Nanofillers for Property Enhancement in Bioplastics

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Bioplastics reinforced with filler enhance the mechanical properties of starch but reduce its hydrophilicity. In recent years, utilization of nano-sized fillers has bloomed in the fabrication of bioplastic due to their merits, such as low density, excellent mechanical properties, low abrasive nature and reactive surface for ease of modification. Numerous studies had reported that nano-sized fillers have a larger surface area than the conventional micro-sized fillers, thus enhancing the properties due to better interfacial interactions with the polymer matrix. Besides enhancing the mechanical and barrier properties, fillers are also capable of imparting specific functional properties to the bioplastics, e.g., electric conductivity or an antimicrobial character. Another added advantage of filler with nanoscale is in retaining the inherent transparency of the film, especially for the neat matrix.

starch-based bioplastic nanofiller bioplastic fabrication plasticizer

1. Layered Silicates

Nanoclays are also known as layered silicates [1]. They are readily available, environmentally friendly and of low cost. As a filler with high stiffness, nanoclay improves the mechanical properties of the soft polymer matrix by impeding the free movement of polymer chains. Nanoclay also behaves like a load-bearing constituent if the interfacial adhesion between the filler and the chains is sufficiently strong [2]. This was evidenced by the findings reported by Wahyuningtiyas and Suryanto [3] in which the tensile strength of bioplastic increased from 5.2 MPa to 6.3 MPa in the presence of 5 wt.% nanoclay. Apart from that, the research team discovered that nanoclay could also increase the microbial decomposition rate of bioplastic. For example, only half of the time is required by bioplastic reinforced with nanoclay to fully decompose, compared to a 12-day decomposition period required by the non-reinforced bioplastic. The higher decomposition rate was attributed to the aluminium ions in nanoclay, which acted as Lewis acids to catalyse the hydrolysis process [3]. Li et al. [4] also reported the improvement of the tensile strength of bioplastic from 48.96 MPa to 64.75 MPa after the addition of 5 wt.% of MMT. One point to note is that susceptibility to agglomeration is the unavoidable problem associated with the utilization of nanofiller in polymers. Therefore, ultrasound treatment was employed in the reported studies to disperse the nanofillers in the starch matrix. Homogeneous dispersion of nanofiller in the starch matrix could ensure even transfer of stress between the matrix and the nanofiller, thus enhancing the mechanical properties of polymer nanocomposites [4].

In order to utilize film for food packaging, oxygen and moisture transport must be minimized to extend food shelf-life [5]. In addition to improved mechanical properties, it can be observed from **Table 1** that nanoclay showed barrier property (oxygen and moisture) improvement. Incorporation of nanoclay into the matrix would increase the path

length and enhance the barrier properties of bioplastic to gases such as oxygen, carbon dioxide, organic vapours and moisture. The uniform dispersion of rigid impermeable nanoclay in the matrix might have hindered the diffusion of permeating molecules by forcing them to traverse and diffuse through a more tortuous path and thus reducing their mass transfer efficiency [1][2]. The antimicrobial effect of nanoclay against bacteria could be related to the release of ammonium salts, which affects bacteria-sensitive targets [6].

In the study by Liu et al. [7], retrogradation behaviour of TPS film was investigated with different surface properties of nano-SiO_2. TPS film with hydrophilic nano-SiO_2 had a lower retrogradation rate than that with hydrophobic nano-SiO_2. During gelatinization of starch, the starch granules and crystalline structure were destroyed along with the breakdown of hydrogen bonds and the double helix structure. During short-term retrogradation, the amylose molecules started to crystallize and formed a crystal through a single helix structure. With longer retrogradation time, the amylopectin molecules gradually formed a crystal through a double helix structure. With the addition of nano-SiO_2, the starch structure would be affected through interaction between O-H groups of starch and nano-SiO_2. The addition of hydrophilic nano-SiO_2 produced a V-type starch with a single helix structure. Formation of hydrogen bonds between O-H groups of hydrophilic nano-SiO_2 and starch subsequently destructed the hydrogen bonds between the double helix structure of starch. In contrast, the double helix structure of starch remained with the addition of hydrophobic nano-SiO_2, which was conducive to the regular arrangement of the double helix structure for crystallization. This indicated that the retrogradation degree of TPS was larger with hydrophobic nano-SiO_2. Furthermore, the mobility of starch molecules was affected by the different surface properties of nano-SiO_2. Hydrophilic nano-SiO_2 has many O-H groups on its surface which could form hydrogen bonds with O-H groups of starch and reduce the mobility of starch molecules. On other hand, hydrophobic nano-SiO_2 could not react with starch molecules as there is no O-H group on its surface. Therefore, TPS with hydrophobic nano-SiO_2 had a higher retrogradation rate as a result of the faster movement of starch molecules during retrogradation.

2. Organic Nanofillers

Cellulose is one of the examples of organic nanofillers. There are three types of cellulose in nanoscale: cellulose nanocrystals (CNC), cellulose nanofiber (CNF) and bacterial nanocellulose [8]. CNC are needle-shaped cellulose particles with a typical diameter of 2–20 nm and a length varying between 100 nm to several micrometres. CNC particles are comprised of 100% cellulose and are highly crystallized, with 54% to 88% crystalline zones. The degree of crystallinity, dimensional diversity and morphology depend on the source of the cellulosic materials, the preparation conditions and the experimental techniques used [9]. The amorphous portion of the cellulose can be easily hydrolysed in strong acidic conditions to generate the individual crystallites. The particle size and properties of the isolated CNCs may vary depending on the cellulosic materials and reaction conditions during hydrolysis [10].

Similar to other fillers, CNCs can increase the stiffness of bioplastic based on their nanoscale dimension, low density, high surface area (≥100 m^2/g), high aspect ratio of ≥100, high crystallinity and high inherent rigidity [11][12]. Xu et al. [13] revealed that CNC-reinforced starch film attained higher tensile strength than that without CNC reinforcement. In this case, a 10 vol.% CNC loading successfully improved the tensile strength of starch film by 129% as well as the barrier property of the starch film, with a 17% reduction in WVP. Another report on bioplastic

fabrication by Chiulan et al. [14] revealed that 2 wt.% of bacterial cellulose derived from *G. xylinus* that was used as a reinforcement filler also had increased tensile strength and Young's modulus up to 2 times and 2.1 times, respectively, as compared to that from non-reinforced bioplastic. Similar findings were also obtained in the study conducted by Noshirvani et al. [12]. Indeed, the mechanical properties of TPS-polyvinyl alcohol (PVA) composite film were improved with the addition of CNCs. Even at low loading of 3 wt.%, the uniform dispersion of CNC in the polymer matrix forced the gas molecules to traverse through a more tortuous path to pass through the bioplastic film and thus retarded the gas transmission and increased the mass transfer resistance of CNC-reinforced TPS-PVA composite film to water vapour. However, excessive CNC would cause particle agglomeration and reduce the effective content of CNC and thus facilitate the water vapour permeation.

Chitosan is another example of an organic nanofiller. It can be obtained from the deacetylation of chitin, which can be found in shell waste and skeletal materials of insects and crustaceans [15][16]. It is appealing to employ it as a filler as it serves the purpose of reusing the waste and being a biodegradable material. In addition, it is well-known for its antimicrobial properties. TPS/chitosan film was found to reduce the microbial growth of *S. aureus* and *E. coli.* The reduction of microbial activity was more pronounced at a higher chitosan concentration [15]. However, chitosan is insoluble in water, strong base solutions and some organic solvents such as alcohol and acetone. Therefore, an aqueous acidic solution such as hydrochloric acid (HCl) or acetic acid is required to dissolve the chitosan [17].

3. Inorganic Nanofillers

Metal or metal oxides are examples of inorganic nanofillers. Metallic nanoparticles such as Ag-NP are known to have antimicrobial and inhibitory activity against a variety of microorganisms such as bacteria, fungi or viruses [5][18][19][20]. From **Table 1**, Ag-NP was reported by Abreu et al. [5] to have a microbial effect against *S. aureus*, *E. coli* and *C. albicans.* Ag-NP would release Ag^+ ions and penetrate into the bacteria, damaging the cell or disrupting the metabolic processes [21]. With the incorporation of hybrid nanofiller of Ag-NP/nanoclay into TPS, both the WVP and OP values were lower than the TPS with Ag-NP only. It was evidenced from the SEM images that incorporation of Ag-NP into nanoclay improved the clay dispersion in the starch matrix, which resulted in higher homogeneity of the film and thus better WVP and OP. Similar to Ag-NP, ZnO nanofillers also exhibit antimicrobial activity. In addition to their ability to be synthesized into different shapes [22], they are suitable to be incorporated into TPS films for food packaging application as they are considered Generally Regarded as Safe (GRAS) by the Food and Drug Administration (FDA) to be used in plastics and food contact materials [23]. From the study by Estevez-Areco et al. [23], TPS/ZnO could not inhibit the bacterial growth completely but it could delay the replication of bacterial growth, which could serve as a bacteriostatic agent.

Table 1. List of nanofillers incorporated in starch-based films with the reported findings or properties enhancement.

Nanofiller	Proposed Application	Findings/Enhancement as Compared to the Control Film	Ref.
Layered silicates			

Nanofiller	Proposed Application	Findings/Enhancement as Compared to the Control Film	Ref.
Nanoclay	Food packaging film	Reduction of water vapour permeability (WVP) by 14% Reduction of OP by 15% Presence of microbial growth against *C. albicans* Reduction of microbial growth against *S. aureus* and *E. coli* (bacteriostatic effect)	[24]
Nanoclay	Packaging material	Improvement of tensile strength from 5.2 to 6.3 MPa Increase in moisture absorption from 44.44% to 69.58% Complete degradation of thermoplastic starch (TPS)/nanoclay film on the 6th day	[10]
Nanosilica (nano-SiO_2)	Packaging material	TPS film with hydrophilic nano-SiO_2 had lower retrogradation rate than that with hydrophobic nano-SiO_2.	[25]
MMT	Packaging material	Improvement of tensile strength by 32% with MMT loading of 5 wt.% Improvement of Young's modulus from 2338 to 3237 MPa Improvement of surface hydrophobicity of film (from 51.97° to 67.77°) Reduction of moisture uptake by 11%	[26]
Organic nanofillers			
Cellulose nanofibers (CNF)	Packaging material	Improvement of tensile strength by 33% with CNF loading of 3 wt.% Improvement of Young's modulus from 2338 to 3173 MPa Improvement of surface hydrophobicity of film (from 51.97° to 53.89°) Reduction of moisture uptake by 13%	[26]
Cellulose nanocrystals (CNC)	Packaging film	Reduction of water absorption and water solubility by 21% and 50% with CNC loading of 20 wt.%, respectively Reduction of WVP by 8% with CNC loading of 15 wt.%.; WVP value increased with 20 wt.% CNC loading Optimum tensile strength of 4.59 MPa at 10 wt.% CNC loading; reduction in tensile strength with addition of 15 and 20 wt.% CNC loadings	[27]

Nanofiller	Proposed Application	Findings/Enhancement as Compared to the Control Film	Ref.
Cellulose nanocrystals (CNC)	Food packaging film	Improvement of tensile strength by 56% with CNC loading of 10 vol.% Reduction of WVP by 17%	[28]
Chitosan	Packaging film	Improvement of tensile strength by 17% with chitosan loading of 10 wt.% Improvement of Young's modulus by 13% Reduction of WVP by 35% TPS/chitosan film had higher opacity than TPS film Reduction of microbial growth against *S. aureus* and *Escherichia coli*	[29]
Chitosan	Packaging film	Optimum tensile strength of ~6.79 MPa at TPS/chitosan ratio of 4:6 Higher biodegradation rate with increase of starch content	[1]
Inorganic nanofillers			
Zinc oxide (ZnO) nanorods	Food packaging film	Improvement of tensile strength (47 to 90 MPa) and Young's modulus (2.1 to 3.2 MPa) Slight reduction of elongation at break from 50% to 47%. Reduction of WVP by 42%. Improvement of antimicrobial activity against *E. coli* from 1.5×10^7 to 9×10^5 CFU/mL	[30]
Silver nanoparticles (Ag-NP)	Active packaging film	Improvement of tensile strength (2.8 to 9.0 MPa) and Young's modulus (50 to 530 MPa) Reduction of EB from 63% to 20% Improvement of antibacterial activity against *E. coli* from 5.0×10^7 to 1.5×10^6 CFU/mL Film with AgNP disintegrated slower than the control film in soil (after 2 weeks vs. after 1 week)	[31]
Ag-NP	Food packaging film	Reduction of WVP by 16% Reduction of OP by 11% No microorganism growth against *S. aureus*, *E. coli* and *C. albicans* (microbiostatic effect)	[24]
Ag-NP/nanoclay	Food packaging film	Reduction of WVP by 33% Reduction of OP by 35%	[24]

Nanofiller	Proposed Application	Findings/Enhancement as Compared to the Control Film	Ref.
		No microorganism growth against *S. aureus*, *E. coli* and *C. albicans* (microbiostatic effect)	
Carbonaceous fillers			
Multi-walled carbon nanotubes (MWCNT)	For packaging and electroconductive applications	Improvement of tensile strength by 327% and Young's modulus by 2484% at MWCNT loading of 0.5 wt.% Highest electrical conductivity of 56.3 S/m with 5 wt.% loading as compared to control film (1.08×10^{-3} S/m) Shifting of thermal degradation temperature to lower temperature with increasing MWCNT loading	[32]
Multi-walled carbon nanotubes functionalized with cetyltrimethylammonium bromide (MWCNT-CTAB)	Production of conductive film	Improvement of 2,2′-azino-bis-(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) radical scavenging activity (from ~2.5% to 30.2% after 1.5 h) Improvement of electrical conductivity (from 2.03×10^{-6} S/m to 14.75 S/m)	[33]
Multi-walled carbon nanotubes functionalized with ascorbic acid (MWCNT-AA)	As adsorbent for removal of methylene blue (MB) dye from aqueous solution	Enhancement of thermal stability Suitable to be used as adsorbent for removal of MB dye but not reusable	[34]
Multi-walled carbon nanotubes functionalized with ascorbic acid (MWCNT-AA)	As adsorbent for removal of methylene range (MO) dye from aqueous solution	Enhancement of thermal stability Suitable to be used as adsorbent for removal of MO dye but not reusable	[35]
Multi-walled carbon nanotubes functionalized with fructose (MWCNT-Fr)	As adsorbent for dye removal from aqueous solution	Film was too brittle for tensile test	[36]
Multi-walled carbon nanotubes functionalized with Valine (MWCNT-Valine)	As adsorbent for removal of copper ions from aqueous solution	Enhancement of thermal stability Suitable to be used as adsorbent for removal of copper ions but not reusable	[37]
Graphene oxide (GO) [4]	Food packaging film [39]	Improvement of tensile strength (from 57.97 to 76.09 MPa) and Young's modulus (from 20.59 to 35.91 MPa). Slight reduction of EB from 6.60% to 3.13%. Enhancement of thermal stability Improvement of surface hydrophobicity of film (from 71.33° to 112.04°)	[38]

in starch-magnetic, orm either amount of s and also dispersion of multi-walled CNTs in the starch matrix. Furthermore, the findings also indicated that the better interfacial adhesion obtained could avoid the formation of holes and sustain a higher degree of deformation [40].

Nanofiller	Proposed Application	Findings/Enhancement as Compared to the Control Film	Ref.
		Improvement of water vapour permeability Starch/gelatin/GO film had lower biodegradability than the control film (~30% vs. 50%) after 6 weeks of soil burial degradation.	[42]

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Nonetheless, the highest antioxidant activity and electrical conductivity were attained by the TPS with MWCNT-CTAB. SC interacted more tightly with the MWCNT surface than CTAB and SDS due to its rigid structure, so that the MWCNT surface was not so exposed. This subsequently reduced the availability of MWCNT to interact with the radical, which resulted in the lowest antioxidant activity [42]. In view of the electrical conductivity, TPS with MWCNT-SDS presented the lowest value, which might be due to agglomeration of nanotubes and weaker dispersibility, as observed in the SEM images. Higher adhesion of SC to the MWCNT surface gave rise to a blocking effect of charge transport in MWCNT network and diminished the contact points between nanotubes [43]. Therefore, the electrical conductivity value was lower. In addition, TPS with functionalized MWCNT could serve as an adsorbent for dye removal. From **Table 1**, TPS with MWCNT-AA, MWCNT-Fr and MWCNT-Valine was capable of removing dye. They are simple to prepare, cost little and are environmentally friendly. However, non-reusability is their chief drawback, as the dye adsorbed on the adsorbent surface cannot be separated completely from the absorbent for next use after dye removal.

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