Absorptive protective padding with electrospinned polyester fibers with hydrogel matrix

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Abstract. Hip fractures has been prevalent especially among aged elderly. This can lead to permanent disability of the elderly as they are wheel-chaired bound after suffering from hip fractures. In this work, we explore the design of a protective hip pad which encapsulate the hydrogel and fibres composite in a laminated sheet. The hydrogel was fabricated using Polyvinyl alcohol (PVA) with distilled water. Two types of electrospinned fibres, Nylon-6 fibres and polyester fibres were used as filler. The fabrication of hydrogel matrix composite was varied by the weight percent of nylon 6,6 pellets dissolving in formic acid as compared to Hydrolysed Poly(Vinyl alcohol) to form crosslinked PVA with water. The impact absorption concept was to allow the gel-like hydrogel to flow through the fibres pores and during this process, part of the energy would be dissipated in the matrix composite. This lower the impact force being transferred to the user’s hip and prevent the facture of the elderly’s hips during fall. The protective padding with 20 layers of polyester fibres with 2.5wt % of PVA had the lowest impact force of 0.8 kN as compared to conventional protective padding with measured 1.07kN impact force for impact study.

1. Introduction

Falls are considered a major public health problem in the world. The total number of hip fractures are expected to be more common among elderly woman due to a disease known as osteoporosis which weakens the bone structure and caused them to fracture more easily [1]. As such, the World Health Organisation (WHO) has positioned falls as the second leading cause of accidental or unintentional injury deaths worldwide. Typically a hip fracture occurs after a lateral fall. Majority of the elderly is unable to break the fall and this result in the transfer of the primary impact during a fall onto the great trochanter of the proximal femur. [2]

There are various strategies to target those who are at risk of a hip fracture due to a fall which included wearing of hip protectors, floor mats and other former of early detection of fall and sensory devices. [3] Hip protectors can be widely found and there are many different designs available commercially. Each design had also claimed its own advantage. However, one commonality amongst the typical hip
protector design was that it is incorporated with a pair of protective padding that prevents all the fall impact to be directly transferred to the hip. The protective padding generally comes in the form of hard-shell or soft-shell where the hard-shell type is typically used to shunt energy and the soft-shell type substantially reduced the total impact force during simulated sideways falls via energy absorption. [4] However, there has been report of inadequate validation of existing protector due to the lack of standardization of test system. [5]

Polyvinyl alcohol has been utilized for preparation of hydrogel by physical cross-linking mechanism due to its non-toxicity and biocompatibility. [6] Varying freeze/thaw cycle can be applied to attain different viscosity level based on the degree of cross-linking [7]. Hence in this work, we will like to explore the use of hydrogel based matrix with electrospinned fibers as a filler to strengthen the polymeric composite for use in soft protector pad. Impact test will be carried out to test the absorbance nature of the hip protector pad using the drop tower configuration. [5] The rationale for using the following material combination is to benefit from both energy absorbing nature of the cross-linked PVA composite matrix and high tensile properties of the porous electrospinned nylon fibers.

2. Experimental Details

2.1 Materials used

Hydrogels are polymer materials which is made up of three-dimensional network that exhibits high moisture retention property with proper encapsulation. In this work, we have explored the use of Hydrolyzed Poly(Vinyl alcohol) from Sigma Aldrich for making of hydrogel. Different weight ratio of PVA is mixed with deionized water which serve as solvent. The PVA will have to undergo heat treatment at 95°C for 1hr and metallic rolling for another 15 min before undergoing the freeze-thaw cycle. [8] As most hydrogels are extremely soft material with a modulus of 0.1MPa, fillers can be added to strengthen the composite. [9] For this reason, in our study two types of materials are explored, (i) commercial continuous filament polyester and (ii) electrospinned nylon 6 fibers. The fabrics of polyester has a thickness of 0.1mm and size of 22.5 cm by 22.5 cm. The electrospinned nylon 6 fibers on the otherhand is obtained by dissolving the Nylon6, 6 pellets with 1,1,1,3,3,3-Hexafluoro-2-propanol, 99% (HFP) from Matrix Scientific. Nylon 6,6 is a semi-crystalline polyamide material which exhibits moisture retention property of up to 8.5% of its mass. Water serves as a solvent to alter the nylon 6,6 tensile properties.

2.2 Sample Preparation

Figure 1a shows the Electrospinning system used to spin nylon 6 fibers at a high potential with source solution prepared with Nylon 6,6 pellets and HFP. The fibres were collected on a planar Aluminium surface collector in the system. The flow rate, distance of separation and potential between the needle tip of the syringe head with the collector stage can be adjusted. The heat treated gel-like PVA solution is prepared in a metal tray as shown in Figure 1b before placing it into the fridge for freeze-thaw cycles. The freeze-thaw cycles and duration was varied so as to verify the effectiveness of cross-linked formation between adjacent porous polymeric chains in the viscous hydrogel on the overall composite treated PVA solution for freeze-thaw cycle treatment (c)
performance as a protector pad. [8]. Figure 1c shows an image of the gel-like viscous hydrogel obtained after 2 freeze-thaw processing steps.

Once the fibers and fabric are prepared, they are infused into the gel-like hydrogel by layering process. Part of the viscous hydrogel is first poured into the tray before placing the nylon fibers or the polyester fabric. The remaining of the hydrogel will then be poured in the tray once the fibers are completely immersed in the hydrogel. Figure 2a shows the step to fold up layers of the hydrogel infused nylon fibers or polyester fabric. The hydrogel matrix composite with the fibers are then heat sealed in thermoplastic polyurethane film to form the protector pad.

Air void formation can be avoided in the process by ensuring that layers of polyester fabric is completely wetted with gel-like viscous hydrogel layer (which has been thawed for 30min). The layers of gel-like hydrogel during the thaw cycle can be sliced out in accordance with the dimension of the hip pad to be heated sealed in a stretchable thermoplastic polyurethane film. An image of the sealed composite in polyurethane film (left) with the commercial protector pad (right) is as shown in Fig. 2b. Thermoplastic polyurethane film is chosen as the outer layer of the protector pad as it is elastic, and resistance to oil, grease and abrasion

3. Results and Discussion

3.1 Morphology of the electrospinned fibers and commercial polyester fabrics

To have a better understanding of the structure and the dimension of these fibres, SEM imaging is carried out for the electrospinned fibers generated at different condition as well as fibers embedded in the hydrogel.

3.1.1 Different concentration used for the Nylon 6,6 pellets with formic acid

Figure 3 shows the comparison of the electrospinned fibers using formic acid with varying flow rates. When the fibers are spun at a 10 wt % of Nylon 6 and formic acid, the electrospinned fibers are very fine (from 5nm to 200nm in dimension as shown inset of Fig. 3a). The network of fibers are also prone to beads formation as illustrated in Fig. 3a. This is undesirable as it can impedes the flow of the hydrogel through the fibers during impact and they are too fine for ease of the gel to flow through, resulting in poor energy absorption. Figure 3b shows the electrospinned fibers at 15 wt % of formic acid which results in thicker bead-less fibers network. It could be seen that the fibres thickness of the fibers are
much thicker (between 0.5\(\mu\)m to 2\(\mu\)m) but with poor uniformity. At some of the regions, the fibers are flatten which can result in poor fibre integrity and prone to fiber fracture during load impact.

3.1.2 Solution of Nylon 6,6 pellets with HFP for electrospinning as compared to commercial polyester fibres fabric

The positive effect of using Formic acid and mixtures of formic acid/dichloromethane, such as clear dissolution of polyamide-6 has allowed for subsequent electrospinning to obtain fibers of high aspect ratio [10]. However, the network of main fibers structures with varying thickness and existence of flatten fibers is not ideal for our work. The existence of a finer Nylon 6 mesh with high aspect ratio structure may hinder the flow of hydrogel into the mesh. There is also the risk of incomplete evaporation of formic acid, leading to defective fibers [11]. Due to the challenge in obtaining well-aligned, uniform thickness of electrospinned nylon 6 fibers with formic acid as the solvent, we have attempt to use Hexafluoro 2 propanol (HFP) instead [12,13].

Figure 4(a) shows the electrospinned fibres using Nylon-6 with HFP solvent. The dimension of the fiber ranges from 0.7 \(\mu\)m to 0.9 \(\mu\)m which is fairly well-controlled in terms of its physical dimension. By
comparing it with the polyester fibres, it could be seen that the polyester fibres were more spaced apart with a thickness of about 2 to 3 $\mu$m as shown in Fig. 4(b). As such, there were be greater amount of voids and gaps for the hydrogel to pass through the network of fibers of the polyester fabric. Since there was more bond stretching for polyester, more energy was absorbed and hence the impact force transferred to the user would be much lower.

3.1.3 Embedded structure of the fibers and fabrics in hydrogel

Figure 5 shows the embedded structure of both types of fibers with hydrogel. Hydrogel has been known to have autonomous self-healing properties with diverse reversible non-convalent bonding [14], hydrophobic interaction [15] and $\pi$-$\pi$ stacking [16]. In our stack embedded structure as shared in Figure 2a under sample preparation, the fibers strengthened the hydrogel matrix and prevent them from undergoing matrix deformation. Figure 5a shows that the infused hydrogel matrix are coated into patches of the fiber. The strand of the fiber appears to have broaden due to its interaction with the hydrogel matrix. It is likely that the hydrophilic Nylon 6 fiber absorbed the moisture content and interact with the gel to form a lump of composite at some of the regions. On the otherhand, for the polyester fibre, they appear to have retained its structure which is affirmed by their hydrophobic nature [17]. The hydrogel matrix forms a web-like structure sticking onto some parts of the hydrophobic polyester fiber. Due to the bigger voids between the polyester fibers, this enables the hydrogel cross-linked matrix to be compressed in the fabric and force to the side of the encapsulated thermoplastic polyurethane film. This mechanism differ from the nylon fiber interaction with hydrogel where the matrix soaked nylon 6 fibers will be squeeze out from the nylon 6 fabric under the dynamic impact.

3.2 Dynamic Impact study

The fabric of embedded nylon 6 fiber and the polyester fiber are then encapsulated in the thermoplastic polyurethane film. Dynamic impact test is then done on both samples as well as the commercial hip pad. Figure 6a shows the impact test system which is used for our study. The impact load is 15kg dropped from a height of 20 cm. The commercial hip pad is placed on the stage as shown and the impact force is determined by the load cell. The dwell time is measured from the fast speed camera connected at its side which triggered and measure the relative position of the load cell to the stage.
The samples were subjected to a mechanical impact drop test to find out its impact force and dwell time. This test was done as to simulate the amount of force being absorbed by the protective padding samples and the remaining force being transferred to the user during a fall. The drop test consists of a 15kg load cell that would be dropped from a height of 0.2m onto the test samples to obtain the results. Figure 6(a) shows the drop test being conducted on the commercial protective padding. The load cell (in black) covers the test area of all the test samples’ sufficiently so that full area of the pad can be used for absorbance. The maximum amount of gravitational potential energy would be converted to work done as the load cell drops from a height and comes in contact to the test sample. Work done is related to force and distance. Hence, the remaining amount of force after it has been absorbed by the test pad samples would be transferred to the load cell and hence be detected on the monitoring system. The dwell time indicates the period of time when the system load remains in physical contact with the sample. The area under the force time graph was determined to obtain the average force of impact, $F_{ave}$ by dividing the total integrated area over the dwell time.

Table I shows the tabulation for the average force and dwell time for the commercial pad, Nylon 6 fiber with hydrogel and lastly polyester fiber with hydrogel. The results show that the conventional

| Sample  | Materials                                      | Average force, $F_{ave}$ | Dwell Time |
|---------|-----------------------------------------------|--------------------------|------------|
| Sample A | commercial pad with foams                     | 1.07 kN                  | 18 ms      |
| Sample B | Nylon 6 fiber filler in hydrogel matrix       | 0.85 kN                  | 20.5 ms    |
| Sample C | polyester fiber filler with hydrogel matrix   | 0.80 kN                  | 18 ms      |

Figure 6(a) Mechanical impact drop test on the commercial protective padding (b) Plot of the the force versus the relative time to determine the average impact force with the dwell time.
Commercial pad has a highest average force of 1.07kN as compared to the two samples with the hydrogel matrix. The polyester fiber with hydrogel matrix, Sample C gives the lowest value of average impact force. This could be attributed to the larger gap between the lower density polyester fiber which allows the greater ease of viscous hydrogel to infuse into it. With the impact force, it is harder for the more dense Nylon 6 fiber to allow the hydrogel to diffuse through. For this reason, Sample B has higher average impact force as compared to Sample pad C. However, the advantage of having B is that the dwell time is much longer which allows the impact force to be better dissipated. This is possible due to its hydrophilic nature of the nylon 6 fiber which allows the absorbed water and hydrogel to be gradually squeeze out from the fiber. This also account for Sample B to be having the highest dwelling time of 20.5 ms.

4. Conclusion

The viscosity of the hydrogel, the nature and the thickness of the fibers can affect the impact absorbent properties of the pad. The generation of the nylon 6 fiber by electrospinning allows the user to gather the fibers to be infused with hydrogel. The hydrophilic nature of the nylon 6 fibers has the advantage over the polyester fiber in that it can soaked up more hydrogel which dispense the gel when a higher load is applied. This called for further work on optimizing the nature of the fiber by varying the freeze-thaw cycle and its duration and possibly different weight composition of the Nylon 6,6 is a semi-crystalline polyamide with solvent water. The impact test affirmed the effectiveness of the hydrophilic nature of nylon 6 fiber to absorb the hydrogel so as to infuse into the fabric for effective impact absorbance.

5. References

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