Effect of storage environment on the crystallinity and compressive load of starch based biodegradable cup

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Abstract. The effect of storage environment on the overall crystallinity and compressive load of commercially sold starch based biodegradable cup was determined. Using FTIR and DSC, the components of the cup was identified as starch, polypropylene (PP) and organic acid as compatibilizer. Using TGA, the weight percentage of starch and PP components were 13 and 58%, respectively. The samples were stored 20°C, 80% RH and 40°C, 40% RH for 4 months. Using DSC, the overall crystallinity was evaluated based on the heat of fusion ($H_f$). Using XRD, the crystalline structure was evaluated based on peaks and full width at maximum height (FWHM). After 4 months, DSC results showed only one endothermic peak with melting point of ≈165°C at both conditions. The $H_f$ was remained ≈50 J/g. Based on XRD results, there were no development of new crystalline peaks and the peak FHWM remained unchanged. Initially, the percentage samples below the set limit of compressive load was ≈20%. The percentage below the set limit was ≈40% for samples stored at 20°C, 80% RH, whereas ≈20% for samples stored at 40°C, 40% RH. The 80% RH at 20°C increased the moisture content from 2% to 3.1%. The overall crystallinity remained unchanged after storage. Water became a plasticizer for the starch component. The increase in moisture content could have decreased the compressive load during storage.

1. Introduction
Thermoplastic starch (TPS) is composed mainly of starch and plasticizer [1,2]. The components are processed to have thermoplastic properties. It can then be converted into films, tray, cup, cutlery, foams and sheets using standard equipment used in conventional polymers. TPS is a very attractive material because its raw material comes from a renewable resource. It is biodegradable and non-toxic. TPS can also be blended with other polymers to improve its mechanical and water barrier properties [1].

Though TPS is very promising material to combat solid waste generation, TPS can become brittle during long term storage [1,2]. The environmental storage conditions can induced recrystallization of starch (i.e. retrogradation) [3] and migration of plasticizer out of the TPS matrix [1,2]. When polymers are stored above its glass transition ($T_g$), the polymer chains has some mobility and it can form more orderly structures during storage. This phenomenon is called recrystallization. Exposure to high humidity environment will increase the moisture content of TPS. Water is effective in plasticizing TPS because it is capable of hydrogen bonding with the hydroxyl groups of the starch chains [3]. The molecular size of water is also smaller than conventional plasticizers like glycerol, thus, it is more mobile to penetrate between the starch chains. The effectiveness of water as a plasticizer which is coupled with storage temperature above $T_g$ will increase the rate of retrogradation.
The recrystallization of polymers can be evaluated using differential scanning calorimeter (DSC) and x-ray diffraction (XRD) techniques [3,4]. Using DSC technique, the presence of crystalline structures can be detected by the melting peak. The heat of fusion of the melting peak is an indicator of the relative amount crystalline structures that are present [5,6]. Using XRD technique, the peaks of crystalline structures can be detected. Recrystallization can also be detected by formation of a new peak [6,7]. The increase in crystallite size can also be evaluated using the full width at maximum height (FWMH). A decrease in FWMH implies increase of crystalline size [7] as effect of storage.

The changes in crystallinity and moisture content during storage can affect the mechanical properties of TPS [8-10]. For films, the increase in crystallinity will increase the tensile strength and modulus of elasticity and will decrease elongation at break. When the film is stored in ≥ 75% relative humidity (RH), the moisture content will increase and films will become very elastic [10]. There are many ageing studies of TPS materials [3,8-10]. In TPS composites, individual components can be influence by ageing and can affect the mechanical properties of the composite [11]. Ageing studies can be conducted to monitor the properties of the packaging and to assure its service life.

In this study, the commercially sold starch-based biodegradable cup is in its final and functional form. The cup is a takeaway packaging. The cup is subjected to compression when the lid is applied as closure or when covered cups were stacked in food delivery. The body section is more likely to be deformed during compression. The objective was to evaluate the effect of storage environment on the overall crystallinity and compressive load of starch based biodegradable cup.

2. Materials and methods

2.1. Materials
Starch-based biodegradable cup (12 oz.) was purchased from a local supplier in the Philippines. The cups with defects such as dents, holes and tear were eliminated.

2.2. Identification of plastic components
Fourier Transform Infra-red (FTIR) spectrum of the body section was recorded using Shimadzu IR-Prestige coupled with attenuated total reflectance (ATR). Using 32 accumulated scans, the absorbance was examined between 400 and 4,000 cm\(^{-1}\) wavenumber using a spectral resolution of 4 cm\(^{-1}\) [12].

Using differential scanning calorimeter (Shimadzu DSC-60), the melting point temperature (\(T_m\)) of the body section was determined. The heating and cooling rates were set at 10°C/min based on ASTM D3418 [13]. The sample was heated from 30 to 250°C and then was cooled under nitrogen atmosphere. The measurement was performed in duplicate.

Using thermogravimetric analysis (TGA), the weight percent (%) of the plastic components were estimated. The TGA thermogram was obtained using a STA 6000 (PerkinElmer, USA). About 20 mg sample was used. It was heated from 30 to 900°C at a heating rate of 10°C/min under a nitrogen atmosphere with N\(_2\) flow rate of 50 ml/min.

2.3. Crystallinity analysis

2.3.1. Overall crystallinity analysis. The overall crystallinity was estimated based on the heat of fusion (\(H_f\)) [6,14]. From the DSC result of Section 2.2, the \(H_f\) (J/g) was calculated using TA-60WS software.

2.3.2. Crystalline structure analysis. X-ray diffraction (XRD) pattern of the body section was analyzed with Shimadzu Maxima XRD-7000. Sample was scanned at diffraction angles (2\(\theta\)) from 5 to 35° using a scan rate of 0.02/s. The crystalline peaks and full width at half maximum (FWMH) of each peak were determined using Jade Version 6.0 software (MDI, USA).

2.4. Compressive load
The samples were conditioned at 23°C, 50% RH for 2 days prior to compressive load test. The compressive load was measured using a compression tester (Shimadzu EZ-SX) equipped with upper and lower compression plates. The jig plate diameter was 118 mm. The speed was set at 1.3 mm/min based on ASTM D695 [15]. The 15 replicates tested. The sample was positioned facing up wherein the upper jig would be in contact with the cup opening.

2.5. Moisture content
The sample was taken from the body section and cut into 5 cm x 5 cm sheet. The sheet was dried using vacuum oven (France Etuves XFL020, France) at 70°C under – 1 bar for 18 hours. The test was performed in triplicate.

2.6. Effect of storage environment
The samples were stored in two conditions: 1) 20°C, 80% RH and 2) 40°C, 40% RH for 4 months. The incubator used can only control the temperature. The relative humidity was monitored.

The overall crystallinity analysis by DSC, compressive load test and moisture content were monitored every month. The crystalline structure analysis by XRD was conducted at 0 month and after 4 months of storage.

To further evaluate the effect of storage on compressive load, the lower limit of compressive load was set to be the average compressive load subtracted by the standard deviation. The percentage of samples below the set lower limit was also calculated.

3. Results and discussion

3.1. Identification of plastic components
The FTIR spectrum of the body section (no figure) exhibited a broad band between 3600–3000 cm\(^{-1}\). This was the absorbance band of O–H stretching of hydroxyl group [16]. Other absorbance bands were at 2949, 2914 and 2849 cm\(^{-1}\) (C–H stretching), 1730 cm\(^{-1}\) (C=O stretching of carbonyl group), 1454 and 1375 cm\(^{-1}\) (C–H blending), 1016 cm\(^{-1}\) (C–O stretching), and 872 cm\(^{-1}\) (C–C vibrations) [16,17].

The absorbance bands of O–H stretching of hydroxyl group and C–O stretching were attributed to the starch component. The sharp peaks of C–H stretching with very strong absorbance were attributed to polypropylene (PP) component. The C=O stretching indicated presence of carboxylic acid group which was not a functional group of the starch and PP components. This implied possible usage of organic acids as compatibilizer in TPS - PP blend [18].

![Figure 1](image1.png)

**Figure 1.** DSC thermogram of body section at 0 month and after 4 months of storage.

Using DSC technique, the heating scan of the body section is shown in figure 1. There was only
one endothermic peak with melting point temperature \((T_m)\) of 166°C. The peak \(T_m\) indicated a PP component in the composite. One endothermic peak of the TPS – PP composite also indicated a degree of miscibility as an effect of the compatibilizer [18].

DSC and FTIR techniques identified the starch, PP and organic acid components of the starch-based biodegradable cup.

Using TGA technique, the mass loss curve (figure 2) was used to estimate the weight percent (%) of components. The maximum rate of weight loss \((T_{\text{max}})\) was observed at 119, 315 and 464°C [14,19]. These were attributed to water, starch and PP components with weight percent of 1.7, 13 and 58%, respectively. The \(T_{\text{max}}\) of the compatibilizer was not detected probably because it has degraded in the same temperature range of starch and PP components.

![Figure 2. TGA curve of body section.](image)

### 3.2. Crystallinity analysis

It was assumed that the PP and TPS components could recrystallized during storage because the storage temperature was above \(T_g\) of the PP component (‒10°C) [20]. The actual \(T_g\) of the components could not be measured because of the limitation on operational temperature range of DSC. In DSC results, it was projected that the \(H_f\) would increase [5]. The single melting peak could also separate into individual peaks of TPS and PP components as each component recrystallized in the blend [11]. In XRD results, the increase in peak intensity and an increase of crystalline size could be observed [6]. New crystalline peaks could also be formed as observed in the study of van Soest et al [7].

#### 3.2.1. Overall crystallinity analysis

The heat of fusion \((H_f)\) was used to estimate the overall crystallinity of the TPS-PP composite [6,14]. Initially, there was only one endothermic peak with \(H_f\) of \(45.9 \pm 4.1\) J/g. After 4 months, DSC results exhibited only one endotherm in both storage conditions (figure 1). The melting point range was 164–166°C. Figure 3 shows the effect of storage on the \(H_f\). After 4 months, the \(H_f\) of the samples were \(47.3 \pm 5.0\) J/g for samples stored at 20°C, 80% RH and 49.3 ± 0.1 J/g for samples stored at 40°C, 40% RH. The \(H_f\) did not increase significantly for both storage conditions. The DSC results suggested that the overall crystallinity did not increase significantly with storage.

#### 3.2.2. Crystalline structure analysis

The crystalline pattern of body section at initial stage was shown in figure 4. The characteristic peaks are at \(2\theta = 9.8, 14.4, 17.3, 19.3, 29.0, 29.8, 31.4\) and 31.9°. The crystalline peaks at \(2\theta = 14.4\) and 29.0° were identified to be PP [17,21]. The peak at \(2\theta = 29.0°\) was sharp and intense. This peak was usually of low intensity in crystallinity studies of PP materials [6,17]. The peak at \(2\theta = 29.0\) and 29.8° could also be processed induced crystallinity during the manufacturing process of the cup.
Figure 3. Effect of storage on the heat of fusion (body section).

Figure 4. X-ray diffraction patterns of body section at initial stage and after 4 months of storage.

Table 1. XRD results of FWHM intensity of body section at initial stage and after 4 months storage.

| 2θ(°) | Full width at half maximum (FWHM) | 0 month | 20°C, 80% RH | 40°C, 40% RH |
|-------|----------------------------------|---------|--------------|--------------|
| 9.8   | 0.24 ± 0.03                      | 0.22 ± 0.03 | 0.24 ± 0.01  |
| 14.4  | 0.45 ± 0.03                      | 0.44 ± 0.03 | 0.43 ± 0.01  |
| 17.3  | 0.46 ± 0.00                      | 0.45 ± 0.03 | 0.46 ± 0.00  |
| 19.3  | 0.54 ± 0.05                      | 0.52 ± 0.04 | 0.49 ± 0.01  |
| 29.0  | 0.32 ± 0.05                      | 0.31 ± 0.02 | 0.31 ± 0.01  |
| 29.8  | 0.32 ± 0.05                      | 0.31 ± 0.02 | 0.31 ± 0.02  |
| 31.4  | 0.36 ± 0.12                      | 0.31 ± 0.02 | 0.34 ± 0.05  |
| 31.9  | 0.43 ± 0.14                      | 0.37 ± 0.01 | 0.33 ± 0.04  |

The crystalline peak at 2θ = 17.3° could be an overlapped of B-type of the starch component (2θ = 16.8°) [7] and PP component (2θ = 16.8°) [17]. The wide peak at 2θ = 19.3° could also be an overlapped of Vh-type of the starch component (2θ = 19.5°) [7] and PP component (2θ = 18.5°) [17]. The crystalline peak at 2θ = 9.8° was not a characteristic peak of starch and PP component. This could
also be processed induced crystallinity during the manufacturing process of the cup. After 4 months of storage, there were no developments of new crystalline peaks. The FWHM of the sharp peaks did not decrease (table 1) which would imply increase in crystallite size. For the PP component, the FWHM was expected to increase as the sample was stored above the T_g of PP. The FWHM of PP peaks at 2θ = 14.4, 29.0 and 29.8° did not decrease. Thus, an increase of crystalline size was not observed [7] as effect of storage. The XRD results agreed with the DSC results.

3.3. Compressive load
The compressive load of the starch-based biodegradable cup was 100 ± 31 N. After 4 months of storage, the compressive load was 95 ± 36 N for samples stored at 20°C, 80% RH whereas 94 ± 21 N for samples stored at 40°C, 40% RH. It was evident that the standard deviation was large (≈30 N) in all samplings. This could be due to manufacturing method of the cup. The lower limit of compressive load was set to be 69 N based on 0 month and the percentage of samples below 69 N was ≈27%. After 4 months of storage (table 2), the percentage of samples below 69 N was ≈40% when stored at 20°C, 80% RH while ≈27% when stored at 40°C, 40% RH. The compressive load of samples stored at 20°C, 80% RH decreased during retention while the samples stored at 40°C, 40% RH remained the same.

Table 2. Percentage of samples below the lower limit of compressive load during storage.

| Storage time (month) | Percentage (%) of samples below 69N* |
|---------------------|-------------------------------------|
|                     | 20°C, 80% RH | 40°C, 40% RH |
| 0                   | 27           | 27           |
| 1                   | 7            | 0            |
| 2                   | 40           | 13           |
| 3                   | 40           | 27           |
| 4                   | 33           | 13           |

* Lower limit of compressive load based on 0 month

3.4. Moisture content
After 4 months of storage, the moisture content of the samples stored at 20°C, 80% RH increased from 2 to 3.1%. The high humidity environment of 80%RH increased the moisture content of the samples. The TPS component absorbed water, thus increasing its plasticizer content [3,10]. The increase in moisture content decreased the compressive load when stored at 20°C, 80% RH. When samples were stored at 40°C, 40%RH, moisture content decreased from 2 to 1.6%. The loss of moisture was due to the evaporation of water at low humidity environment of 40% RH. The loss of moisture of the TPS component could equate to decrease in plasticizer content and it could lead to embrittlement [2]. The compressive load of samples stored at 40°C, 40% RH was not affected by the decrease in moisture content.

4. Conclusion
The body section of the starch-based cup was identified as the area that more likely to be deformed during excessive compression. Different characterization techniques were used to understand its mode of failure as a takeaway packaging. The recrystallization phenomenon was not observed based on DSC and XRD results after 4 months of storage. When stored at high relative humidity of 80%, the starch component absorbed moisture which would become its additional plasticizer. The material became more flexible which leaded to the decrease of compressive load during storage. It is recommended to measure T_g for further studies on retrogradation of TPS blend composites.

Acknowledgments
This work was financially supported by Industrial Technology Development Institute, Department of
Science and Technology, Philippines. The authors were grateful to Advanced Device and Materials Testing Laboratory (ADMATEL) for TGA analysis.

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