Mechanical Properties of Thermoplastic Starch Biocomposite Films with Hybrid Fillers

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Abstract. Thermoplastic starch (TPS) was studied extensively to replace conventional plastic in packaging application. In this study, granule corn starch was first plasticized with water and glycerol to form TPS films and two different fillers were incorporated with TPS to form hybrid biocomposite films (TPSB). Two different fillers: Microcrystalline cellulose (MC) and Nano bentonite (NB) fixed at 1:4 ratios in various loadings were incorporated in TPS to study effect of hybrid fillers on the mechanical properties of TPSB films. The effect of different loading of MC/NB on TPSB films was investigated through structural, morphological and mechanical testing. Fourier Transform Infrared Spectroscopy (FTIR) shows TPS matrix and hybrid fillers are highly compatible due to hydroxyl bonding and verified through the shifting of spectra band. Scanning Electron Microscope (SEM) showed even distribution of fillers in the matrix of TPS. The TPSB films exhibited significant improvement 40% in elongation at break compared to pure TPS films. In this study, 5wt% is best loading of the hybrid fillers to incorporated in TPSB films as it achieved the highest value of tensile strength (8.52MPa), Young’s Modulus (42.0 MPa) and elongation at break (116.3%). Generally, previous studies showed flexibility of TPS composite films reduced with incorporating filler; however in this study, the flexibility TPSB show significant improvement compared to previous studies and exhibit promising potential in dry food packaging application.

1 Introduction

It was not a secret where plastic pollution is one of the biggest threats to all the world. With the efforts and collaboration of several environmental organizations around the world, the awareness of the public regarding plastic pollution on the earth seemed to increase significantly over the past few decades [1]. Social media also played a huge part in the publicity to driven up the awareness and consciousness of the public toward plastic pollution. The increased awareness has successfully triggered a shift in public behavior to go against the usage of single used plastic such as plastic bags, drinking straws and plastic cutlery, etc. [2]. However, this initiative was seemed to only slightly alleviate the plastic pollution by slowing down the rate of plastic waste accumulating in landfills. Even though many policies and programs were implemented by the government or local authorities, none of the approaches was deemed as the ‘perfect solution’ to make a dent in the growing plastic waste in the landfill.

Bio-polymer starch was seemed as the next ideal biopolymer to replace conventional plastic as it is low cost, biodegradable and abundant in nature[3]. One of the most interesting properties of starch is the rheology of granule starch can be transformed into thermoplastic behavior by adding a plasticizer and it can be processed by a similar processing technique as conventional plastic. Starch is mainly comprised of two different structures: long straight chain amylose and highly branched structure amylopectin. During the plasticization process, the original structure of granule starch was disturbed and destroyed, and synchronously reformed with a plasticizer such as glycerol, water, polyol etc. to form thermoplastic starch (TPS) under shearing and heating conditions [4].

However, compared to conventional polymer, TPS possessed three main disadvantages such as low mechanical strength, high water sensitivity and brittle which impeded the TPS to be used in packaging application. Therefore, the mechanical strength of TPS must be enhanced in several such as altering the chemical structure of TPS or adding reinforcement fillers or additive components to achieve the required mechanical strength in packaging applications [5]. Natural organic filler such as microcrystalline cellulose and inorganic filler, bentonite, often to be used as a single filler to improve the physical and mechanical properties of the films. Othman et al. studied the effect of different loading amounts of microcrystalline cellulose (MCC) on the mechanical properties of TPS. They found out the 3wt% of MCC is
the optimum percentage to produce the highest performance of the TPS films. However, the elongation at break of the films decreases by almost 10-15% after incorporating the filler [6]. Meanwhile, Mansour et al. studied the effect of clay on the properties of TPS films. The elongation at break of films was compromised 20-25% after adding the nanoclay into TPS [7]. Both studies concluded the same outcome where adding filler into will reduce the flexibility of the films. Deceasing the flexibility of films is not a favored characteristic in films packaging application.

Therefore, in this study, TPSB was enhanced by combining the organic filler and inorganic filler (microcrystalline cellulose and bentonite) to improve the tensile properties of the films. The combination of both fillers not only improve the TPS films’ tensile strength, but also enhanced the films’ flexibility. Both fillers have a great interaction with TPS chains due to the highly compatible hydroxyl group chemical structure. The interaction of both fillers with TPS chain alter the dynamic chain interaction and resulted in improved TPS films’ flexibility. The effect of different loading of hybrid filler (1-6wt%) was studied and evaluated in this study.

2 Experimental

2.1 Material

Corn starch (73% amylopectin, 27% amylose), microcrystalline cellulose, nano bentonite clay, glycerol, distilled water, sodium bicarbonate, and formulation of TPSB films is showed at Table 1.

| Sample name       | TPSB percentage (wt%) | MCNB in 1:4 ratio (wt%) |
|-------------------|-----------------------|-------------------------|
| TPS               | 100                   | 0                       |
| TPS 1MCNB         | 99                    | 1                       |
| TPS 2MCNB         | 98                    | 2                       |
| TPS 3MCNB         | 97                    | 3                       |
| TPS 4MCNB         | 96                    | 4                       |
| TPS 5MCNB         | 95                    | 5                       |
| TPS 6MCNB         | 94                    | 6                       |

2.2 Sample Preparation of TPSB films

The corn starch was plasticized with distilled water and glycerol in the ratio 1:20:0.4. The mixture was stirred for 20 minutes at temperature 75-85 °C by using magnetic stirrer until the gel form TPS obtained. The hybrid filler suspension was treated with ultrasonication and added into the TPS solution. The mixture was continuously stirred for another 15 minutes. After that, 0.5 grams of sodium bicarbonate was added into the TPS mixture under stirring condition. Then, the mixture was poured into round shape Teflon-coated pan and put into the oven for 24 hours under 45 °C. The TPSB films was removed from the pan after drying and the testing sample was cut out according to the dimension of ASTM. The process for making following TPSB film samples were repeated for the other formulation.

2.3 Testing and characterization

Tensile test according to ASTM D638 Type V was conducted to analyze the tensile properties of TPSB films. The detail of the testing is listed at below:

| Test Speed | 5mm/min |
|------------|---------|
| Room Temperature | 23 °C |
| Thickness of the films | 0.2-0.25 mm |
| Humidity | 53% |

SEM and FTIR was conducted to analyze the surface fracture morphology and the functional group interaction within the TPS matrix.

3 Result and discussion

3.1 Tensile Strength

Table 2 summarizes the tensile properties of TPS/MCNB films with different loading of hybrid fillers. The mechanical properties of the films were analyzed by tensile test. Fig. 1. (a) depicted the tensile strength of TPS/MCNB films. The pure TPS films has the lowest tensile strength, 3.44 MPa meanwhile TPS5MCNB films exhibited the highest tensile
strength, 8.52 MPa. The tensile strength of the TPS/MCNB films increased significantly by adding of the MC and NB. This trend of result was like most others TPS biocomposite films studies [8-10]. TPS5MCNB showed 60% improvement in tensile strength compared to pure TPS. This improvement was due to good compatibility between TPS and hybrid filler as showed by FTIR result. High compatibility trigger the efficient load transfer from matrix to filler and resulted in higher tensile strength [11]. However, the tensile strength of TPSB drop significantly when the loading of filler reaching 6wt%. This may be due to agglomeration of filler in matrix and result in poor stress-transfer in TPSB.

3.2 Young's Modulus

The Young’s Modulus of TPSB films increased with adding hybrid filler. The addition of 5% MC/NB increase the Young’s Modulus from 11.7 MPa to 42.0 MPa compared to pure TPS films. This indicated hybrid fillers have strong interfacial bonding with TPS matrix and disperse evenly in the TPSB as seen in SEM image. However, unexpected drop of Young Modulus when 6wt% of hybrid fillers was incorporated. This may be due to agglomeration of fillers which result in inferior dispersion of fillers in TPS matrix and causing uneven stress transfer in TPSB matrix [11].

3.3 Elongation at break

The most notable result in this study is the significant improvement of the TPSB films’ elongation at break. All the hybrid fillers TPS/MCNB films showed improvement in elongation at break, and the TPS5MCNB films achieved the highest elongation at break (116.3%) among all the films. This result indicated that hybrid fillers not only can produce a high mechanical strength film, it also can enhance the films’ flexibility. The enhancement in the elongation at break of the TPSB films may be due to the high effectiveness of hybrid filler to retain the plasticizer within the matrix of TPS matrix and causing lubricant effect during the straining of the films[12]. Meanwhile the different shapes and structure of MC and NB may react differently in term of enforcement direction or confirmation within the TPS matrix which can create more free volume for the mobility of the TPS chains. However, the flexibility of the films was reduced after the optimum percentage (5wt%). This may due to the agglomeration of fillers which causing premature failure to happen in the matrix of TPSB films and reduce the strength [13].

Table 3. Tensile Strength, Young’s Modulus and Elongation at break of TPS/MCNB biocomposite film.

| Sample          | Tensile strength (MPa) | Young’s Modulus (MPa) | Elongation at break (%) |
|-----------------|------------------------|-----------------------|------------------------|
| Pure TPS        | 3.44 ± 0.24            | 11.7 ± 1.93           | 76.1 ± 4.5             |
| TPS1MCNB        | 3.00 ± 0.34            | 20.6 ± 2.4            | 80.2 ± 3.2             |
| TPS2MCNB        | 4.62 ± 0.14            | 26.9 ± 1.2            | 83.2 ± 5.5             |
| TPS3MCNB        | 5.74 ± 0.35            | 30.8 ± 2.3            | 100.32 ± 6.2           |
| TPS4MCNB        | 6.38 ± 0.2             | 38.0 ± 3.4            | 112.3 ± 3.4            |
| TPS5MCNB        | 8.52 ± 0.32            | 42.0 ± 2.7            | 116.3 ± 5.3            |
| TPS6MCNB        | 4.38 ± 0.43            | 28.3 ± 1.89           | 83.2 ± 4.6             |
3.4 FTIR Analysis

FTIR spectroscopy was performed to analyze the functional group interaction between the components in the TPSB films. The FTIR spectra of all the films showed an absorption band in the wavelength around 3200-3300 cm\(^{-1}\), corresponding to the O-H bond stretching. The presence of this broad band showing the existence of hydrogen bonding interaction within the films. Besides that, for all the films also exists a peak around 1656-1640 cm\(^{-1}\) which associated the angular O-H bending of water molecules bound in the TPSB films [7]. By comparing the spectra of neat TPS and TPS/MCNB films, notice there was a shift of wavenumber and intensity of peak at the region 3100-3500 cm\(^{-1}\) after adding the hybrid filler. This suggesting that there was a physical bonding form between MC and NB with the TPS chain through the strong hydrogen bonding.

3.5 Surface fracture of TPS/MCNB

The morphology of fracture surface of TPS3MCNB and TPS6MCNB were studied and compared by SEM. The TPS3MCNB show a slightly rough surface, homogenous and crackless compact surface which indicated excellent distribution of hybrid filler in matrix of TPS [14]. However, as the filler loading increase to 6wt\%, the fillers tend to agglomerate and appear domain in white color spot on the fracture surface (circle in red). The agglomeration of fillers in
the matrix of TPS may contribute to the decreasing tensile properties of TPS6MCNB films [15]. Both TPSB films fractured surface appears slightly rough texture which indicated the hybrid filler TPSB films experiences some deformation before failure, and this may lead to increase of elongation at break.

**Fig 3:** SEM image (x500 magnification) for (a) TPS3MCNB, (b)TPS6MCNB

**4 Conclusion**

The effect of different MC/NB filler loading on the tensile properties of TPSB films was studied and investigated. The combination of MC and NB showed that hybrid filler can significantly enhanced the tensile strength, Young’s Modulus and achieved high elongation at break. The optimum percentage for the hybrid filler is 5wt%. High loading of hybrid fillers, 6wt% can lead to agglomeration of filler and resulted in decreasing tensile properties. Besides, FTIR also showed that both fillers have high compatibility and strong interaction with TPSB matrix by forming hydrogen bonding.

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