Biocomposites: Their multifunctionality

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During the last decade, tissue engineering has shown a considerable promise in providing more viable alternatives to surgical procedures for harvested tissues, implants and prostheses. Due to the fast development on nano- and biomaterial technologies, it is now possible for doctors to use patients’ cells to repair orthopaedic defects such as focal articular cartilage lesions. In order to support the three-dimensional tissue formation, scaffolds made by biocompatible and bioresorbable polymers and composite materials, for providing temporary support of damaged body and cell structures, have been developed recently. Although ceramic and metallic materials have been widely accepted for the development of implants, their non-resorbability and necessity of second surgical operation (like for bone repair), which induce extra pain for the patients, limit their wide applications. The development of different types of biocomposites for biomedical engineering applications is described. These biocomposites include (i) basic biomaterials; (ii) natural fiber-reinforced biocomposites and (iii) nanoparticle-reinforced biocomposites. Their multifunctionality is discussed in terms of the control of mechanical properties, biodegradability and bioresorbability.

Keywords: multifunctional materials; biocomposite

1. Introduction

The musculoskeletal system of a human body involves the integration of tissues and other structural members such as bones, cartilages, tendons, ligaments, peripheral nerves and spinal nerve roots, skeletal muscles, etc. In connecting those bones, there are three types of joints that exist in the human body, namely fibrous, cartilaginous and synovial, but only the synovial or diarthrodial joints allow a large degree of motion. The coverage of the diarthrodial joints is a layer of hyaline articular cartilage, which is a thin, dense, white but translucent connective tissue, which forms articulating surfaces of the diarthrodial joints. The articular cartilage is a soft tissue composed primarily of a large extracellular matrix (ECM) with a sparse population of chondrocytes distributed throughout the tissue. ECM is mainly composed of collagen, which forms insoluble tightly woven fibers; water and proteoglycan are dispersed through the collagen framework as a soluble gel making the matrix biphasic. Collagen fibrils can withstand tension but not in compression in general, and thus the matrix possesses high tensile strength, whereas for proteoglycan macromolecules, which are the main protein in hyaline articular cartilage, they withstand compression by attracting and entrapping large amount of water. The
articular cartilage, as a load-bearing material, supports joints movement with relatively low
coefficient of friction and high wear resistance.

The articular cartilage is predominantly loaded in compression and is viscoelastic in
nature; its defects are usually caused by congenital diseases, paediatric growth plate dis-
orders, trauma-induced injuries and others. Once injured, the capacity of tissue regeneration
and self-recovery for full-thickness defects is very low, because of its nature of no contact
with blood and exhibits low cell to matrix ratio [1]. Statistically, it has been reported that
more than 900,000 Americans suffer from articular cartilage injuries each year and they have
been waiting for organ transplants. This leads to the situation that the transplantation of organs
from compatible donors is severely insufficient to go around. Driven by the shortage of the
organ transplants, tissue engineering offers a tremendous promise for providing more viable
alternatives to surgical procedures for harvested tissues, implants and prostheses [2]. In the
past decades, most of the surgical inventions to repair damaged cartilage have been directed to
the treatment of clinical symptoms rather than the regeneration of hyaline cartilage, such as
pain relief and functional restoration of joint structures and articulating surface [3].

Currently, there are three approaches in tissue engineering: (i) usage of segregated cells
or cell substitutes to replace those functional cells; (ii) delivery of tissue inducing substances
to targeted locations including growth and differentiation factors; and (iii) seeded and
growing cells in three-dimensional scaffolds [4]. On the other hand, there are three general
strategies for joint surface restoration; they are (i) enhancement of intrinsic healing capacity
of cartilage, (ii) replacement of damaged articular cartilage with osteochondral transplants
and (iii) regeneration of articular cartilage surface with the growth of new cartilage [5].

Autologous chondrocyte implantation, where donor tissue is harvested and separated into
isolated cells which are then attached and cultured onto some suitable substrates ultimately
implanted to the wound site, has yielded promising results in treating articular cartilage
defects [1], however, the usage of suspended cells and a periosteal flap for holding chon-
drocytes in positions have certain difficulties on theoretical and experimental results [6].
Moreover, tissues in vivo are generally three-dimensional construction; cells cultured in
three-dimensional substrates are more likely to reflect in vivo scenarios. In order to address
these problems, three-dimensional cell seeded matrices are studied in cartilage tissue
engineering to facilitate in vivo implantation and promote cartilage repair [7].

2. Biomaterials

As the growth and regeneration of neo-tissues can be greatly influenced by the biological
environment that essentially provides to the cells and also the scaffold characteristics including
biocompatibility, biodegradability, micro- or macro-porosity and interconnectivity, etc., dif-
f erent sorts of considerations on the design and build of scaffolds has to be clearly understood
by all researchers and scientists working in or intending to fit into this area. This section
intends to provide a review on the effects and relationships of the choice of different types of
biomaterials for fabricating scaffolds. The advantages and limitations of these biomaterials are
also discussed in detail. To select an appropriate type of material for designing and manufac-
turing scaffolds, several key factors, listed as follows, have to be studied in detail.

2.1. Biocompatibility

The biocompatibility of materials inside the human body plays a key role in tissue engineer-
ing, which ensures the materials are safe for use in the human body and in the endogenous
fluids. Being an ideal implant for repairing tissue defects and regenerating neo-tissue for
wound sites, the materials used must be biocompatible, i.e. the materials must not induce any inflammatory response, extreme immunogenicity or cytotoxicity to native cells, tissues or organs in vivo. Since the implants are normally imbedded into the human body and last for a period of time, by-products resulting from the degrading process of the implants should not produce any harmful material and/or element to the body. For recent polymer-based scaffold design and development, the basic requirement is that the scaffolds must be naturally degraded with time, and gradually absorbed by the human body itself without generating any side effect. This process allows the functionality of the human body to gradually recover without relying too much on the support of the scaffolds. Due to the fact that demand for scaffolds and implants has been increasing, many comprehensive studies on the biocompatibility of scaffolds and the toxicity of their decomposed products have been progressed rapidly in the past 10 years.

2.2. Biodegradability and bioresorbability

The field of biodegradable polymers is a fast-growing area of polymer science because of the interest in such compounds for temporary surgical and pharmacological applications. With reference to the definitions of these two phenomena, biodegradable materials like polymers can be decomposed naturally but their degraded products will remain inside the human body. For bioresorbable materials, they will degrade after a certain period of time of implantation, and non-toxic products will be produced in the ways of elimination with time and/or metabolism. For chemical degradation, two different modes are defined; they are (i) hydrolytic degradation or hydrolysis, which is mediated simply by water, and (ii) enzymatic degradation, which is mainly mediated by biological agents such as enzymes. Scaffolds should be biodegradable, allowing ECM to occupy the void space when the biomaterial is degraded. Today, there are many types of materials, as listed in Table 1, that are widely used as bioabsorbable implants and their market is expanding rapidly worldwide. In fact, the advantages of using biodegradable polymers over the traditional metallic materials for implant development include the reduction of stress-bearing capability over time since the polymer will be degraded naturally, and the alleviation of pain, both physically and physiologically, due to the need of second surgical operation for removing metallic implants.

2.3. Degradation rate, pore size and surface morphology

The major function of a biodegradable polymer-based scaffold must be able to retain at the implantation site while maintaining its physical characteristics and ordinary mechanical properties, as well as supporting the attachment, proliferation and differentiation of cells, until the regeneration of tissues on an injured site. Ideally, the degradation rate of the scaffold

| Polymer                  | Abbreviation | Purpose                                           |
|--------------------------|--------------|---------------------------------------------------|
| Poly(glycolide)          | PGA          | 3D polymer scaffolds for cell transplantation     |
| Poly(lactic acid)        | PLA          | 3D polymer scaffolds for cell transplantation     |
| Poly(L-lactide)          | L-PLA        | Fracture fixation, suture anchor, ACL reconstruction, rotator cuff repair, meniscus repair |
| Poly(D,L-lactide)        | D,L-PLA      | Fracture fixation, ACL repair, suture anchor      |
should be matched with the rate of neo-tissue formation so as to provide a smooth transition of the load transfer from the scaffold to the tissue. However, based on recent research investigations, it was found that the degradation rates of different types of biodegradable polymer are different, depending on the composition of the polymer, conditions of loading and ambient environment. The enzymatic degradation rate proceeds from the surface of the polymer, so therefore surface area and condition (porosity) of the polymer is one of the important factors to control the degradation rate [8].

To date, there are many ways to manufacture porous scaffolds; they are porogen leaching, emulsion freeze-drying, expansion in high temperature gas, 3D printing, phase separation techniques, thermal phase separation [9]. Figure 1 shows two porous films of PLA and PCL fabricated by using the freeze-dry method. It was found that the degradation rate of the films varied with the pore size and density. The two porous films decomposed faster than films without pores, as shown in Figure 2 [8]. Large numbers of pores may be able to enhance the mass transport and neo-vascularization within the implants, whereas a smaller diameter of pores is more preferable to provide larger surface per volume ratio. Moreover,
instead of adjusting the pore size, the shape of the pores is also a key to affect the efficiency of tissue regeneration. It is important to note that some specific pore sizes can enhance the cellular activity, but optimal size and geometry are highly dependent on specific cell types grown on injured sites. For bone in-growth, the optimal pore size is in the range 75–250 μm. On the other hand, for in growth of fibro-cartilaginous tissue, the recommended pore size ranges from 200 to 300 μm [9]. Figure 3 shows the percentage of cells attached onto scaffolds with different pore sizes [10] and it further proves that the control of pore size for different scaffolds is necessary.

Most organ cells require a suitable substrate to retain their ability to adhere, proliferate and perform the later differentiated functions, including spreading and differentiating seeded cells. Therefore, the design of scaffolds for tissue regeneration, the control of surface topography and roughness is important to allow the migration of the cells on the scaffold surface. A rougher surface also enhances the diffusion rates to and from the scaffolds as well as facilitating vascularization and improving the oxygen and nutrients supply and waste removal. Figure 4 shows osteoblast-like cells grown on poly(L-lactic acid) (PLLA) substrates with different surface morphologies; one was a smooth flattened surface, whereas the other had PLLA islands [11]. The height of the cells on the smooth surface was higher than

Figure 3. Percentage of cells attached to the collagen–glycosaminoglycan (CG) scaffolds with different pore sizes [10].

Figure 4. SEM images of OCT-1 osteoblast-like cells attached on the (left) smooth surface of PLLA substrate and (right) island-patterned PLLA substrate [11].
that of the cells on the island-patterned PLLA, which implies that the cells preferred to stretch on a rough surface. The uniformity of the cells grown on the smooth PLLA substrate was also relatively poor as compared with that grown on the island-patterned PLLA substrate. In addition, Figure 4 also clearly indicates that the total contact area of the cells to the PLLA was much larger as compared with the one without the island-patterned structure built on the PLLA surface [11].

2.4. Mechanical integrity

In order to fulfill the physiological loading requirement, tissue engineered scaffolds should act as temporary physical supports (or so-called “structural members”) to withstand the external and internal stresses until neo-tissues are generated. As for a native cartilage, its metabolism, synthesis and the organization of ECM are affected by the mechanical environment experienced by chondrocytes. These forces are usually generated during both the implantation procedure and the mechanical forces experienced at the joint surfaces. In vitro, the scaffolds have to be able to resist the culturing mechanical environment such as direct compressive, hydrostatic pressure and static loads. Especially for the dynamic functional environment of the scaffolds, this can have a significant effect on the scaffolds’ in vitro degradation as well as release of bioactive agents. Consequently, the properties of the scaffolds should be as similar as the properties of neo-tissues generated, in order to provide a proper structural support in the stage of healing. At the later stage, all the loads have to be totally transferred to the neo-tissues since the scaffolds should be degraded gradually. Neves, Kouyumdziev, and Reis [12] have studied the change of mechanical properties of starch with poly(lactic acid) (SPLA) with time, and the results showed that the strength of the SPLA dropped substantially after being immersed in isotonic saline solution (0.154M NaCl) for three days, and in spite of the change its deformation was small.

3. Natural fiber biocomposites

In the past few years, there has been a dramatic increase in the use of natural fibers such as leaves from flax, jute, hemp, pineapple and sisal for making new types of environmentally-friendly composites. Recent advances in natural fiber development, genetic engineering and composite science offer significant opportunities for improved materials from renewable resources with enhanced support for global sustainability. A material that can be used for medical application must possess a lot of specific characteristics. The most fundamental requirements are related to biocompatibility, that is, not to have any adverse effect on the host tissues; therefore, those traditional composite structures with non-biocompatible matrix or reinforcement are substituted by bioengineered composites.

Biocomposites consist of biodegradable polymer as matrix material and usually biofibers as reinforcing elements, which are generally low cost, low density, high toughness, acceptable specific strength properties, good thermal properties, ease of separation, enhanced energy recovery and biodegradability. Biofibers are chosen as reinforcements since they can reduce the chance of tool wear when processing, dermal and respiratory irritation. Conversely, these fibers are usually small in cross-section and cannot be directly used in engineering applications; they are embedded in matrix materials to form biocomposites. The matrix serves as binder to bind the fibers together and transfer loads to the fibers. In order to develop and promote these natural fibers and their composites, it is necessary to understand their physico-mechanical properties.

Natural fibers are subdivided based on their origin, coming from plants, animals or minerals. Generally, plant-based natural fibers are lignocelluloses in nature and are
composed of cellulose, hemi-cellulose and lignin, such as flax, jute, sisal and kenaf; whereas animal-based natural fibers are of proteins, like wool, spider and silkworm silk. The enhanced environmental stability of silk fibers in comparison to globular proteins is due to the extensive hydrogen bonding, the hydrophobic nature of much of the protein, and the significant crystallinity.

Silk proteins – known as silk fibroins – are stored in the glands of insects and spiders as an aqueous solution. During the spinning process, a silkworm accelerates and decelerates its head in arcs to each change of direction, and the concentration of silk in the solution is gradually increased and finally an elongation stress is applied to produce a partly crystalline, insoluble fibrous thread in which the bulk of the polymer chains in the crystalline regions are oriented parallel to the fiber axis. Faster spinning speed leads to stronger but more brittle fibers, whereas slower speed leads to weaker and more extensible fibers. At even greater speed, silk toughness decreased, mainly due to the loss of extensibility [13].

Cocoons are natural polymeric composite shells made of a single continuous silk strand with length in the range of 1000–1500 m and conglutinated by sericin [14]. This protein layer resists oxidation, is antibacterial, ultra-violet (UV) resistant, and absorbs and releases moisture easily. This protein layer can be cross-linked, copolymerized and blended with other macromolecular materials, especially artificial polymers, to produce materials with improved properties. On average, cocoon production is about 1 million tonnes worldwide, and this is equivalent to 400,000 tonnes of dry cocoon (see Figure 5). In the tissue engineering area, silks have been identified as a kind of biomaterial, useful for the healing process in bone, tendon or ligament repairs. Slowly degrading biomaterials that can maintain tissue integrity following implantation, while continually transferring the load-bearing burden to the developing biological functional tissue are desired. In such phenomena, the gradual transfer of the load-bearing burden to the developing and/or remodelling tissue should support the restoration and maintenance of tissue function over the life of the patient. A normal compact cocoon exhibits a high ability of elastic deformation with an elastic strain limit higher than 20% in both longitudinal and transverse directions. Anisotropic properties, mainly due to the non-uniform distribution and orientations of silk segments and the inner layer of cocoon, have low porosity (higher silk density) and a smaller average diameter of silk, therefore, there is an increase in elastic modulus and strength from outside to inside layers. That is, the thinner the silk, the higher the elastic modulus and tensile strength and the maximum values at the innermost layer. On the other hand, temperature above the glass transition temperature, the cocoon and its layers become softer and softer and behave similarly to a rubber-like material. Silk fibers have higher tensile strength than glass fiber or synthetic

![Figure 5. Raw cocoon silks (a) and side view of the silk fiber (b).](image-url)
organic fibers, good elasticity, and excellent resilience [15]. They resist failure in compression, are stable at physiological temperatures and sericin coating is water-soluble proteinaceous glue. Table 2 shows a comparison of the mechanical properties of common silk types (silkworm and spider dragline) to several types of biomaterial fibers and tissues commonly used today.

Silk fibers spun out from silkworm cocoons consist of fibroin in the inner layer and sericin in the outer layer: all are protein based. From outside to inside layers of cocoon, the volume fractions of sericin decreases, whereas the relative content of fibroin increases. Also, it is known that silk fibroin consists of both hydrophilic and hydrophobic regions, which is a block-like polymeric system. These fibers have a highly non-uniform cross-sectional geometry with respect to both shape and absolute dimensions. By changing the reeling conditions, silkworm silks can be stronger, stiffer and more extensible, approaching the properties of spider dragline silks [16]. Each raw silk thread has a lengthwise striation, consisting of two separate but irregularly entwined fibroin filaments (brin) embedded in sericin. Silk sericin is a minor protein that envelops silk fibroin fibers and glues them together to form a cocoon shape. Fibroin and sericin in silk account for about 75 and 25 wt %, respectively. Silk fibers are biodegradable and highly crystalline with a well-aligned structure.

Chicken feather fibers (CFFs) have attracted much attention to different product design and engineering industries recently, so the use of CFF as reinforcements for polymer-based

| Natural fibers | UTS (Mpa) | Elongation at break (%) | E (GPa) |
|----------------|-----------|-------------------------|---------|
| Flax           | 300–1500  | 1.3–10                  | 24–80   |
| Jute           | 200–800   | 1.16–8                  | 10–55   |
| Sisal          | 80–840    | 2–25                    | 9–38    |
| Kenaf          | 295–1191  | 3.5                     | 2.86    |
| Abaca          | 980       |                         | 106psi  |
| Pineapple      | 170–1627  | 2.4                     | 60–82   |
| Banana         | 529–914   | 3                       | 27–32   |
| Coir           | 106–175   | 14.21–49                | 4–6     |
| Oil palm (empty fruit) | 130–248  | 9.7–14                  | 3.58    |
| Oil palm (fruit) | 80        | 17                      |         |
| Ramie          | 348–938   | 1.2–8                   | 44–128  |
| Hemp           | 310–900   | 1.6–6                   | 30–70   |
| Wool           | 120–174   | 25–35                   | 2.3–3.4 |
| Spider silk    | 875–972   | 17–18                   | 11–13   |
| Cotton         | 264–800   | 3–8                     | 5–12.6  |
| Cocoonsilk     |           |                         |         |
| Bombyx Mori    | 209       | 20                      | 6.1     |
| Tussah         | 248       | 34                      | 5.79    |
| Human Tissues  |           |                         |         |
| Hard tissue (tooth, bone, human compact bone, longitudinal direction) | 130–160 | 1–3                     | 17–20   |
| Skin           | 7.6       | 78                      |         |
| Tendon         | 53–150    | 9.4–12                  | 1.5     |
| Elastic cartilage | 3        | 30                      |         |
| Heart valves   | 0.45–2.6  | 10–15.3                 |         |
| Aorta          | 0.07–1.1  | 77–81                   |         |

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biodegradable materials has emerged gradually. The advantages of using these natural fibers over traditional reinforcing fibers in biocomposite materials are low cost, low density, acceptable specific strength, recyclability, biodegradability, etc. Natural fibers generally have high specific mechanical properties.

Due to an increasing public awareness of environmental protection, the application of natural fibers in biocomposite materials has been increased rapidly in the past few years. CFFs, because of their renewable and recyclable characteristics, have been appreciated as a new class of reinforcements for polymer-based biocomposites. However, the full understanding of their mechanical properties, surface morphologies, environmental influences due to moisture and chemical attacks, bonding characteristics between silk fibroin and surrounding matrix and manufacturing process is essential.

The moisture content of CFF is an important factor that can highly influence their weight and mechanical properties. The moisture content of processed CFFs can vary depending upon processing and environmental conditions. The glass transition temperature ($T_g$) of the feather fibers and inner quills is approximately 235°C, whereas for outer quills it is 225°C. High $T_g$ represents the fact that a tighter keratin structure is formed to which water is more strongly bonded. Fibers and inner quills do not begin to lose water below 100°C. The moisture evolution temperature of the CFF and quill occurs in the range of 100–110°C [17]. This suggests that it may be possible to have fully-dry fibers and inner quills at 110°C. Figure 6 and Table 3 show the SEM image of the down CFF and its strength compared with other type of feathers. It was found that the development of chicken feather fiber biocomposites have been increasing in recent years, and the outcome are expected to be able to alleviate the global waste problem.

![Figure 6](image_url)  
(a) Flight chicken feather fiber (a) and down chicken feather fiber (b).

| Sample                                           | Modulus of elasticity (GPa) |
|--------------------------------------------------|----------------------------|
| Pure PLA                                         | 3.8                        |
| CFF/PLA (fiber from upper (flight) portion of feather) | 3.4                        |
| CFF/PLA (fiber from lower (down) portion of feather) | 4.2                        |

Table 3. Comparison of the modulus of PLA and CFF/PLA composites.
3.1. Applications

Silk fibers have been used in biomedical applications particularly as sutures by which the silk fibroin fibers are usually coated with waxes or silicone to enhance material properties and reduce fraying. But in fact, there are lots of confusing questions about the usage of these fibers as there is the absence of detailed characterization of the fibers used including the extent of extraction of the sericin coating, the chemical nature of wax-like coatings sometimes used, and many related processing factors. For example, the sericin glue-like proteins are the major cause of adverse problems with biocompatibility and hypersensitivity to silk. The variability of source materials has raised the potential concerns with this class of fibrous protein. Yet, silk’s knot strength, handling characteristics and ability to lay low to the tissue surface make it a popular suture in cardiovascular applications where bland tissue reactions are desirable for the coherence of the sutured structures [9].

3.2. Silk-based biocomposites

Annamaria, Maria, Tullia, Silvio, and Orio [18] discovered in their studies that environment-friendly biodegradable polymers can be produced by blending silk sericin with other resins. Nomura, Iwasa, and Araya [19] identified that polyurethane foams incorporating sericin are said to have excellent moisture-absorbing and -desorbing properties. Hatakeyama [20] has also reported producing sericin-containing polyurethane with excellent mechanical and thermal properties. Sericin blends well with water-soluble polymers, especially with polyvinyl alcohol (PVA). Ishikawa, Nagura and Tsuchiya [21] investigated the fine structure and the physical properties of blended films made of sericin and PVA. Moreover, a patent reported on a PVA/sericin cross-linked hydrogel membrane produced by using dimethylurea as the cross-linking agent had a high strength, high moisture content and durability for usage as a functional film [22].

Silk fibroin film has good dissolved oxygen permeability in the wet state but it is too brittle to be used on its own when in the dry state, whereas chitosan is a biocompatible and biodegradable material that can be easily shaped into films and fibers. Park, Lee, Ha, and Park [23] and Kweon, Ha, Um, and Park [24] have introduced an idea of silk fibroin/chitosan blends as potential biomedical composites, as the crystallinity and mechanical properties of silk fibroin are greatly enhanced with increasing chitosan content.

Another type of biocomposite is the silk fibroin/alginate blend sponge. For biotechnological and biomedical fields, silk fibroin’s reproducibility, environmental and biological compatibility, and non-toxicity benefit many different clinical applications. As the collective properties, especially mechanical properties of silk fibroin sponges in dry state are too weak to handle as wound dressing, thus, they can be enhanced by blending silk fibroin films with other synthetic or natural polymers, for example, polysaccharide–sodium alginate.

Furthermore, Katori and Kimura [25] and Lee et al. [26] examined the effect of silk/poly (butylenes succinate) (PBS) biocomposites. They found that the mechanical properties including tensile strength, fracture toughness and impact resistance, and thermal stability of biocomposites could be greatly affected by their manufacturing processes. Moreover, a good adhesion between the silk fibers and PBS matrix was found through the observation and analysis by scanning electron microscope (SEM) imaging.

The mechanical properties of Bombyx mori, twisted Bombyx mori and Tussah silk fibers were also investigated through tensile property tests. It was found that Tussah silk fiber exhibited better tensile strength and extensibility as compared with others. However, the
stiffness of all samples was almost the same. This may be due to the distinction of silkworm raising process, cocoon producing and spinning conditions. Based on the Weibull analysis, it was shown that the Bombyx mori silk fiber has a better reproducibility in terms of experimental measurement, than that of the Tussah silk fiber. This may be due to the degumming treatment, which has an effect on the microstructure of the fiber.

By using silk fiber as reinforcement for biodegradable polymer, the mechanical properties do have a substantial change. Cheung, Lau, and Tao [27] have demonstrated that the use of silk fiber to reinforce poly(lactic acid) (PLA) can increase its elastic modulus and ductility to 40% and 53%, respectively, as compared with a pristine sample. It was also found that the biodegradability of silk/PLA biocomposites was altered with the content of the silk fiber in the composites. This reflects the fact that the resorbability of the biocomposites used inside the human body can be controlled, which in this is the key parameter of using this new type of material for bone plate development.

3.3. PLA biocomposites

By mixing CFF with biopolymers like PLA, a biodegradable composite can be formed for use in plastic products and implant applications. In preparation of the composites, chicken feather was immersed in alcohol for 24 h, then washed in a water-soluble organic solvent, and dried under 60°C for 24 h [10]. CFFs with a diameter of about 5 μm and length of 10–30 mm were separated from the quill and then used. Figure 7 shows the relationship between CFF content and peak stress and modulus of elasticity, respectively. The modulus of elasticity of CFF/PLA composite increases with the CFF content and reaches the maximum modulus of 4.38 GPa (increment up to 35.6%) at the CFF content of 5 wt %. These results reveal that the incorporation of CFF into the matrix is quite effective for reinforcement. The decrease of modulus for the composite with the CFF content above 5 wt % will be due to the insufficient filling of the matrix resin; designating 5 wt % CFF is the critical content.

It can also be shown from the peak stress that the tensile strength of PLA after the addition of CFF is lower than that of pure PLA. This phenomenon, also reported by other researchers [17,28], is an indication of poor adhesion between the CFF and the matrix. Although the CFF surface is rough and the hydrophobic consistency of CFF and PLA, the adhesion between
them is a problem needed to be solved. And the stress could not be transferred from the matrix to the stronger fibers. Another possible explanation of this phenomenon can be that the CFFs were randomly oriented inside the composite; the failure of the composite might be initiated by the failure of the matrix and then followed by fiber breakage. These conclusions could be proved by the fractured morphology of the microstructures observed by SEM. Thermal properties, such as glass transition temperature \( T_g \), crystallization temperature \( T_c \), melting temperature \( T_m \), crystallization enthalpy \( \Delta H_c \) and melting enthalpy \( \Delta H_m \), obtained from the DSC studies are summarized in Table 4.

### 4. Nanoparticle-reinforced biocomposites

Nanocomposites are novel materials with drastically improved properties due to the incorporation of a small amount (about less than 10%) of nano-sized fillers into a polymer matrix. In biomedical and tissue engineering applications, in bio-nanocomposites, these nano-fillers are added into biopolymers, which can be compatible and/or bioresorbable to form stiffer materials, in which their strength is enhanced while the biodegradability/bioresorbability rate can be controlled.

Many attempts have focussed on using nanoparticles like carbon nanotubes, nanoclay and nano-apatite to reinforce biodegradable polymers in order to enhance their mechanical and thermal properties. The focus on using these particles for controlling their biodegradability is clear. There are many reports addressing the fact that the use of these particles can enhance the Young modulus and glass transition temperature of thermoset polymers, like epoxies commonly used in aerospace engineering applications. They function by blocking the linkage between polymer chains, or act like fiber, in nanoscale level to allow stress transfer from the polymer matrix to the particles.

Carbon nanotubes have been well recognized as among the strongest materials in the world compared with other traditional materials. In addition, their geometry allows them to be an excellent means of delivering hydrogen and drugs, respectively, for different fuel cell and biomedical engineering applications. Nanotubes actually can be classified into three types: they are (i) zigzag; (ii) armchair and (iii) chiral. Each of these has its own mechanical, electrical and fractural properties. Harrison and Atala [29] have reported that nanotubes can be used in tissue engineering materials for improved tracking of cells, sensing of microenvironments, delivering of transfect ion agent and scaffolding for incorporating with the host’s body. These nanotubes can also act as reinforcement to enhance the strength of the materials. Unfortunately, these nanotubes, if mixed with some biodegradable or bioresorbable polymers to form biocomposites, may have potential risk of being trapped in the cells of the human body. The formation of cell-bridge, due to the existence of nanotubes may create neural network. In terms of cytotoxicity, several reports in the literature indicate that carbon nanotubes are cytotoxic. For example, when the nanotubes were incubated with alveolar macrophages, a significant increase in cytotoxicity was observed after 6 h of exposure.

| CFF content (wt %) | \( T_g \) (°C) | \( T_c \) (°C) | \( \Delta H_c \) (J/g) | \( T_m \) (°C) | \( \Delta H_m \) (J/g) |
|-------------------|----------------|----------------|----------------|----------------|----------------|
| 0                 | 58.7           | 112.9          | 38.8           | 163.4          | 169.5          | 43.2           |
| 2                 | 59.8           | 112.2          | 42.1           | 164.0          | 171.9          | 44.7           |
| 5                 | 59.2           | 112.4          | 42.6           | 163.7          | 170.0          | 43.7           |
| 8                 | 59.3           | 112.0          | 43.5           | 163.5          | 170.0          | 44.7           |
| 10                | 57.5           | 102.9          | 44.5           | 166.7          |                | 46.9           |
addition, there are some limitations in adopting these materials for implant applications because of their poor biodegradability.

In general, for nanoparticles like carbon nanotubes, due to their small size, individual nanomaterials and small agglomerates may be deposited deep within the lungs when inhaled, reaching areas that are not as easily accessed by larger materials. Also, their size may also permit them to pass directly through tissues and cell membranes allowing them to translocate from their initial site of exposure to their organ in the body. There are three generally accepted factors that determine the potential of a particle to cause harm:

- The surface area/mass ratio of the particle – a large surface area gives the particle(s) a greater area of contact with the cellular membrane, as well as greater capacity for absorption and transport if toxic substances;
- The particle retention time – the longer the particle stays in contact with the cellular membrane the greater the chance of damage. This factor also incorporates the concept of particle mobility, either through clearance or migration to surrounding tissue;
- The reactivity or inherent toxicity of the chemical(s) contained within the particles.

For the nanoclays, a commonly used polymer is layered silicate, which forms an ordered layered structure. In general, there are three types of structures forming in nanopolymer composites; they are [30]:

1. A microcomposite when the clay layers are still stacked and the polymer is not intercalated within the clay platelet, forming clusters due to poor polymer–clay affinity; the material thus exhibits phase separation. In this structure, a poor tensile and impact strength normally results.
2. An intercalated composite for which the polymer is partially intercalated between the silicate layers; these latter are still stacked but the interlayer spacing has increased.
3. Eventually, an exfoliated nanocomposite showing individual and well-dispersed clay platelets in the matrix; in this case, the layered structure does exist anymore.

Our newly-developed nanoclay-supported nanoparticles improve dispersion and exfoliated properties of the clay structure in the polymer environment.

Recent research has been focussed on some applicative directions, like the preparation of porous ceramic materials or scaffolds as support for tissue regeneration by using PLA/nanoclay biocomposites with the aim of obtaining high cell density and a controlled morphology varying from microcellular to nano-cellular structures.

The latter research has shown that, in general, a desirable percentage of nanoclay placed into the polymer for biocomposites should not exceed 5% as it would cause substantial degradation of their mechanical properties, such as flexural strength. The softening of biocomposites may also be due to the change of chemical structures, of the biocomposites after nanoclay being added.

Nano-hydroxyapatite has also been used for orthopaedic/dental implants because of its similar chemical composition and structure to the mineral phase of human bone. Zhang et al. [31] used nano-hydroxyapatite (n-HA) to reinforce polyamide 66 (PA 66) to form a biocomposite. In their work, it was shown that the biodegradability can be controlled. Besides, the thermal stability of the biocomposites is much better than that of pure PA 66, which is due to the hydrogen bonds between the amide group of PA 66 and hydroxyl group
(–OH) of n-HA into PA66 caused an apparent increase in the $T_c$, despite a decrease in the percentage of crystallinity.

5. Conclusion

Recently, research on new types of biodegradable materials for biomedical engineering applications has been the hottest topic in both advanced composites and biomaterials communities. The integration of composite techniques to fabricate high-strength and durable biodegradable polymer-based composites is of great interest to all researchers and engineers. Properly applying the right polymer with the considerations of pore size, degradation rate and surface morphology, as a parent material with mixing with high-strength fibers can indeed provide a good alternative to existing polymer and metallic-based biocompatible materials for scaffold applications. The use of natural fiber and nanoparticles to reinforce the basic polymer materials as well as control their biodegradability/bioresorbability is the most promising method for both scaffolding development and bone repair. This review article provides fundamental information for researchers and engineers working in advanced composite industry, to open a new step to the development of bioengineered composites. In the view of using nanoparticles, the most common challenges facing ahead are (i) on the establishment of the test procedures to ensure safe manufacture and use of nanoparticles in the marketplace is urgently required and achievable and (ii) as nanoparticles can vary with respect to composition, size, shape, surface chemistry, and crystal structure, it is not appropriate to establish general safety regulations for all nanomaterials.

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References

[1] E.M. Darling and K.A. Athanasiou, Bioactive scaffold design for articular cartilage engineering, in Biomedical Technology and Devices Handbook, J. Moore and G. Zouridakis, eds., CRC Press, Boca Raton, 2004.
[2] M.A. Wimmer, S. Grad, T. Kaup, M. Hanni, E. Schneider, S. Gogolewski, and M. Alini, Tribology approach to the engineering band study of articular cartilage, Tissue Eng. 9–10 (2004), pp. 1436–1445.
[3] J.K. Francis Suh, and H.W.T. Mattew, Application of chitosan-based polysaccharide biomaterials in cartilage tissue engineering: A review, Biomaterials 21 (2000), pp. 2589–2598.
[4] S. O’Driscoll, Current concepts review – the healing and regeneration of articular cartilage, J. Bone Joint Surg. Am. 80 (1998), pp. 1795–1812.
[5] S.R. Frenkel, B.C. Toolan, D. Menche, M. Pitman, and J.M. Pachence, Chondrocyte transplantation using a collagen bilayer matrix for cartilage repair, J. Bone Joint Surg. 79B (1997), pp. 831–836.
[6] Y. Dausse, L. Grossin, G. Miralles, S. Pelletier, D. Mainard, P. Hubert, D. Baptiste, P. Gillet, E. Dellacherie, P. Netter, and E. Payan, Cartilage repair using new polysaccharidic biomaterials: Macroscopic, histological and biochemical approaches in a rat model of cartilage defect, Osteoarthr. Cartil. 11 (2003), pp. 16–28.
[7] J.S. Dounchis, W.C. Bae, A.C. Chen, R.L. Sah, R.D. Coutts, and D. Amiel, Cartilage repair with autogenic perichondrium cell and polylactic acid grafts, Clin. Orthop. 377 (2000), pp. 248–264.
[8] K. Mizuno, H. Kido, T. Narita, M. Dohmoto, T. Ogawa, and S. Osawa, Control of degradation rate of porous biodegradable polymers, Paper presented at the 8th Polymer for Advanced Technologies International Symposium, Budapest, Hungary, 2005, September.
[9] Y.S. Nam and T.G. Part, Porous biodegradable polymeric scaffolds prepared by thermally induced phase separation, J. Biomed. Mater. Res. (1999), pp. 8–17.

[10] F.J. O’Brien, B.A. Harley, I.V. Yannas, and Gibson, The effect of pore size on cell adhesion in collagen-GAG scaffolds, Biomaterials 26 (2005), pp. 433–441.

[11] Y.Q. Wan, Y. Wang, Z.M. Liu, X. Qu, B.X. Han, J.Z. Bei, and S.G. Wang, Adhesion and proliferation of OCT-1 osteoblast-like cells on micro- and nano-scale topography structured poly(L-lactide), Biomaterials 26 (2005), pp. 4453–4459.

[12] N. Neves, A. Kouyumdziev, and R.L. Reis, The morphology, mechanical properties and ageing behaviour of porous injection molded starch-based blends for tissue engineering scaffolding, Mater. Sci. Eng. C 25 (2005), pp. 195–200.

[13] Z. Shao and F. Vollrath, Surprising strength of silkworm silk, Nature 418 (2002), p. 741.

[14] H.P. Zhao, X.Q. Feng, S.W. Yu, W.Z. Cui, and F.Z. Zou, Mechanical properties of silkworm cocoons, Polymer 46 (2005), pp. 9192–9201.

[15] J. Perez-rigueiro, C. Viney, J. Llorca, and M. Elices, Silkworm silk as an engineering material, J. Appl. Polym. Sci. 70 (1998), pp. 2439–2447.

[16] E. Atkins, Silk’s secrets, Nature 424 (2003), p. 1010.

[17] R.D.B. Fraser and D.A.D. Parry, The molecular structure of reptilian keratin, Int. J. Biol. Macromol. 19 (1996), pp. 207–211.

[18] S. Annamaria, R. Maria, M. Tullia, S. Silvio, and C. Orio, The microbial degradation of silk: A laboratory investigation, Int. Biodeterior. Biodegradation 42 (1998), pp. 203–211.

[19] M. Nomura, Y. Iwasa, and H. Araya, Moisture absorbing and desorbing polyurethane foam and its production. Japan Patent No. 07-292240A, 1995.

[20] H. Hatakeyama, Biodegradable sericin-containing polyurethane and its production, Japan Patent No. 08-012738A, 1996.

[21] H. Ishikawa, M. Nagura, and Y. Tsuchiya, Fine structure and physical properties of blend film composed of silk sericin and poly(vinyl alcohol), Sen’i Gakkaishi 43 (1987), pp. 283–287.

[22] K. Nakamura and Y. Koga, Sericin-containing polymeric hydrous gel and method for producing the same. Japan Patent No. 2001-106794A, 2001.

[23] S.J. Park, K.Y. Lee, W.S. Ha, and S.Y. Park, Structural changes and their effect on mechanical properties of silk fibroin/chitosan blends, J. Appl. Polym. Sci. 74 (1999), pp. 2571–2575.

[24] H. Kweon, H.C. Ha, I.C. Um, and Y.H. Park, Physical properties of silk fibroin/chitosan blend films, J. Appl. Polym. Sci. 80 (2001), pp. 928–934.

[25] S. Katori and T. Kimura, Injection moulding of silk fiber reinforced biodegradable composites, in High performance structures and composites, C.A. Brebbia and W.P. de Wilde, eds., WIT Press, Boston, 2002, pp. 97–105.

[26] S.M. Lee, D. Cho, W.H. Park, S.G. Lee, S.O. Han, and L.T. Drzal, Novel silk/poly(butylenes succinate) biocomposites: The effect of short fiber content on their mechanical and thermal properties, Compos. Sci. Technol. 65 (2005), pp. 647–657.

[27] H.Y. Cheung, K.T. Lau, and X.M. Tao, A potential material for tissue engineering: Silkworm silk/PLA biocomposite, Composites Part B: Eng. 36 (2008), pp. 1026–1033.

[28] Environment Hong Kong. Annual report. Environmental Protection Department, The Government of the Hong Kong Special Administrative Region, Hong Kong, 2005.

[29] B.S. Harrison and A. Atala, Carbon nanotube applications for tissue engineering, Biomaterials 28 (2007), pp. 344–353.

[30] P. Bordes, E. Pollet, and L. Averous, Nano-biocomposites: Biodegradable polyester/nanoclay systems. Pro. Polym. Sci. 34 (2009), pp. 125–155.

[31] X. Zhang, Y. Li, G. Lv, Y. Zuo, and Y. Mu, Thermal and crystallization studies of nano-hydroxyapatite reinforced polyamide 66 biocomposites, Polymer Degrad. Stabil. 91 (2006), pp. 1202–1207.