Summaries of Training in

Japan for JICA project

A. Research project tittle: **Preparation and properties testing of TPS/PHBV/PBAT and TPDW/PHBV/PBAT blends**

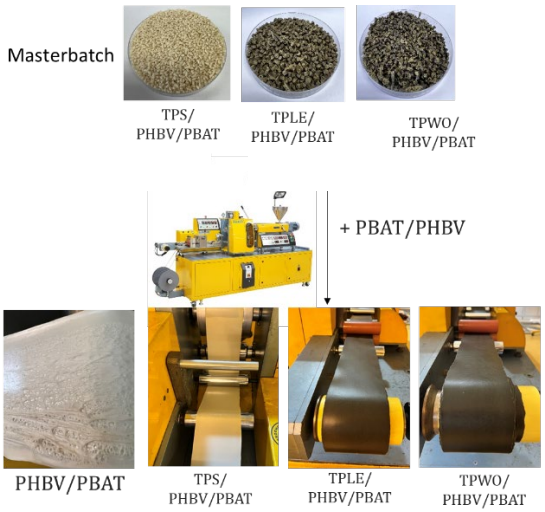
B. Project progress

1. Time table

Activity	October (week)				November (week)			
	1	2	3	4	1	2	3	4
Training for using machines and equipment								
Molecular weight determinization by GPC								
Chemical analysis by ^{1}H-NMR								
Thermal properties of DSC								
Migration of glycerol								

2. Method

2.1. Preparation of PHBV/PBAT/TPS and PHBV/PBAT/TPDW blends



2.2. Molecular weight determinization by GPC

The PHBV/PBAT/TPS and PHBV/PBAT/TPDW blend sheets were first dissolved in Chloroform ($CHCl_3$) to precipitate TPS, TPLE and TPWO. The obtained mixtures in $CHCl_3$ were centrifuged, following by refined to archive clear solvent of PHBV/PBAT solution.

The PHBV/PBAT mixtures were further dissolved in tetrahydrofuran (THF) to precipitate PHBV. The procedure to remove precipitated PHBV and obtain clear PHBAT solution was similar to the above process.

The obtained PHBV and PBAT from the PHBV/PBAT/TPS and PHBV/PBAT/TPDW blends were dissolved in $CHCl_3$. All solutions were heated t until complete dissolution arrived. Molecular weights were measured by using exclusion chromatography equipped with two tandem 806L column. The number-average (Mn) and weight-average (Mw) molecular weights were calculated using a calibration curve from polystyrene standards.

2.3. Chemical analysis by ^{1}H-NMR

The ^{1}H-NMR spectra of pure PHBV and PBAT in the blends were recorded on a Bruker AMX-3000 apparatus using $CDCl_3$ as the solvent.

2.4. Thermal properties of DSC

Thermal analyses were carried out on 5-8 mg of PHBV/PBAT/TPS and PHBV/PBAT/TPDW blends with various concentration of TPS and TPDW at 60 °C. Thermal properties, i.e., glass transition temperature (T_g), cold crystallization temperature (T_{cc}), crystallization temperature (T_c), and melting temperature (T_m), were analyzed using a differential scanning calorimeter (DSC) (DSC3+, Mettler Toledo, Switzerland). The measurements were conducted at temperatures ranging from -80 °C to 250 °C.

2.5. Migration of glycerol

The migration of glycerol to water was determined by using Amplite® Colorimetric Glycerol Assay Kit. the PHBV/PBAT/TPS and PHBV/PBAT/TPDW blend sheet was soaked in water for 24 h and 72 h. The solution was then mixed with Amplite® glycerol working solution and measured OD at 575 nm. The amount of glycerol released from swelling blend sheets was calculated using glycerol standard curve.

3. Results and Discussion

3.1. Chemical analysis by 1H-NMR

Many polymer properties rely on the chemical structure of the monomer, its stereochemistry, chain length, and the distribution of chain structure. Therefore, the following techniques were utilized to confirm the chemical structure and purity of each polymer.

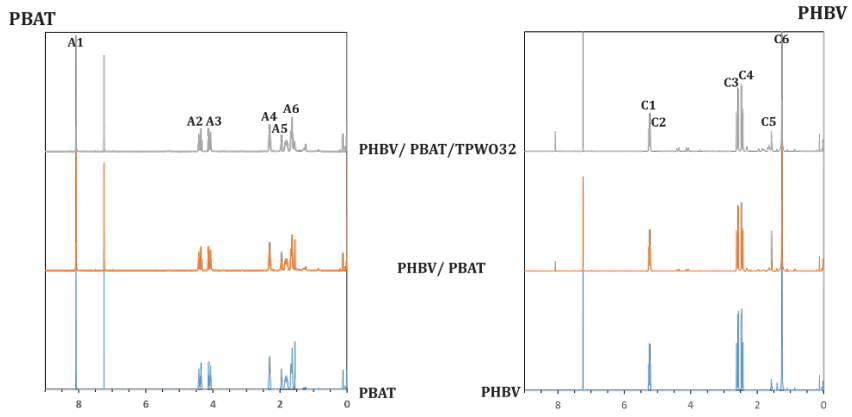


Figure 1. ^{1}H-NMR spectra of PBAT and PHBV

^{1}H-NMR technique was used to determine each sample's polymer composition and microstructure. In this study, NMR spectra were obtained to compare with the literature and prove the pristine composition. As we can see in Figure 1, the ^{1}H-NMR spectra of neat PBAT, and PHBV confirmed the chemical structure of each polymer by the presence of characteristic protons. The signal of aromatic protons of PBAT appears at 8.09 ppm, indicating the phenylene structure. Some signals of the CH_2 are located at 4.37, 4.14, 2.33, 1.96, and 1.66 ppm as seen as a match with chemical structure. Both PHBV CH signals are shown in multiple peaks at 5.24 and 5.14 ppm, CH_2 signals are also multiplet at 2.59, 2.49, and 1.62 ppm, where the latest corresponding to the CH_2 within the ethyl group. The CH_3 have signals at 1.27 and 0.89 ppm.

The result of PBAT and PHBV extracted from PHBV/PBAT and PHBV/PBAT/TPWO32 blend sheet showed almost identical ^{1}H-NMR pattens as

compared to neat PBAT and PHBV. The result suggested that PBAT and PHBV were successfully isolated from the blends PHBV/PBAT and PBV/PBAT/TPDW blend sheets.

3.2. Molecular weight determinization by GPC

Through GPC, the molecular weight of the polymer was determined. By comparing these molecular weights, it was possible to determine the effects of localized shear heating in the extrusion process that resulted in a drop in molecular weight. Figure 2 illustrated the results of the GPC analysis on PHBV and PBAT in PHBV/PBAT and PHBV/PBAT/TPDW blends after isolating process to purify PBV and PBAT. The results of neat PBAT and PHBV showed that the M_w and M_n of PHBV was over twice higher than for PBAT.

The molecular weights of PHBV and PBAT in PHBV/PBAT blend were slightly lower than the neat PHBV and PBAT, indicating the degradation occurred with both PHBV and PBAT after thermal extrusion processes. However, the decreased molecular weight was even more significant with the blends containing TPS and TPLE and TPWO. In addition, the higher content of TPS and TPLE and TPWO caused much lower M_w and M_n.

As compared the rate of decreasing molecular weight of PHBV and PBAT among PHBV/PBAT/TPS, PHBV/PBAT/TPLE and PHB/PBAT/TPWO blends. The highest reduction of molecular weight was PHBV/PBAT/TPWO blend, following by PHBV/PBAT/TPLE and PHBV/PBAT/TPS, respectively.

The hydrolyzation of PHBV was higher than PBAT at the same material and its content.

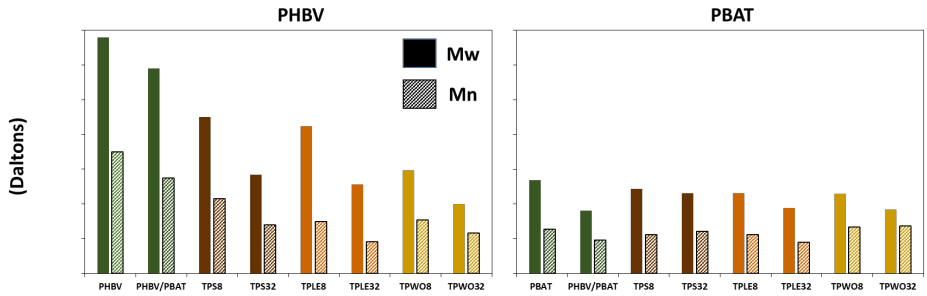


Figure 2: GPC analysis of near PHBV, neat PBAT, and PHBV and PBAT in PHBV/PBAT and PHBV/PBAT/TPDW blends with 8 wt% and 32 wt% of TPS, TPLE and TPWO.

3.3. Thermal properties of DSC

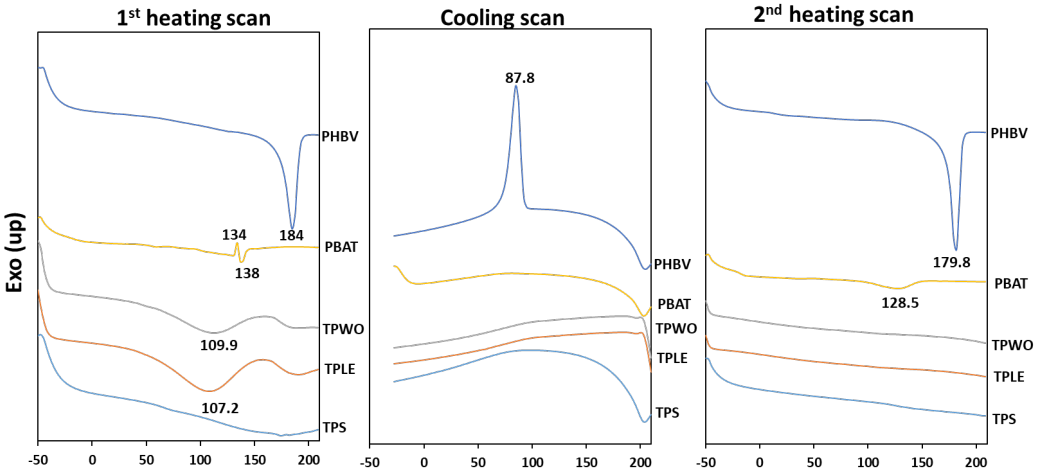


Figure 3. DSC analysis of neat TPS, TPLE, TPWO, PBAT, and PHBV.

- PHBV appeared T_m at 184°C and 179.8 °C for 1st heating scan and 2nd heating scan, respectively, while Tc appeared at 87.8 °C at cooling scan
- PBAT showed Tcc at 134 °C and T_m at 138 °C and 128.5 °C for the 1st heating scan and 2nd heating scan
- TPWO showed T_m at 109.0 °C for 1st heating scan and no information at cooling and 2nd heating scan
- TPLE showed T_m at 107.2 °C for 1st heating scan and no information at cooling and 2nd heating scan
- No information of T_m of TPS appeared in the 1st heating scan

3.4. Migration of glycerol

Due to its small molecular weight, it is very common that glycerol will migrate or leak out to the polymer surface during long time storage. This phenomenon created negative effect to polymer material, which used for producing end-used packaging product for food storage (e.g. tray, utensils, etc.). Therefore, the study about migration of glycerol is required to know about the amount of glycerol migrates to the sheet surface during storage. The result showed that significantly higher glycerol migrated to water with increasing soaking time due to higher swelling.

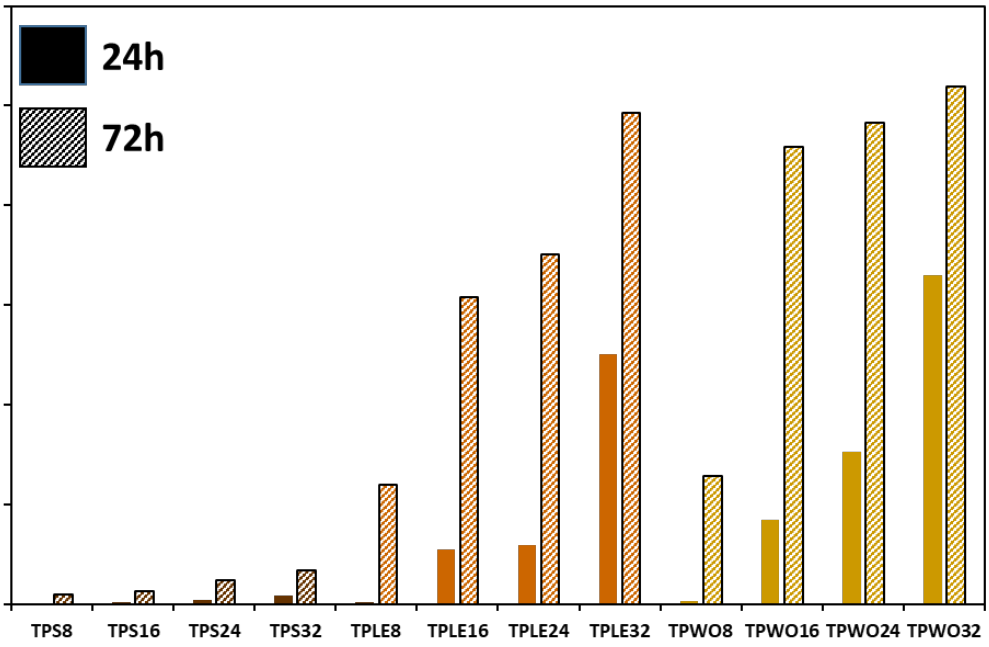


Figure 6. Migration of glycerol from PHBV/PBAT/TPS8, PHBV/PBAT/TPS32, PHBV/PBAT/TPLE8, PHBV/PBAT/TPLE32, PHBV/PBAT/TPWO8, PHBV/PBAT/TPWO32 blends.

TPS/PHBV/PBAT exhibited much lower migration of glycerol than TPLE/PHBV/PBAT and TPWO/PHBV/PBAT. 8 wt% of TPS, TPLE and TPWO showed almost no leakage of glycerol after 24h. TPWO/PHBV/PBAT exhibited the highest migration of glycerol after 24h and 72h. However, the migration of glycerol was still very small compared to the added glycerol to the matrix.

C. Outdoor activities

I am so lucky to visit Hokkaido during Autumn season, the weather is so good and the scene is magnificent.

First place that I visited was Maruyama Park and Hokkaido Jingu, located inside Maruyama park. There was some activities on that day, so that a lot of kids with uniform and photograph with their family

Hokkaido Jingu by KhanhDang

During the peak of Autumn at the end of Occtober, I took a day trip to visit Hōheikyō Dam at Jozankei area. I spent almost of my time for transportation from Sapporo city to Jozankei, then took another bus from Jozankei to Hōheikyō. However, it is totally worth my time to visit there. One of my best place I ever visit in my life.

Hōheikyō Dam by KhanhDang

Last place but It is one of the most beautiful place I visited in Sappro, The Gingko tree tunnel at Hokkaido University. I passed the Gingko trees almost everyday, I had seen them since the leaves were green, then changing slowly to light yellow and finally golden color. It is worth waiting to see that moment. I believe that not only me but everyone in Sapporo also waited to see that moment. I joined the Konyousai Festival, and dived myself in the crowd, I enjoyed the atmosphere there.

Gingko thee tunnel at Hokkaido University by KhanhDang

Last activity that I joined was the presentation from Professor. Rangrong Yoksan, she arrived Japan just 1 day before I went back Thailand, it is so good that I have a photo with Professor Morikawa, Professor Matsumoto, Professor Rangrong and all members in Prof. Matsumoto's laboratory. It's one of my best moment ever!

D. Acknowledgments

First of all, I would like to express my sincere gratitude to Professor Morikawa and JICA scholarship for giving me a big chance to go to Sapporo City, Japan for visiting, learning and enjoying there. At the moment, when I am writing these words, all memories come back to me, the best moment ever!

Secondly, I would like to thank Professor Rangrong Yoksan. I have worked with her since I studied M.Sc degree. She always support me when I have problems and give me many chances to visit other countries for archiving more knowledge and opening up my mind.

Last but not least, I would like to acknowledge Professor Matsumoto and all of my friends in Professor Matsumoto's laboratory. They are really kind and friendly, they fully supported me when I needed any equipment and guideline to use the machine there. Without them, I am sure that I cannot finish my work there.