4] Micron-sized perfume microcapsules are found in many detergent powders and fabric softeners as a way to deposit fragrance and essential oils.[1, 3, 5-7] Microcapsules attach to the fabric during washing and, when worn, the encapsulated perfume is released through either permeation or *via* sudden rupture of the microcapsules through abrasion.[8] The long-lasting fragrant notes that the clothes emit after washing is one of the biggest factors in consumers choosing specific laundry products.[9] For this reason, detergent manufacturers are actively interested in improving both the deposition and retention of such active species onto fabrics during a wash cycle.

The deposition and retention rate of spherical particulates onto textiles during a wash cycle is dependent on particle size; nanoparticles, due to their large surface area-to-volume ratio and high surface energies, have been shown to have high affinity for textile surfaces and are able to penetrate the interstices of fibres and fill the pore spaces. In addition, hydrophilic textiles such as cotton that can swell (upon wetting) and contract (on drying) can enhance particle uptake and retention.[10] Other nanoparticle examples used on textiles include semiconductor oxides, such as TiO_2, ZnO, SiO_2 and Al_2O_3 that impart UV-protection,[11-13] anti-bacterial[14, 15] and wrinkle-resistance[16, 17] properties to the fabric, with these desired effects lasting after 50 wash cycles.[11, 18]

In contrast, the deposition/retention rate of micron-sized spherical particles is typically low, as demonstrated through experimental studies conducted using perfume microcapsules that have non-reactive shells. Teixeira *et al.*[19] studied the efficiency and durability of textiles (composed of 60% wool, 38% polyester, and 2% elastane) impregnated with commercial lemon perfume microcapsules (mean particle size ~6 µm) using a laboratory-scale Foulard. The textiles are placed in a finishing bath containing the microcapsules, a softener and a self-crosslinking substance, and then subjected to drying (100 °C; 3 min) followed by curing (140 °C; 3 min); it should be noted that this process forces the deposition of particulates onto the surface of the fabric and is therefore not fully representative of exhaust deposition that occurs in a washing cycle. Using a combination of SEM, GC-FID-Headspace, and mass balance analysis, it was found that after one domestic wash cycle, the mass of limonene present in the textiles had reduced by 46% (and by 97% after 20 washes). Panisello *et al.*[20] deposited 2.5–40 µm polysulfone/vanillin based microcapsules by fixing them onto commercially coated cotton fabrics (under pressure) and assessed their retention after laundering within a washing machine. Using image analysis, they reported that 30% of the initial deposition was lost after the first wash, with ~87% lost after the second wash. After a total of 5 washes, only 2% of the initial microcapsule deposition remained. Additionally, it was found that the smaller microcapsules

(2.5–10 μm) were able to survive the longest with increasing number of wash cycles due to a thin layer of the coating remaining on the textiles which kept the microcapsules adhered to the fabric.

To overcome these low retention values, researchers have proposed the use of binders to improve the adhesive interaction between the microcapsules and textiles, leading to wash durability. Two main groups of binders have been used: polymeric resins[21-23] and polyfunctional cross-linking agents.[24, 25] Although improvements in laundering durability is achieved, these methods require additional processing steps (*e.g.* elevated heat treatment), which can lead to the microcapsules aggregating together on the fabric surfaces, leading to non-uniform deposition.[22] The application of chemical coatings can provide an attractive surface for soil deposition in the wash cycle and also be sensitive to the chemical surface that will change as the fabric chemistry changes.

For domestic laundering applications, detergent manufacturers tend to oversaturate their formulations with the micron-sized particulate actives in a bid to ensure a sufficient amount adhere and remain impregnated within the fabrics both during and after the laundering process. However, this means increased levels of active loaded products end up in the wastewater stream at the end of the wash cycle, which is inefficient and poses environmental concerns, such as microplastic pollution as a result of the limited biodegradability of the polymeric microcapsule shell.[26, 27]

The work herein aims to evaluate the influence of particle characteristics on the mechanical entrapment of particulates within textiles during a wash cycle. Using a laboratory scale mixer (to mimic the mechanical processes encountered in a washing machine) and a combination of image and mass balance analysis, the influence of particle and textile characteristics (fabric weave, yarn structure and fibre density) on deposition and retention is investigated. The impact of wash time, mixer speed and mixed fabrics is also assessed.

MATERIALS AND METHODS

Materials:

The particles used in this study were: 1) spherical polyethylene microspheres (aspect ratio = 0.99) (where aspect ratio distribution by number is; d_{10} = 0.986, d_{50} = 0.993 and d_{90} = 0.997) and a circle equivalent particle diameter $d_{4,3}$ of 59.42 µm (where size distribution by volume is d_{10} = 53 µm, d_{50} = 59 µm and d_{90} = 65 µm) purchased from Cospheric LLC, U.S.A with a density = 0.96 g cm^{-3}; and 2) irregular polypropylene purchased from Diamond Plastics GmBH, Germany with a mean aspect ratio = 0.64 (where aspect ratio distribution by number is; d_{10} = 0.42, d_{50} = 0.65 and d_{90} = 0.86) and a circle equivalent particle diameter $d_{4,3}$ of 75 µm (where size distribution by volume is d_{10} = 37 µm, d_{50} = 75 µm and d_{90} = 108 µm), (density = 0.92 g cm^{-3}). The full distributions can be accessed in S1 of the Supplementary Information. These particles sizes are similar in size to fragrance microcapsules that are typically found in detergent formulations. Representative micrographs of these particles are presented in Figure 1. Tween 20 (Sigma Aldrich) was used to aid the dispersion of the powders in water. The textiles studied were purchased from Whaley's Bradford Ltd., U.K. and were chosen to probe the effect of: i) fibre type; ii) yarn structure (twists per cm and fibre structure); iii) yarn packing density (tightness of the weave) and weave structure, such as plain, twill, etc.[28] Further details are provided in Table 1. All fabrics were of a similar weight (g m^{-2}) to ensure that results were comparable.

Methods

Particle deposition via tumbling cycle:

The fabrics were cut into 25 x 25 mm pieces and placed into petri-dishes and dried at 60 °C for 20 min in a convection oven (Memmert, Germany) to enable removal of any bound water on the surface of the fabrics prior to weighing in order to improve the accuracy of mass balance measurements conducted using a microbalance. Once dried, these fabrics were then placed into polypropylene centrifuge tubes (either as singular piece or two pieces from mixed fabrics) containing ~0.05 wt.% dispersion of the particles (either spherical or irregular) in 50 mL of distilled water at pH 7. The zeta potential and contact angle measurements of both particles can be accessed in S2 and S3 of the supplementary information. The diameter of the tubes had to be larger than the diameter of the fabric pieces to ensure that they were able to move freely during the deposition experiments. Tween 20 (0.5 wt.%), a non-ionic surfactant, was added to the solution to ensure a homogenous dispersion of the particulate powders into water; this was the minimum amount required to prevent particle aggregation and minimise their effects on the deposition process. The centrifuge tubes were then placed on a RotoFlex tube rotator (Argos Technologies) that rotates 360° to mimic the tumbling action of a simple washing cycle that fabrics would experience in a washing machine, as depicted in Figure 2. The effect of rotation speed and duration was examined. It should be noted that using Stokes' Law, the calculated unhindered creaming velocity for the two particle systems were 87 µm/s (spherical) and 275 µm/s (irregular). If we consider the slowest tumbling rpm used in this study (20 rpm), then the maximum distance travelled by the particles (in-between tumbling due to creaming) would be ~830 µm (based on the larger irregular particles) before the creaming direction changes. This means that any particle creaming effects can be regarded as minimal, since the tumbler rotation frequency ensures that the time period is not long enough to provide sufficient separation due to gravity. The wet textile samples were carefully removed from the centrifuge tubes and dried (statically) for 24 h using a convection oven at 60 °C. The dried textile samples were weighed immediately after their removal from the oven to prevent moisture uptake from the environment.

Particle retention during rinse cycle:

For the rinse cycle, the centrifuge tubes were replaced with 50 mL of distilled water only. The textile samples containing deposited particles were placed in each test tube and rotated at various speeds, durations, and cycles. The samples were then removed from the test tube, dried at 60 ºC for 24 hours prior to characterisation and analysis to determine particle retention.

Characterisation:

The textile samples were characterised using an optical microscope (Luxeo 4D, Labomed) and a scanning electron microscope (SEM) (TM3030+, Hitachi) to determine the preferential locations for particle deposition, the deposition number density during tumbling process and the number of these particles retained after a rinse. This was done by taking 5 x 25 mm^2 'quadrats' on each side of every sample and the number of particles counted. This gave a number density (#/mm^2) for each fabric type, which could be compared with the mass balance results. This process was carried out after both the tumbling and rinsing cycles.

RESULTS

Material balance analysis

Influence of fabric structure: Measuring changes in the mass of the fabric after the tumbling cycle was used as a method to determine the percentage of particles that deposit from the bulk on to the fabrics, as well as the percentage of these deposits that are retained after a rinse cycle (Table 2). The fabrics were subjected to a tumble/rinse cycle of 10 min at 40 rpm. This rpm value was chosen as a benchmark as it corresponds well to the average drum speed used in domestic washing machines during the initial wash and rinse cycles.[29, 30] In addition, the values reported take into consideration any mass loss due to fibre shedding occurring during tumbling.

The material balance data shows that the overall deposition when using irregular shaped particles is higher in comparison to spherical particles. In several fabrics, the percentage of particles deposited is increased by up to two/three-fold (*e.g*., loose cotton and the two polyester-based fabrics). These irregular particles were also better retained (after deposition) with values as high as 75% observed compared to a maximum retention of 25% using spherical particles. The disparity in both the deposition and retention values can be attributed to the nature of the motion of the two different shaped particles as they travel along the fabric surface. This is because electrostatic repulsive forces will dominate over van der Waals forces due to similar charges between the fabric and particles and they both have similar wetting (contact angle) characteristics (see S2 and S3 in Supplementary Information). According to Boskovic *et al.*,[31] spherical particles can either slide or roll upon coming into contact with the fabric before coming to rest.

On the other hand, irregular shaped particles will either tumble or slide. This rolling motion of the spherical particles makes particle deposition and retention on fabrics less likely than that of the irregular shaped particles. In the case of the spherical particles, particle-fabric contact surface area does not change as it slides or rolls across the fabric fibres. In contrast, as the irregular shaped particles tumble due to changes in the hydrodynamic flow interactions, the area of the particle in contact with the fabric fibres will significantly change. This makes it more likely for the irregular shaped particles to be entrapped within the fabric fibres. The surface of the spherical polyethylene particles has irregularities in the order of a few tens nanometres (see S4 in Supplementary Information),[32] similar to the surface roughness of a cotton fibre and melamine formaldehyde based microcapsules.[33] Whereas, the irregular particles exhibit roughness in the order of a few hundred nanometers (as seen by the SEM micrographs presented in Figure 1 and roughness measurements conducted on each particle type with an AFM presented in S4 of the Supplementary Information). Therefore mechanical entrapment of the irregular particles within the fabrics is likely to be much higher than the smoother spheres, as previously demonstrated.[34]

SEM was performed to image the fabric surfaces, to probe the effect of fabric characteristics (fibre, yarn, and weave structure) on the particle deposition (location) during the tumbling cycle. There are several key characteristics of the fabrics that need highlighting. Tight cotton consists of a tight plain-woven structure with no wells between yarns and no significant differences in the yarn structure in both the warp (vertical) and weft (horizontal) directions. The yarn is made up of densely packed fibres that are twisted to hold them together with a few fibres that protrude from the yarn surface. Loose cotton in contrast, contains wells due to a looser weave structure and has more fibres protruding from the yarn surface. This looser weave structure is also seen in the linen (containing yarns of uneven widths) and silk fabrics, and both contain large wells. The fibres in silk are continuous filament, which is unusual for a natural fibre and a large number of fibres protrude from the yarn surface; in addition, some of these loose fibres form matted 'bird's nest' structures on the surface of the fabric. Polyester is tightly woven with a twill weave and contains no wells and the twill weave gives the fabric a different appearance when observing the front or the back of the fabric surface; the long sections of exposed yarns (running horizontally across the image) appear slightly twisted, whereas the yarns running vertically do not. Finally, the polyester/polyamide fabric is made of a honeycomb weave. The yarns consist of fibre bundles that are densely packed together and are not twisted. SEM images illustrating the deposition of spherical polyethylene and the irregular polypropylene particles onto these fabrics (after drying) are presented in Figures 3 and 4.

In fabrics that possess a tight weave structure and a high fibre density (tight cotton and polyester), the spherical particles deposit at sites where the yarns interconnect, *i.e.* macro-occlusion.[13, 35] These sites are areas of great topographical variation consisting of depressions (sinks) and ridges. As a result during tumbling, the particles roll and slide[31] into these sites becoming mechanically entrapped and difficult to remove.[36] Deposition in these tightly woven yarns also occurs through 'particle trapping' within loose fibres protruding from the yarn surface;[13, 37, 38] this can be particularly seen in the case of tight cotton in Figure 3, showing two particles underneath a loose fibre. In addition, when the fabrics undergo drying in a convection oven, capillary flow of the unbound and bound water as well as water evaporation will also allow particles to migrate on the fabric surface (macro-occlusion in tightly woven yarns with high fibre densities).[39, 40] Once the fabric is dry, van der Waals attractive forces and mechanical interaction between the particles and the fabric surface will dictate whether successful particle adhesion occurs.[41] The irregular polypropylene particles in contrast are found to deposit within the centre of the yarns (Figure 4) although a few appear where the yarns interconnect. It is mostly likely that due to the particle shape and its roughness, it is more adept in interacting with the fibre threads (within the tightly twisted yarns) due to increased contact surface area leading to successful adhesion and thus deposition.[42]

In fabrics that have a loose weave structure and yarns with high fibre densities (loose cotton, linen, and silk), the sites for spherical particle deposition again occur where yarns interconnect and *via* mechanical entrapment within loose fibres. In addition, deposition is seen to occur in the wells (pores formed between the yarns due to loose weave structure). Considering the liquor-fabric interaction during the tumbling process as dead-end filtration, these wells allow a greater level of fluid flow through the fabric. The loose fibres within these pores will capture particles as the fluid flows through, thus becoming mechanically entrapped. The irregular particles also deposit where the yarns crossover, but the majority of the deposition occurs *via* adhesion onto the surface of fibres within the yarns.

In the case of polyester/polyamide honeycomb fabric, both particle systems are found to reside between interconnecting yarns and in the fibre structure within the yarn. Although the fibre density in the yarn is high, they are simply bundled and not twisted. This means that when the liquor passes through, areas of the yarn (particularly in the centre) will become looser and allow micro-occlusion of the particles to occur.[35]

These observations highlight that the yarn fibre density as well as the weave density plays a crucial role in successful particle deposition and retention. A plot of % particle deposition and retention versus fabric specific area is presented in Figure 5 (annotated with fabric type). The data shows that, in general, the level of successful particle deposition and retention increases as the fabric specific surface area increases. This can be alluded to the fabric topological variations and high weave densities that will allow a greater contact time between the transported particles *via* cross and convective flows and the fabric surface area. Furthermore, the higher surface area of the irregular particles leads to a higher deposition and retention on the fabric compared to the smoother spherical counterparts.

Another factor to account for is the shape of fibres is the corresponding cross-sectional perimeter will dictate the area in contact with the particle. A summary of the fibre shapes and their associated perimeter is summarised in Table 3. A plot of % particle deposition and retention with respect to fibre perimeter (annotated with fabric type) is presented in Figure 6. It is seen that the level of particles deposited generally decreases with increasing fibre perimeter. It is possible that the flatter surface in fibres with higher perimeters offers a greater surface area for particle-fibre interaction, which is driven by a multiplicity of surface van der Waals interactions, hence, greater van der Waals interactions are possible with flatter fibres.

It was also observed that the greatest particle deposition occurred on fabrics that are hydrophobic in nature. Silk and the polyester based fabrics are hydrophobic[45] whilst linen and cotton are hydrophilic.[46] The interaction of the fabrics with water is important as a fully wetted fabric will have an even film across it. Since water acts as the transport medium for deposition, this will affect how easily the particles can be brought into contact with the fabric surface (cross-flow) and also transportation around and within the fabric itself (convective flow). Both the polyethylene and polypropylene particles used in this study are hydrophobic, but become hydrophilic due to the presence of Tween surfactant (S3 of Supplementary information) which will also affect the wettability of the hydrophobic fabrics. It is envisaged that this will make the particle/fabric interaction more favourable during the deposition stage. In contrast, during the rinse cycle, pure water is used so the more hydrophobic fabrics will limit its interaction with water and hence will have an effect on particle retention.

Effect of tumbling speed and time: The influence of the tumbler characteristics on the particle deposition and retention was investigated by varying the rotational speed and duration. Tight cotton and polyester were selected as the fabrics for this study as they possess similar fibre and yarn characteristics that are tightly woven. Figure 7 illustrates the degree of particles deposited and retained from bulk after tumbling and rinse cycles (duration = 10 min) using both particle systems.

As seen in Figure 7, particle deposition increases with increased tumbler rotation speed irrespective of the fabric or particle system used. This increase in deposition number can be attributed to various processes that occur as the fabrics rotate in the wash liquor. Firstly, by increasing the agitation speed the fabric will also move rapidly up and down within the tube that is tumbled. As the fabric moves with each tube rotation, it acts as a filter allowing the solution to pass through the porous structure whilst trapping particles due to the tight weave structure. In addition, the fabric also experiences a crossflow of the liquid over its surface mimicking the processes found in the washing machine. This leads to an increase in the collision frequency between the fabric and the particles, thus a higher proportion of deposition. Secondly, the increased stresses imparted on the fabric as it rotates within the tube will affect the integrity of the yarn producing a greater number of loose fibres due to loosening of the yarn or some fibre shedding occurring (limited in high twist yarns).[47] This provides an excellent location for particle occlusion as they come in close contact with the fabric as seen by the SEM images shown in Figures 3 and 4.

In contrast, when these fabrics are subjected to a rinse cycle the opposite trend is seen as a higher percentage of particle retention is observed at the lower agitation speed. This is because at this lower speed the motion of the fabric in the tumbler is more gentle and may not provide the required energy to disturb a large proportion of the deposited particles. It should be noted that during both the wash and rinse cycles, particles will continually deposit and become removed from the fabric and future studies are needed to extract the impact of each cycle in greater detail. At higher rotation speeds the frequent collision between the fabric and the tumbler tube wall will further loosen the fabric structure allowing deposited particles to escape into the bulk solution.

The influence of cycle duration on particle deposition and retention onto tight cotton and polyester fabric (using an agitation speed = 40 rpm) is presented in Figure 8. It is clear that deposition and retention performance increases as cycle time is decreased from 10 to 5 min using both spherical (Fig. 8a) and irregular shaped (Fig. 8b) particles. With respect to deposition level, it would be expected that this would increase with time, due to longer interaction time between the particles and the fabric surface. Interestingly, Marsh et al.[13] found in their stationary trials that the majority of particle uptake occurs within the first 30 seconds after which the rate decreases and plateaus out. In our case, the two fabrics have a tight weave structure and will 'filter' the particles as they tumble within the tube, which is expected to increase in number with, time. At the same time, the tumbling action will also lead to particles becoming dislodged as the fabric hits the tube wall and localised fluid flow disrupts particles that are not strongly held by the fabric. These processes also influence the retention level obtained during the clean water rinse cycle.

Effect of multiple fabrics: In typical domestic laundry washing, many different textiles will be washed together. To investigate how having a mixture of fabrics affects the particle deposition/retention on each fabric simultaneously, a study comparing linen in the presence of another fabric type was conducted. This study was performed using the irregular shaped particle system only (due to their markedly better performance than the spherical particles as shown in the studies above) and the obtained mass balance and deposition/retention on each fabric type can be found in Table 4.

In general, the percentage of particles deposited on fabrics when multiple fabrics are present decreases in comparison to when only single fabrics are used. The average deposition when singular fabrics were used ranged from ~10–25%, whereas ~2.5–17% is observed with multiple fabrics. This reduction is expected, as the presence of an extra fabric piece will increase competition for capturing particles from the bulk wash liquor.

Based on the data from the single fabric study (Table 2) where linen had the second lowest deposition value, in the case of when multiple fabrics are used, the deposition on linen is much lower compared to the other fabric present (samples TM1, TM3 and TM5). Interestingly, deposition on loose cotton and polyester was much lower than that seen in the single fabric study. The reason for this is that during the tumbling and rinse cycles, it was observed that there was an increased abrasive interaction between linen and the loose cotton/polyester fabrics. This resulted in significant fibre shedding (easily identifiable in the case of TM2 due to the black colour of the loose fabric) and as a result low deposition and retention values. This is the reason why in the case of loose cotton, the percentage of the particle retained during rinsing could not be determined as the average mass loss after rinsing was greater than the average mass gained after tumbling. Since the calculations are mass based, the actual particle retention values may be higher as fibre shedding will influence the calculated retention values.

SEM images in Figures 3 and 4 show that both the loose cotton and polyester fabrics contain a significant number of loose fibres on the fabric surface; another source of loose fibre strands will be at the edges where the fabric was cut to size. During tumbling in water, abrasive forces due to fabric-fabric, fabric-tube wall, fabric-water interaction, and surfactant based lubrication effects could cause these fibres to become expelled into the bulk solution.[48, 49]

Particle deposition/retention based on number density

To corroborate the mass balance analysis on single fabrics, a particle number density analysis (with the spherical particle system) was performed by counting the number of particles within five random 25 mm^2 quadrants (with each quadrant equating to roughly 4% of the total area). The number density results should also give an impression of how uniform the depositions are after both tumbling and rinsing cycles. The number density counted (#/25mm^2) on the front side (side presented to the solution when placed into tube) of each fabric type after the initial tumbling stage (the number of particles initially deposited) and again after the rinsing stage (the number of particles retained) is presented in Figure 9. The value presented for each fabric type is the average of every median value collected from each fabric sample. The error bars (in all figures) represent plus/minus one standard deviation.

The particle number density data for deposition and retention correlate well with the mass balance values presented in Table 2. Silk has a significantly greater number of depositions after tumbling than any of the other fabric samples, whilst both the cotton fabrics yield the lowest deposition. The size of the standard deviations seen on all fabrics suggests that there was a high level of variation in the results suggesting that the deposition is not uniform across the entire front face of the fabric sample. The exact cause of this variance is not known and requires further probing. It is postulated that the orientation that that fabric undergoes as it tumbles may be one possibility, as the fluid flow will influence the fabric contact area with the particle dispersion. The diameter of the tube may also cause restrictions in the fabric tumbling behaviour. Therefore, future experiments will perform analysis over the entire fabric surface to understand if the deposition is indeed random or whether certain areas dominate over others and the cause of this.

To determine if the deposition and retention was uniform on both sides of the fabric, a number analysis was performed as presented in Figure 10. It can be said that after the deposition step there are statistically, significantly fewer particles on the reverse of each fabric compared to the front. This indicates that due to tube geometry restrictions, the front side of the fabric will has a significantly greater contact with the particles in the bulk. If the fabrics were able to rotate more freely it is envisaged that the number density values would be similar. This is an important learning as in a washing machine if the fabric load is high the ability for the fabrics to rotate freely is restricted and as a result one surface side will dominate compared to the other.

DISCUSSION

The particles are dispersed within an aqueous solution containing a trace quantity of non-ionic surfactant. In a real-world scenario, the solution properties will be much more complicated as it includes other ingredients including a wider range of surfactants (with different surface charges), perfumes, colouring agents, bulking agents, bleaches, *etc*. Our observations show that the surfactant in the wash liquor aids particle dispersibility preventing the particles from agglomerating and creaming/sedimentation. At the same time the surfactants reduce the surface tension at the interface between the fabric fibres and water, increasing the fabric wettability.

The transport mechanism is dictated by the flow of fluid around the fabrics which brings particles into close contact with the fabric surface (predominantly the front side). The interactions between the fluid (containing particles) and the fabric can be described as a mixture of dead-end and cross flow filtration. In the cross-flow model, as the fluid flows across the surface some particles will become trapped on the fabric surface. This will be aided by topographical variations and imperfections on the particle surface as well as on the fabric surface (such as ridges, corners, and loose fibres). Simultaneously, particles will be removed by abrasive forces of the fluid flowing tangentially to the fabric surface. In the dead-end model, fluid will flow perpendicular to the fabric surface and travel through the wells or 'pores' within the yarns and weaves of the fabric. A proportion of the particles will become lodged within the wells, depending on their well size. Similarly, some particles will be dragged through the wells and back into solution. In porous fabrics with no obvious wells, particles will be deposited on the fabric surface or within the yarn. By using irregular particles versus smoother spherical particles, the deposition and retention is drastically improved. To determine the actual degree of benefit when using irregular particles, a future assessment is needed with studies conducted in a domestic washing machine.

A major part of the washing process which was not replicated within the lab scale experiment is the draining and spin cycle. This would be another opportunity for deposition to occur. During draining, excess water is removed through the bottom of the drum through holes via gravitational forces. This allows the fluid to flow either through or around the fabric sat at the bottom of the drum, providing further dead end and cross flow filtration interactions. Spinning drives any remaining water towards the outside of the drum and so furthers this process.

In the rinsing stage, the fabric is washed with only fresh water with no further additives. The same abrasive forces as discussed for the tumbling stage apply in the rinsing stage and will remove some of the more poorly deposited particles. If more than one piece of fabric is in the system, abrasive interactions between fabrics will also apply. The final opportunity for particles to perform a 'good quality' deposition is during the drying stage. When the fabric is removed from the solution, the particles are in contact with the fabric either trapped at thread junctions, underneath loose or 'rogue' fibres, or within the wet film, which covers the fabric surface. As the wet film evaporates, particles are drawn to the areas where the evaporation rate is greatest via capillary forces and are eventually deposited. At the same time, particles which are located on the surface of threads can be transported between fibres via capillary forces, should the thread structure allow this, creating high quality depositions within the thread itself.

The current research is exploratory in assessing if particle physical properties such as shape can have at least as important an impact on retention in fabrics as chemical surface modifications. The data highlights that mechanical trapping and particle shape (towards more irregular) may play a dominant role in particle deposition and subsequent retention, and across a wide range of fabric types, which is encouraging for formulators since they have little influence on choosing which fabrics are washed. This study therefore provides impetus to open up the field to better define which of the many different properties have the largest impact, so future work should investigate these properties in a more controlled manner. In doing so, to build a better understanding and develop a predictive model to assist particle engineers in the future. These could include factors (not considered in the current study) such as:- i) particulate properties using particle engineering (material chemistry, controlled size & aspect ratio distribution, roughness, density, rigidity), ii) analysis of size & aspect ratio distribution of deposited and retained particles, iii) studying the effects of gravitational, buoyancy, electrostatic, van der Waals and hydrodynamic flow interactions and iv) impact on process scale up using washing machines. This will additionally have significant impact in the growing area of minimizing microplastic waste within the environment.

CONCLUSIONS

The study explores the deposition and retention of particulates onto fabrics during a wash cycle using a laboratory scale tumbler to mimic the action of a washing machine. It is found that the deposition and retention can be considered as a random event and is heavily dependent on the particle shape and fabric structure. For both particle systems, the distribution of the deposited particles on the fabric surface is inhomogeneous, as particles are predominantly located at weave junctions (higher contact area between particle and fabric) or under loose fibres protruding on the fabric surface (i.e. trapped). The rinse and spin cycle leads to the removal of particles from the fabric surface, but the impact of this is bigger for spherical particles than on irregular ones. The level of retention across all fabrics is found to increase by a factor of up to 3x when moving from the smooth, spherical particles to rough, irregular ones. This is attributed to the higher contact surface area exhibited by the irregular shaped particles.

The laboratory bench scale studies show similar deposition values for spherical particles compared to full scale testing reported in literature. However, the actual magnitude of the benefit of using irregular particles needs to be assessed with testing in a full-sized washing machine. The work highlights ways to optimise the mechanical entrapment of particles to fabrics, but more in-depth studies are required to assess what the best particle shape to use. The research also highlights that whilst improvement is seen in the proportion of particles retained when using non-spherical ones, a notable number are still released during washing. With the issue of microplastics in the ocean in mind, the primary motivator from a sustainability perspective should be to reduce losses to a minimum. This also provides an innovation opportunity to develop particulates from marine degradable materials.

CRediT authorship contribution statement

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. **M.S. Manga:** Conceptualization, Methodology, Data curation, Validation, Formal analysis, Writing - original draft, Writing - review & editing. **T. Adetomiwa:** Methodology, Data curation, Validation, Formal analysis, Writing - review & editing. **S. Marks:** Methodology, Data curation, Formal analysis, Writing - review & editing. **J. Gardy:** Data curation, Formal analysis, Writing - review & editing. **R.S Blackburn:** Conceptualization, Writing - review & editing. **S.J. Russell:** Conceptualization, Writing - review & editing. **D.W. York:** Conceptualization, Methodology, Writing - review & editing.

Notes

The authors declare no competing financial interest.

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