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Biodegradable porous structures derived from multiphase polymer blends

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Reinforcing multiphase porous biopolymer composites with clay platelets increases their mechanical strength, making them a promising candidate for future tissue engineering applications.

In view of their use as scaffolds in tissue engineering applications, biodegradable polymers have attracted a great deal of attention in recent years. In addition to being biodegradable, these polymers are biocompatible and have good processability. Most of them, however, do not have sufficient mechanical strength for applications where the scaffold also plays the role of a load-bearing element. A wide range of nano- and microscaled particulates have been implemented to enhance the mechanical and other properties (e.g., thermal, fire, and barrier) of the scaffold.[1–3] Another requirement for the successful use of these materials in tissue engineering is the formation of a continuous porous 3D network, which enables the flow of biological liquids and thereby increases cell proliferation and growth. Polymer composites consequently represent an attractive approach to obtaining porous scaffolds with enhanced properties.

Although numerous methods have been proposed to create porous structures using biodegradable polymers, the majority suffer from limitations related to the resulting pore-size dimensions. The fabrication of porous structures from a co-continuous morphology, however, represents a cost-effective and environmentally friendly approach that may enable the avoidance of these limitations.[1] Co-continuous morphologies are interpenetrating networks of two phases, with both phases continuous in all three spatial dimensions. A porous structure is achieved by the extraction of one of these two phases. If the obtained porous structure is to be used as a scaffold, the primary constituent of the polymer blend must be biodegradable. We hope to provide new insights by producing porous structures from a co-continuous morphology.

To this end, we have developed porous poly(lactic-co-glycolic acid)—PLGA—hybrid scaffolds loaded with organically modified clay minerals (Cloisite 15A, Cl15A). We obtained these porous structures

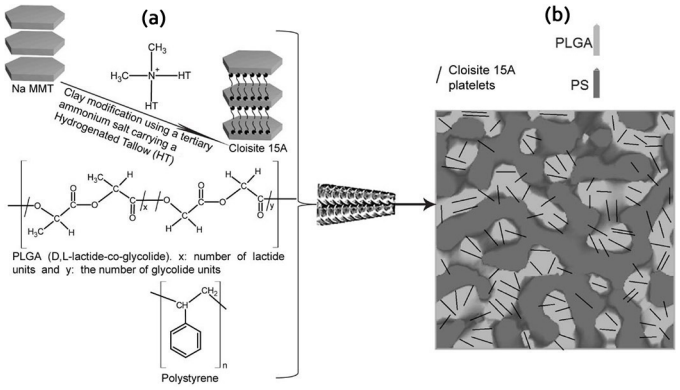

Figure 1. *(a) Chemical structures of the three constituents—Cloisite 15A, Cl15A; poly(lactic-co-glycolic acid), PLGA; and polystyrene, PS—used for the fabrication of (b) co-continuous composite blends via extrusion. Na MMT: Natural montmorillonite, modified to form Cl15A. PLGA (D,L-lactide-co-glycolide): Stereochemical form of PLGA.*

by extracting the polystyrene (PS) phase by dissolution from a ternary composite co-continuous blend of PLGA/PS/Cl15A.[3] An optimal dispersion of Cl15A clay platelets in the biodegradable PLGA phase is highly desirable, due to the increased mechanical resilience and reduced channel blockage afforded in the resulting porous composite. We therefore carefully selected the components of the ternary blend to achieve good dispersion. The chemical structures of the components used in this study and the expected co-continuous composite structure are illustrated in Figure 1. Morphologically, the porous structures consist of a well-formed 3D porous network (see Figure 2).

In addition, we investigated the conformation of the dispersed clay sheets in the final porous materials and the influence of this on the geometrical characteristics of the materials. Specifically, we found that the average pore diameter and the porosity depend on the clay loading and its dispersion (intercalated or exfoliated) inside the PLGA matrix.

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Our results show that the porous structure is refined with the addition of Cl15A.

More specifically, the pore generation seems to occur at the polymer-clay interface. Because the clay is dispersed better in lower clay concentrations (due to exfoliation), smaller pores are created. In the multiphase-polymer-blend fabrication procedure of porous structures, clay minerals play a structural role. Pore generation is realized by the sacrificial extraction of the second polymer. The fillers used generally affect only the geometrical characteristics of the porous structures.[2] In porous samples with a higher clay loading (5 and 10%), a sharp increase of the porosity and average pore diameter is observed: see Figure 2(c) and (d). Moreover, the porous 10% loaded composite exhibits a more refined porous structure. This may be due to the intercalated structure becoming more pronounced and the intercalated clay stacks accumulating at the walls of the porous skeleton. As the clay structure in these porous composites becomes more compact, larger pores are created. This increase could also be ascribed to the greater melt viscosity during processing that occurs as a result of the high loading of clay particles.

Thermogravimetric analysis results show that a high content of clay mineral remains inside the PLGA matrix after the PS dissolution. Additionally, dynamic mechanical thermal analysis results confirm the reinforcing effect of the clay on the storage modulus (E'). The addition of 5% Cl15A leads to an increase in E' of almost 50%. This result could be attributed to the high aspect ratio of the swollen clay particles and to their synergistic relationship with PLGA.

In summary, we have developed environmentally friendly porous composites from a multiphase polymer blend. The pores in our composites are wider than the typical diameter of biological cells used in tissue engineering, making the material suitable for this application. Due to the high clay loading their walls are mechanically reinforced, and because of the pores' size and connectivity these PLGA porous structures represent good candidates for mechanically strong scaffolds. In future work, we intend to employ many different nanofillers (e.g., nanotubes and graphene) for the reinforcement of biodegradable porous structures. We also aim to test these porous materials as scaffolds in tissue engineering.

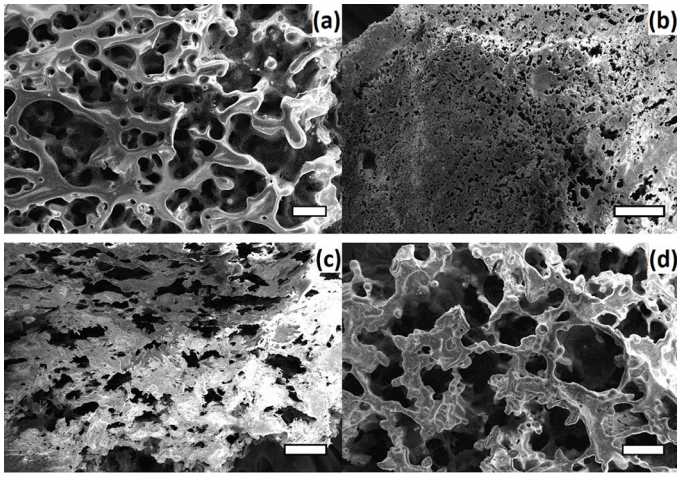

Figure 2. *Porous structure of (a) PLGA+1% Cl15A, (b) PLGA+3% Cl15A, (c) PLGA+5% Cl15A, (d) PLGA+10% Cl15A. Magnification bar is 300μm.*

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