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Novel bioinspired approach to improve the properties of soy protein isolate films

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A casting method is used to incorporate poly(dopamine)-modified montmorillonite reinforcements and ferric iron coordination crosslinking centers into the matrix of nanocomposites.

As part of the search for environmentally friendly alternatives to conventional petrochemical-based polymeric materials, biodegradable materials have received a large amount of attention in recent years.[1–3] Soy protein isolate (SPI), the most abundant plant-derived protein, is one example that is used in a variety of applications (e.g., adhesives, packaging, drug delivery, and tissue regeneration).[4,5] The particularly high protein content of SPI means that it has a strong capacity to form films. Unmodified SPI-based composite films, however, suffer from several problems. These issues—including poor mechanical strength, water resistance, and thermal stability—thus limit the practical uses of these materials.[4,6]

To improve the mechanical properties and reduce the water sensitivity of SPI-based films, a diverse array of modification methods have previously been investigated. To date, the most popular approaches have included physicochemical methods, enzyme treatments, and chemical crosslinking (the latter of which appears to be the most successful).[7–9] Furthermore, it has been shown that the addition of aldehydes and epoxy components can enhance the performance of SPI-based films.[10,11] There are some concerns, however, over the safety and toxicity of such components (especially when used in food packaging).[12]

In this work,[13] we have developed a novel methodology for the preparation of SPI-based nanocomposites. In our bioinspired strategy we use montmorillonite coated with poly(dopamine), PDA, as reinforcements, as well as ferric iron (Fe^{III}) particles as coordination crosslinking centers. In this way, we are able to realize strong interfacial interactions between the SPI matrix and the MMT sheets (i.e., because of the versatility of the reactive groups).

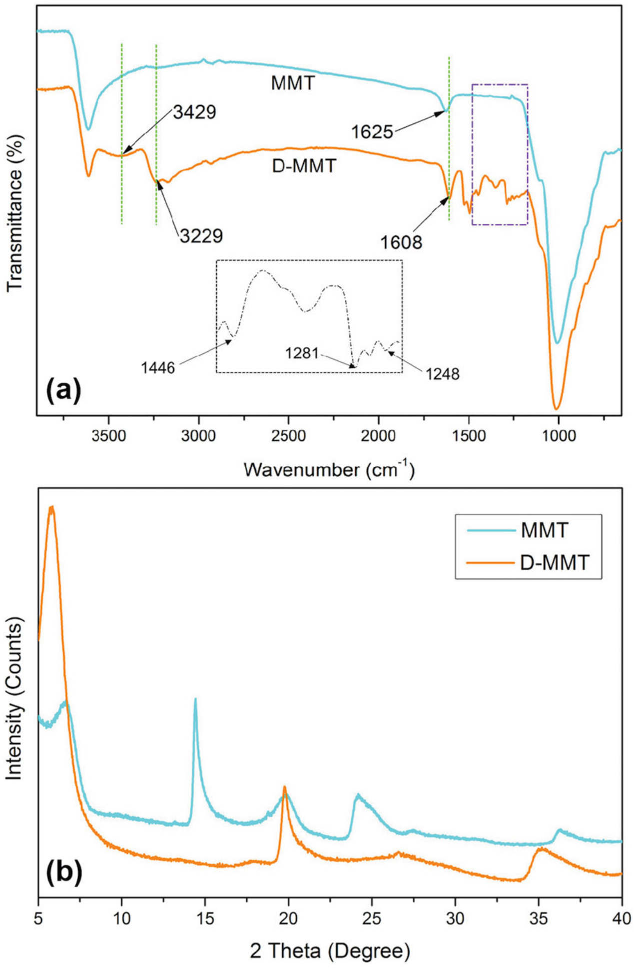

Figure 1. *(a) Fourier-transform IR (attenuated total reflectance) and (b) x-ray diffraction spectra of unmodified montmorillonite (MMT) and poly(dopamine)-coated MMT (D-MMT) samples. The wavenumbers of specific spectral peaks are shown in (a). 2 theta: Measured angle of diffraction.*

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Table 1. Mean measured thickness and mechanical properties of the soy protein isolate (SPI) and SPI nanocomposite film samples. The nanocomposites contained an SPI matrix and either MMT, D-MMT, or MMT and ferric iron (Fe^{III}*). Standard deviation values are given in parentheses.*

Specimen	Thickness (mm)	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)
SPI	0.226 (0.012)	3.86 (0.07)	124.4 (0.4)	141.1 (10.1)
SPI/MMT	0.276 (0.028)	6.04 (0.18)	15.8 (0.2)	308.8 (9.6)
SPI/D-MMT	0.260 (0.027)	6.51 (0.16)	15.4 (0.3)	408.8 (21.0)
SPI/D-MMT-Fe^{III}	0.275 (0.011)	6.77 (0.06)	31.9 (0.6)	331.8 (16.1)

Table 2. Mean measured values for the moisture content, solubility, water uptake, and water contact angle of the SPI-based nanocomposite films. Standard deviation values are given in parentheses.

Specimen	Moisture content (%)	Water uptake (%)	Total soluble matter (%)	Water contact angle (°)
SPI	30.64 (1.06)	21.29 (3.88)	31.66 (2.87)	72.2 (3.0)
SPI/MMT	28.16 (0.97)	30.92 (1.60)	39.98 (5.32)	47.5 (5.0)
SPI/D-MMT	30.24 (1.15)	18.91 (3.78)	27.76 (3.32)	68.6 (4.0)
SPI/D-MMT-Fe^{III}	28.68 (0.63)	17.31 (2.55)	27.34 (4.42)	48.9 (7.1)

To produce the composites for our study, we first dip-coated MMT with self-polymerized poly(dopamine). To characterize the microstructure and chemical composition of the PDA-modified MMT (D-MMT), we used both Fourier-transform IR spectroscopy and x-ray diffraction. The results (see Figure 1) demonstrate that the PDA layer was successfully coated on the surface of the MMT.[14–16] We then used a casting method to incorporate the D-MMT into the SPI matrix (in the presence of the Fe^{III}) and to fabricate the samples. In total we produced and studied four different SPI samples. Our control sample—SPI—contained 5g of SPI, 2.5g of glycerol, and 95g of deionized water. In addition to the SPI matrix, our composite samples contained either 0.5g of MMT (SPI/MMT), 0.25g of D-MMT (SPI/D-MMT), or 0.25g of MMT and 0.3g of Fe^{III} (SPI/D-MMT-Fe^{III}).

The mechanical properties of our resultant SPI-based films are given in Table 1. We find that, compared with the control SPI sample, the tensile strength and the tensile modulus of the SPI/MMT film increased from 3.86 to 6.77MPa and from 141.1 to 331.8MPa, respectively. These results are in good agreement with our previously reported work.[17] Moreover, the tensile strength and modulus of the SPI/D-MMT were 7.8 and 32.4% higher than the control sample, respectively. This improvement in mechanical properties arises because D-MMT is compatible with the matrix and can thus act as a load-bearing bridge between the MMT and SPI matrix. Our results also indicate that the integration of Fe^{III} into the SPI matrix caused an improvement to both the tensile strength and elongation at break of the sample (compared with the SPI/MMT film).

The water resistance characteristics of our modified and unmodified SPI films are presented in Table 2. These results suggest that, by incorporating D-MMT and Fe^{III} into the system, the water uptake and total soluble matter of the films can be reduced by 44.0 and 13.7%, respectively. We ascribe this enhancement of water resistance to improved interfacial interactions that cause the permeation of water molecules to be obstructed. In addition, we find that the surface contact angle (a measure of hydrophilicity) of the SPI/D-MMT film was 75.4% higher (68.6°) than the unmodified SPI/MMT film (47.5°).

In summary, we have investigated the mechanical properties and water resistance characteristics of SPI-based nanocomposite samples that contain modified and unmodified MMT, as well as Fe^{III}, fillers. Our results confirm that the inclusion of PDA-coated MMT molecules enhances the interfacial interactions between MMT nanosheets and the SPI matrix. This, in turn, results in a significant improvement to the tensile properties, water resistance, and thermal stability of the resultant SPI-based films. In our ongoing work, we are continuing to investigate the assembly, design, and physical properties of natural biological materials (e.g., mussel byssus, spider silk, and nacre) for use in food preservation and packaging applications.

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