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Lecture title: Effect of microcrystalline cellulose Reinforcement on Mechanical and Water Barrier Properties of Sugar Palm Starch Biocomposite Films

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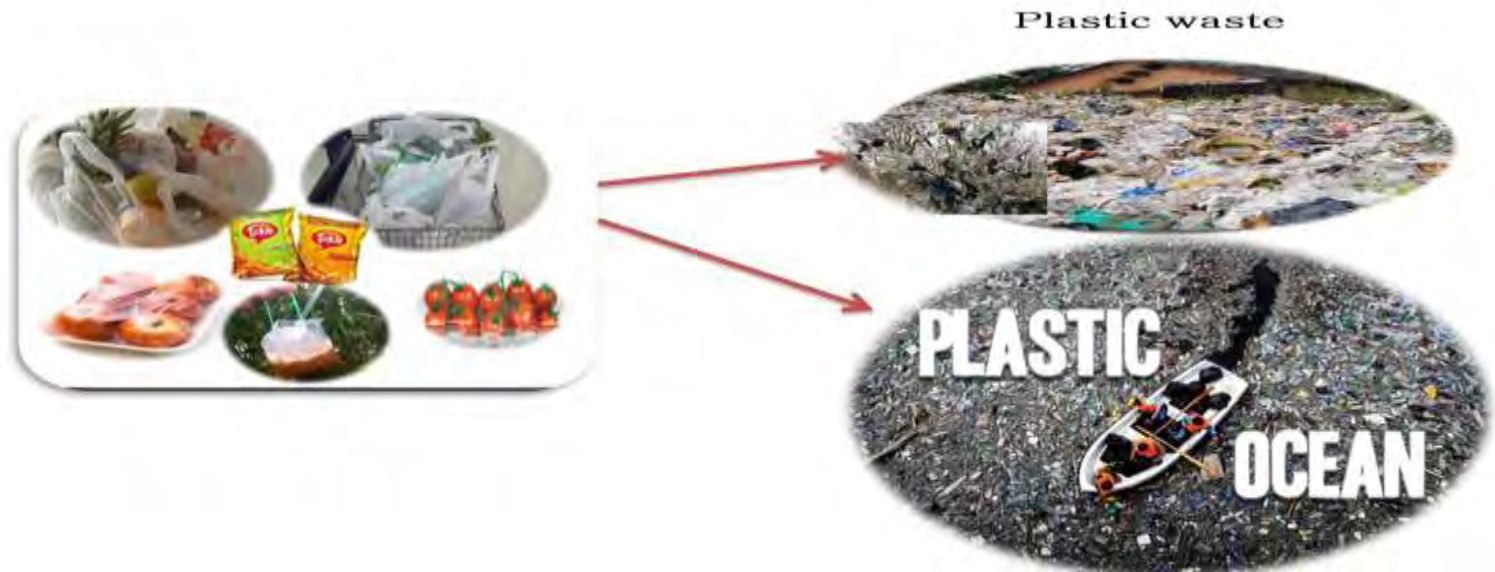


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Effect of microcrystalline cellulose Reinforcement on Mechanical and Water Barrier Properties of Sugar Palm Starch Biocomposite Films

Introduction

- Despite the numerous merits attached with the use of petroleum based plastics, they bring about severe environmental impacts.



- The non-biodegradable nature of petroleum based plastics has posed great environmental challenges which contributes to the rapid exhaustion of landfills.



The growing environmental awareness has directed the attention of most researchers to eco-friendly materials, with attributes such as “**renewable**”, “**recyclable**”, “**sustainable**”, and “**biodegradable**”.

Sugar palm (*Arenga Pinnata*) tree



- Sugar palm (*Arenga Pinnata*) is a multipurpose tree found in most South East Asian countries.
- Of all the palm species, sugar palm tree has probably the widest range of applications, involving almost each and every part of the tree (Mogea et al., 1991).

Palm sugar

“Neera sugar”

'Sugar block'



Food Sweetener



Traditional foods



Neera syrup





Sugar palm fiber



Handicrafts





Brooms/Brushes



Roofing material



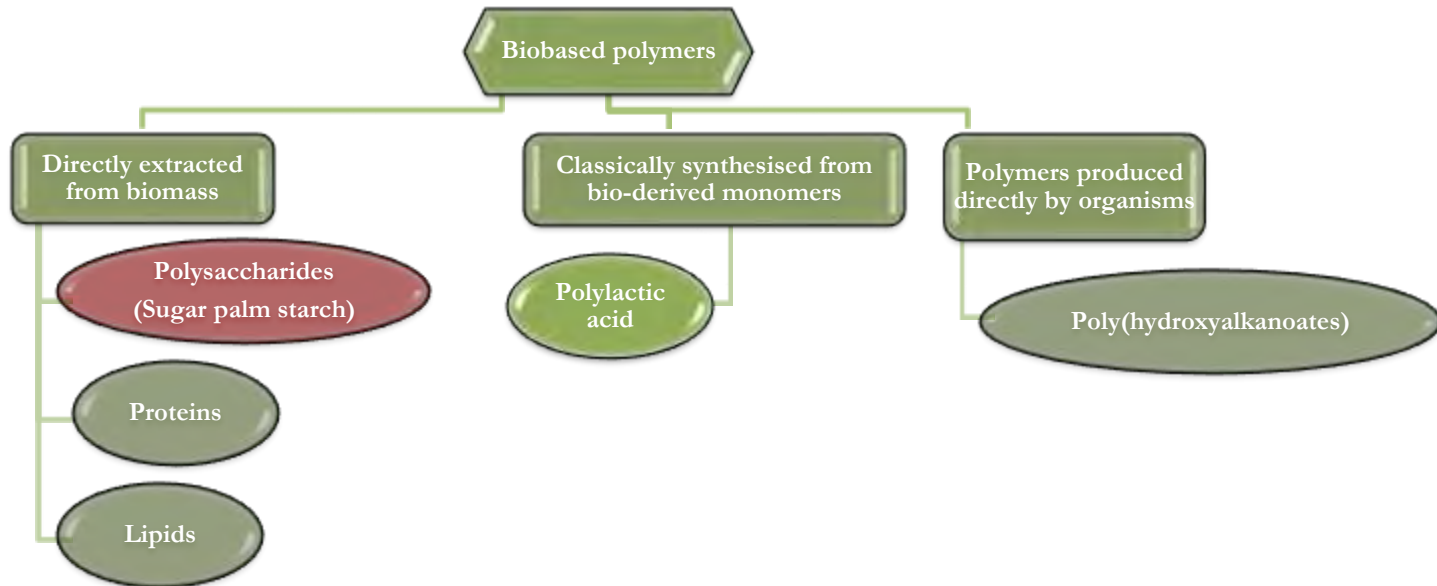
Ropes



Sugar palm starch



□ *Biopolymers are potential alternatives to petroleum-based polymers.*



Sugar palm starch

- Sugar palm starch (SPS) can be obtained from trunk of sugar palm tree (Adawiyah et al., 2013).
- SPS has been traditionally used as raw material for glue substances (Sahari et al., 2011).
- **One tree** can produce approximately **50 – 100 kg of starch** (Sahari et al., 2012a).
- SPS has **higher amylose content (37%)** compared to most commercial film forming starches such as tapioca (17%), potato (20 – 25 %), wheat (26 – 27%), maize (26 – 28%) and yam (30%) (Sahari et al., 2014; (Mali et al., 2004) .
- However, SPS has not yet receive much needed attention required for developing it as an industrial thermoplastic starch.



- Sugar palm is a significant bioresource which is still underutilized.
- Very limited studies have been reported related to their development as a green packaging material.
- Hence, in this study, sugar palm starch was modified by reinforcing with microcrystalline cellulose (MCC) to develop fully biodegradable composite films as environmentally friendly packaging material.

Microcrystalline cellulose (MCC)

- MCC is a white, odourless, and tasteless crystalline powder composed of porous particles.
- They are obtained from the indigestible part of plant material (Głowińska and Datta, 2015).
- In general, it is defined as a purified non-fibrous form of cellulose which is obtained from the partial acid hydrolysis of quality wood pulp (Reis et al., 2014; Kiziltas et al., 2014).
- The performance of MCC in various applications is greatly influenced by their degree of crystallinity.
- In comparison with other conventional cellulose fibers, MCC has the advantage of high specific surface area which grants them better reinforcement ability for polymer matrix (Kiziltas et al., 2014).

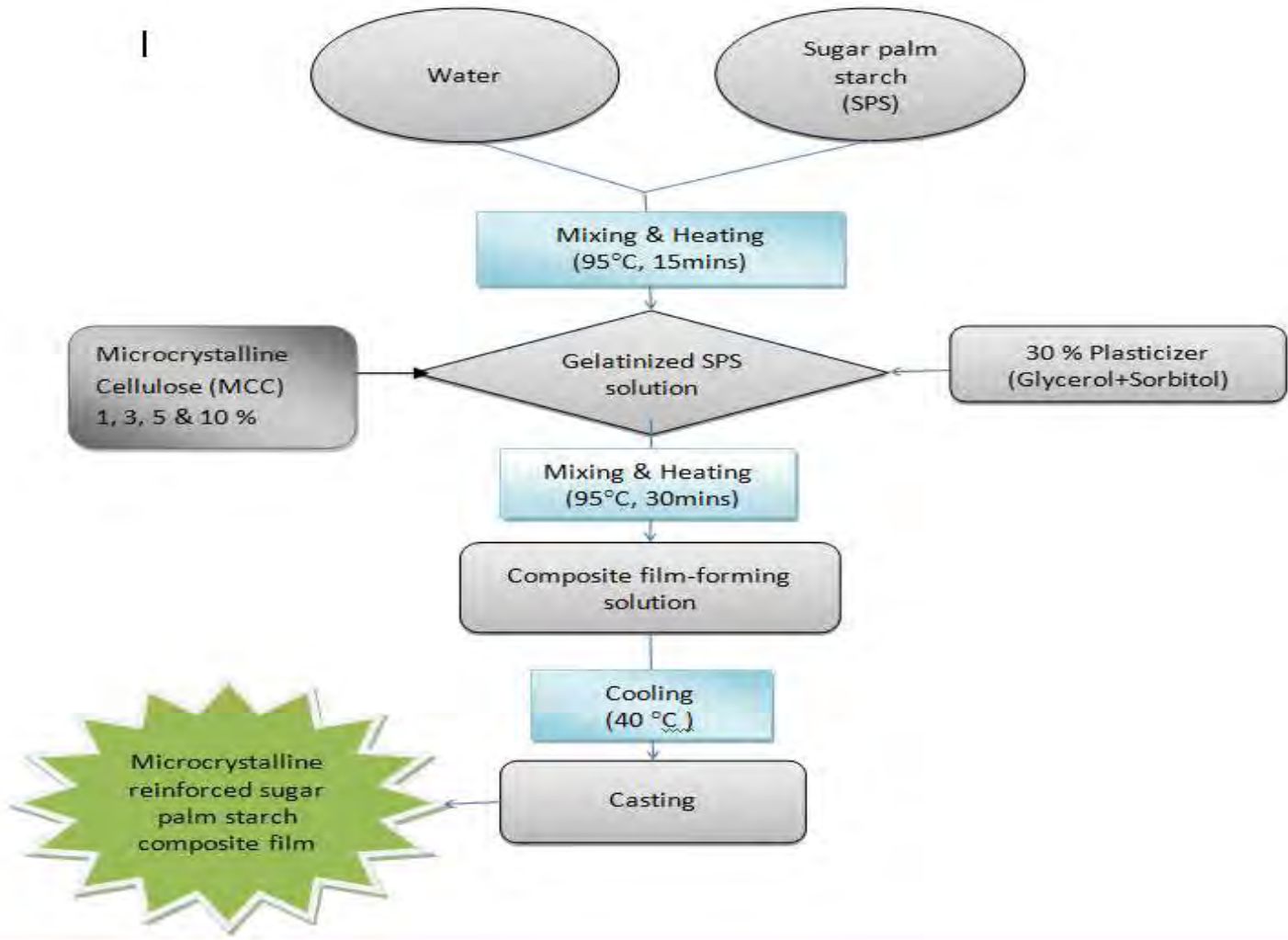
➤ The aim of this study was to evaluate the effect microcrystalline cellulose (MCC) on the mechanical, thermal and water barrier properties of MCC reinforced SPS composite films.

METHODOLOGY

Materials

Material	Source
Sugar palm starch	Jempol, Negeri Sembilan (Malaysia)
Microcrystalline cellulose	SIGMA-ALDRICH
Glycerol and Sorbitol	SIGMA-ALDRICH
Distilled water	

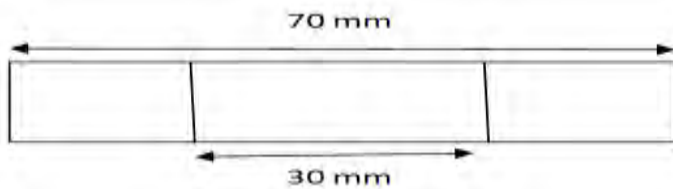
Preparation of composite films



Characterization

- **Tensile test**

- Films were tested using the standard method D882-02 (ASTM, 2002).
- Tensile strength and elongation at break were determined by using Instron 3365 universal testing machine with a load cell of 30 kg.
- Crosshead speed of 2 mm/min.



Sample dimension



Tensile test in progress

Dynamic mechanical analysis (DMA)

- Standard method: ASTM D5026 (ASTM, 2015).
- Operation: Tension mode at frequency of 1 Hz and a pre-load of 0.01N.
- Film dimension: 0.3 – 0.5 mm (thickness), 30 mm (length) and 10 mm (width) .
- Temperature: -150 to 150 °C
- Heating rate: 2 °C/min



Dynamic mechanical analyzer

Water vapour permeability (WVP)

- Standard method: ASTM E96-95
- Operating parameters: 25 °C, relative humidity 75 %, 5 days
- WVP calculation:

$$WVP = \frac{(m \times d)}{(A \times t \times P)}$$

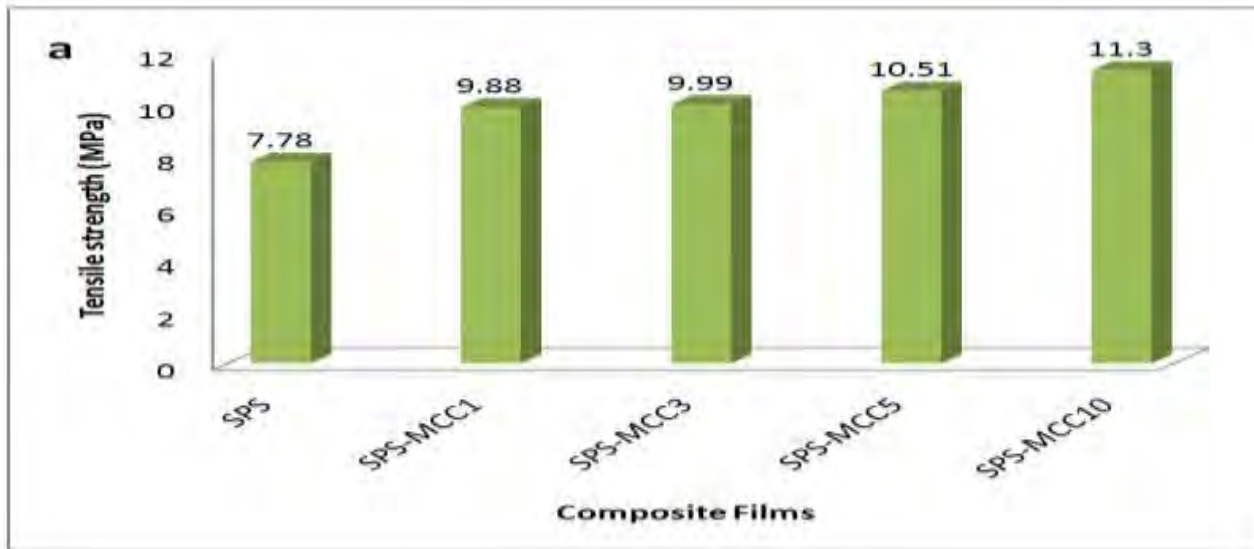
- Where m (g) is the weight increment of the test cup, d (mm) is the film thickness, A (m²) is the area of film exposed, t (s) is the duration for permeation, and P (Pa) is the water vapor partial pressure across the films.
- The results were expressed in g mm s⁻¹ m⁻² Pa⁻¹.

Atomic Force Microscopy (AFM)

- The morphology of the films was investigated using Atomic Force Microscop.
- The film samples were mounted on aluminum stubs with double-sided adhesive tapes and coated with gold to avoid charging.
- Finally, the AFM observation was performed at an acceleration voltage of 5 kV.

RESULTS & DISCUSSION

Tensile properties – Tensile strength



Effect of MCC loading on the tensile strength of SPS-MCC composite films compared with neat SPS films

- The incorporation of MCC in SPS matrix increases the tensile strength of resulting composite films.
- The tensile strength of films increased from 7.78 Mpa (control, SPS) to 9.88 Mpa (SPS-MCC1) when 1 % MCC was added to the SPS matrix.
- Further addition of MCC content up to 10% for SPS-MCC10 shows 45.24 % increase in their tensile strength values compared to neat SPS films.

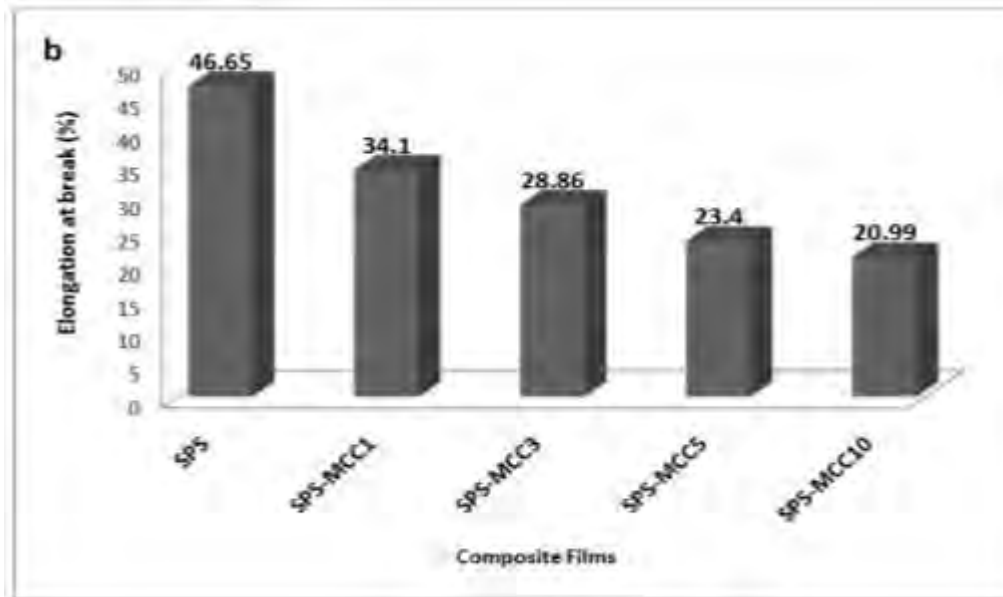
Tensile strength

- SPS matrix and MCC have similar functional groups.
- Hence, the incorporation of MCC filler with SPS produces strong hydrogen bridges, due to the interactions among OH groups of both materials.
- Therefore, increasing the MCC content gives higher reinforcement by enhancing the hydrogen bonds in the SPS matrix of the film.

Tensile strength

- Ma et al. (2008) reported that the strong intrinsic adhesion of filler-matrix interface caused by the chemical similarity of starch and cellulose derivatives, remarkably improve the tensile strength of composite films.
- This concur with the obtained results in this study, that the reinforcement effect of MCC increased with the concentration of MCC at constant starch content.
- The exhibited increase in tensile strength of SPS-MCC composite films can also be attributed to the good compatibility between SPS matrix and polar MCC.

Tensile properties – Elongation at break



Effect of MCC loading on the elongation at break of SPS-MCC composite films compared with neat SPS films

- It can be observed from the figure that MCC demonstrates significant effect on the elongation at break of SPS-MCC composite films.
- The elongation at break of neat SPS is 46.65 % and this value decreased from 34.1 to 11.3 % as the MCC content of composite films increased from 1 to 10%.

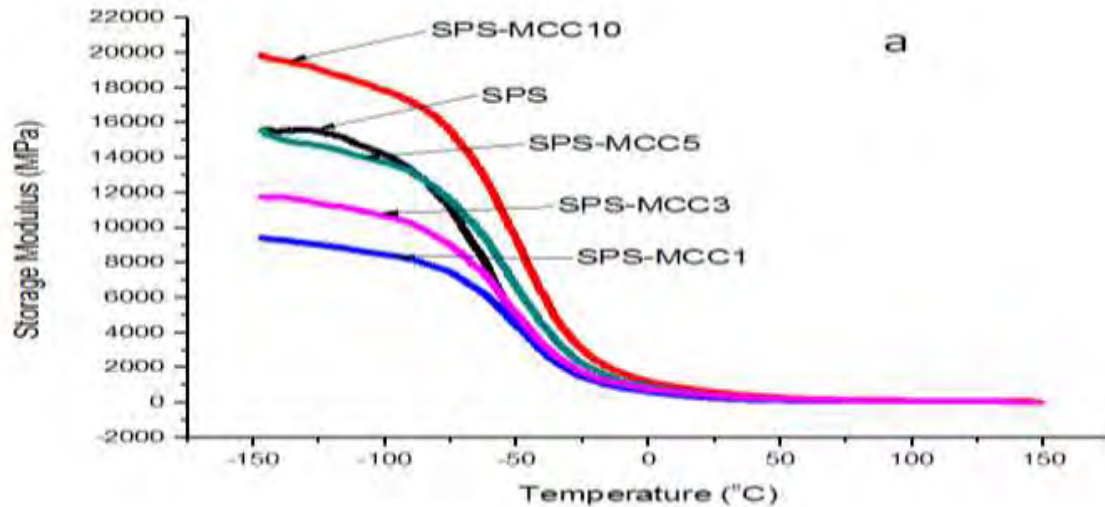
Elongation at break

- The obtained results clearly suggest that the good compatibility between SPS matrix and MCC filler reduce the mobility of molecular chains of films.
- This causes a drop in their elongation at break.
- Thus, the addition of MCC content promotes the formation of extensive three-dimensional network between starch and filler through hydrogen bonds which restrict the flexibility of the composite films.
- This results agrees with the report of Teaca et al. (2013).

Dynamic mechanical analysis- Storage modulus

- The viscoelastic behavior of neat SPS films was evaluated as well as their MCC reinforced composite films using DMA.
- The storage modulus obtained from the DMA data provides the stored energy which reflects the elastic portion of the film samples.
- In simple terms, it is the measure of elastic behavior of film samples when subjected to temperature changes.
- It also indicates the stiffness of samples (Sanyang et al., 2015).

Storage modulus



Effect of MCC loading on the storage modulus of SPS-MCC composite films compared with neat SPS films

- SPS composite films reinforced with MCC shows higher storage modulus values than pure SPS films.
- The storage modulus of composite films significantly increased with the increasing of MCC contents from 1 to 10 %.
- Overall, it can be seen that the storage modulus of films decreased as the temperature increased.

Storage modulus

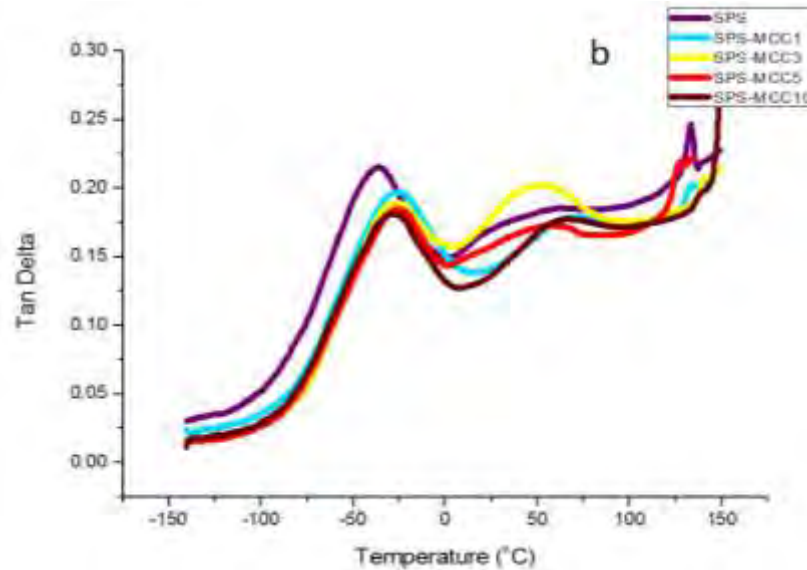
- This increment in storage modulus relates to the incorporation of MCC in the SPS matrix, can be attributed to the interaction between SPS and MCC.
- Piyada et al. (2013), Ma et al. (2008) and Lu et al. (2006) also reported similar effect on storage modulus of reinforced thermoplastic starch composite films.

Storage modulus

- Exposing the films to higher temperature enhances the chain mobility and increases their free volume.
- Thereby reducing the intermolecular interaction and keeping adjacent chains of the matrix far apart.
- Thus, considerable reduction in the storage modulus of all the films was observed.

Loss factor ($\tan \delta$)

- Loss factor ($\tan \delta$) is one of the data obtain from DMA and it relates to the ratio between the lost energy and the stored energy (Ren et al., 2009; Dogan and Mchugh, 2007).
- The $\tan \delta$ results help to determine the glass transition temperature (T_g) of the films.
- The observed T_g of the films indicates the transition from the glassy state to more elastic state, which is known as the rubbery state (Reis et al., 2014).



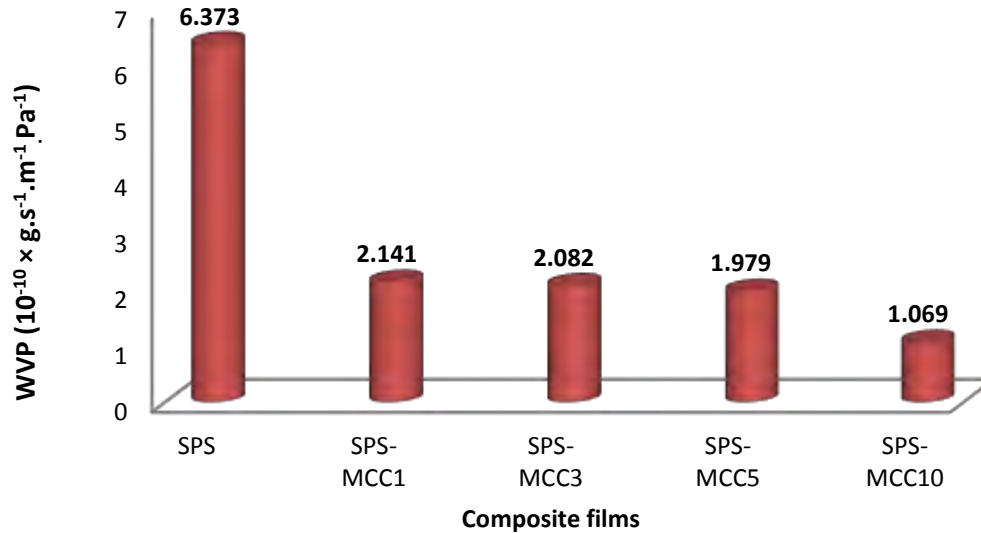
Effect of MCC loading on the tan delta of SPS-MCC composite films compared with neat SPS films

- The $\tan \delta$ curve of samples shows two thermal transition peaks indicating two separate phases of film samples especially in SPS-MCC composite films.

Loss factor

- The addition of MCC in SPS films shifts the first transition and second transition to higher temperature.
- The presence of MCC generates favourable intermolecular interaction with SPS matrix , which draws adjacent molecular chains closer, reducing the free volume and , thus, elevating the T_g of composites.
- This is an indication of reinforced rigidity (increased strength) of the SPS-MCC composite films.
- The increased strength in these composite films can be attributed to the strong interfacial interactions between large specific MCC surface and SPS matrix.

Water vapor permeability (WVP)



Effect of MCC loading on the WVP of SPS-MCC composite films compared with neat SPS films

- SPS film has the highest WVP ($6.373 \times 10^{-10} \times \text{g}\cdot\text{s}^{-1}\cdot\text{m}^{-1}\cdot\text{Pa}^{-1}$) due to its high hydrophilic nature.
- The presence of MCC drastically improves the WVP of the neat SPS film.
- The incorporation of MCC significantly decrease the WVP value of composite films because it is less hydrophilic than starch.

Water vapor permeability

- The MCC also reduce the diffusion coefficient of the composite films by obstructing the pathway for water molecules to pass through.
- Similar observation was reported by Reis et al. (2014), who used MCC as reinforcement in thermoplastic starch/poly(butylene adipate-co-terephthalate) films.

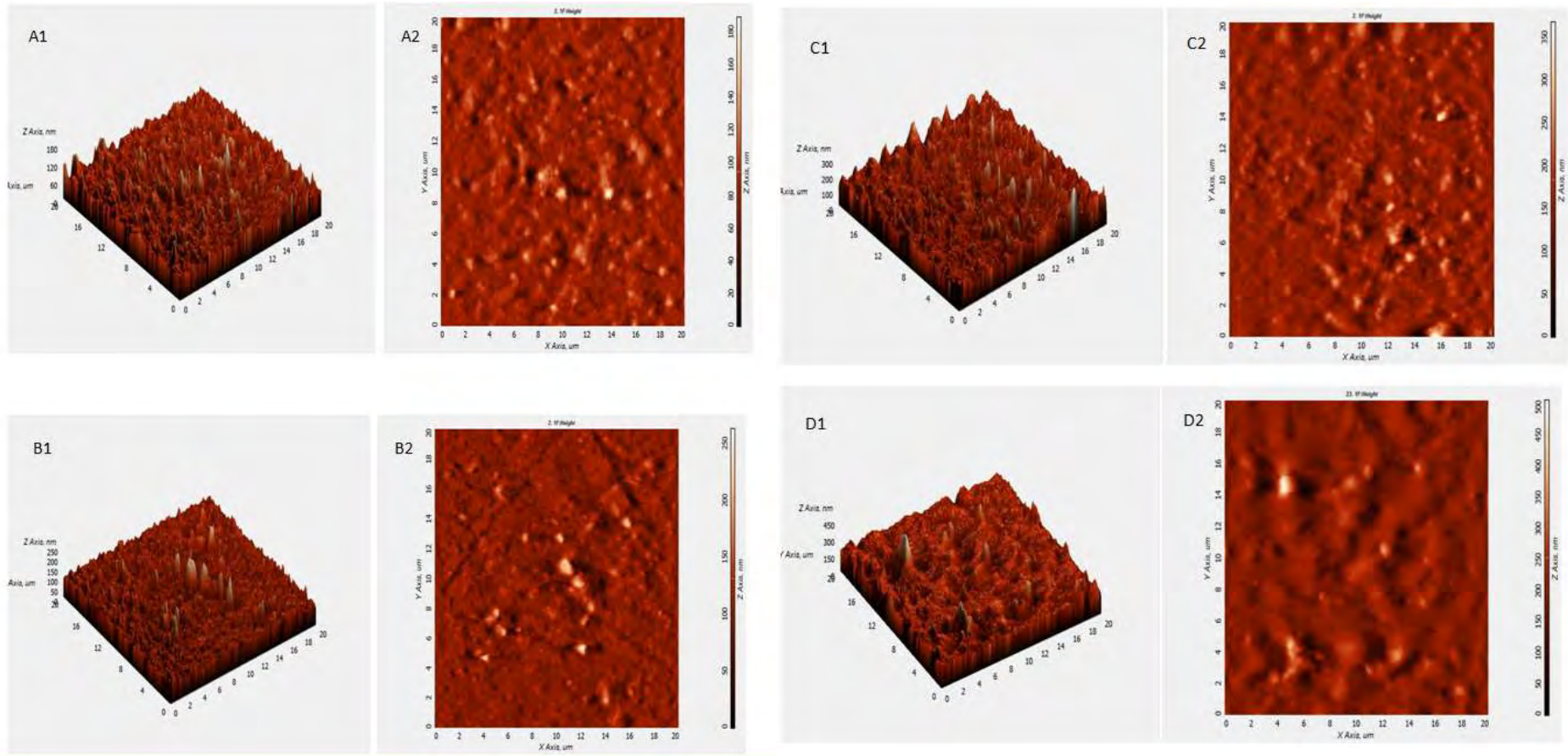
Water vapor permeability

- The addition of 1 % MCC into SPS films decreases their WVP value by 66.41 %.
- This reduction can be attributed to the tortuous path caused by the dispersed MCC in the starch matrix which hinder or prolong the path for water molecules to pass.
- Therefore, increasing the MCC concentration from 1 to 10 % shows slight decrease in the WVP of composite films from $2.141 \times 10^{-10} \times \text{g}\cdot\text{s}^{-1}\cdot\text{m}^{-1}\cdot\text{Pa}^{-1}$ to $1.069 \times 10^{-10} \times \text{g}\cdot\text{s}^{-1}\cdot\text{m}^{-1}\cdot\text{Pa}^{-1}$.
- Thus, SPS-C10 displayed 83.23 % improvement in WVP compared to the neat SPS film.

Surface morphology

- Investigating the morphology structure of composites provide crucial information which helps to determine various properties of the material.
- Hence, the use of AFM is a more detail technique to evaluate the morphology structure of polymer composites.
- It clearly exhibit the topography of films reinforced or filled with micro- and nanofibers (Sanchez-Garcia et al., 2008).
- AFM is famously utilized to examine the nanoscale surface chemistry and the surface topography of polymer composites when SEM images are not satisfactory.
- Therefore, observation of the effect of MCC as reinforcement on the surface structure of SPS-MCC based composites films was performed with AFM.

Surface morphology



Effect of MCC loading on the AFM surface morphology images of SPS-MCC composite films containing (A) 1 % MCC, (B) 3 % MCC, (C) 5 % MCC and (D) 10 % MCC

*Number 1 and 2 denote 3D and 2D images

Surface morphology

- The obtained images clearly illustrates that the MCC are thoroughly dispersed and covered by the SPS matrix.
- The increase of MCC contents in SPS from 1 to 10 % significantly increase the roughness of the film surface from 10.81 to 26.42 nm.
- This might significantly contribute to the improved mechanical strength and water vapor permeability of SPS-MCC composite films especially for SPS films containing 10 % MCC.

Surface morphology

- The SPS-MCC10 composite film surface became rougher with no noticeable clusters or agglomerate of MCC.
- Therefore, the good dispersion of MCC evident shown in AFM images is a good indication of strong interfacial adhesion between the two components of the SPS-MCC composite films.
- This strong interfacial adhesion translates into its high tensile strength.
- Our findings concur with the ones reported by Bilbao-Sainz et al. (2011) and Savadekar and Mhaske (2012).
- In fact, Bilbao-Sainz et al. (2011) reported that cellulose fibers must be well dispersed in the polymeric matrix to enhance the functional properties of the composite.

Conclusions

- In the effort to resolve the alarming environmental crisis caused by non-biodegradable plastics, natural biopolymers are potential alternatives to rescue our ecosystem.
- Hence, in this study, environmentally friendly (SPS/MCC) composite films were prepared as potential biodegradable films for packaging.
- The incorporation of MCC improved the mechanical strength of the composite films as compared to the neat SPS films.
- MCC also enhanced the water vapor resistance of the composite films which was associated with the good interaction between MCC and SPS as manifested by the AFM images.

Conclusions

- This study also add to the effort to unveil the potential of using SPS in developing green products.
- Else, such abundant bioresources may be underutilized.



Sugar Palm Tree

Without Research



UNUTILIZED

Research



BIOPOLYMER/BIOCOMPOSITES

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- SEARCA, The Philipines
- Universiti Putra Malaysia

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