KRICT Korea Research Institute of Chemical Technology

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# Toughened Biodegradable PLLA/PBAT Composites Prepared via Reactive Compatibilization with Poly(Styrene-*co*-GMA) Polymeric Compatibilizers


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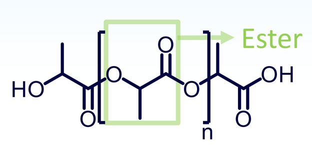
## Motivation & Objectives

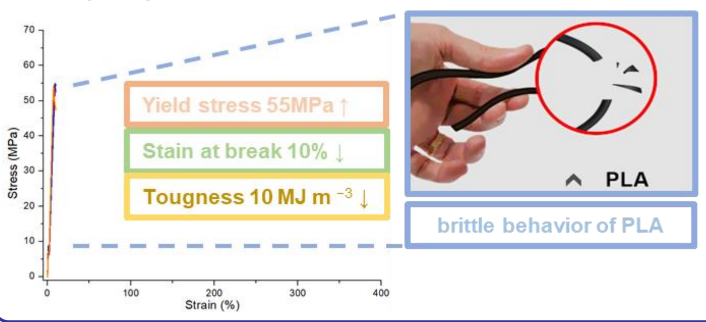
Mechanical property enhancement of PLLA through PBAT blending with styrene-GMA compatibilizer

### PLLA Overview




Polylactic acid (PLLA)
Rigid bio-based polymer

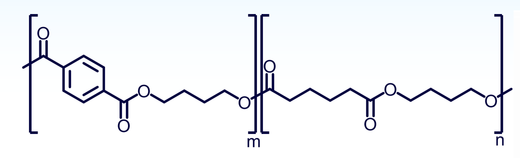
- Renewable
- Biodegradable
- Biocompatible





PLA application

### PBAT: Biodegradable Copolymer

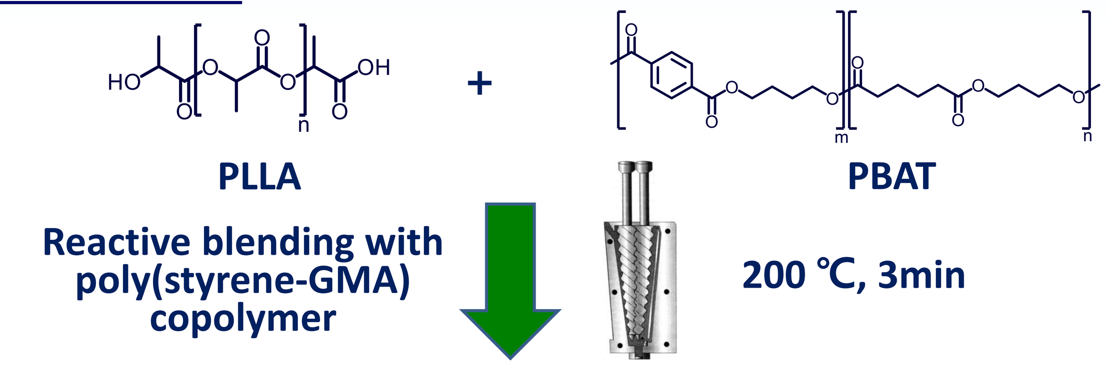


Polybutylene adipate terephthalate (PBAT)


Soft biodegradable polymer


PBAT Market
*https://www.transparencymarketresearch.com*

### Solving PLLA Brittle Disadvantages by Blending with PBAT



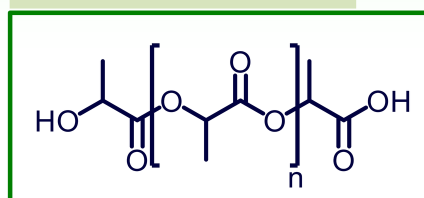

Tough PLLA/PBAT Composites

- Increase in packaging because of biocompatibility, biodegradability of PLLA and PBAT
- high mechanical strength and excellent processability

## Experimental Section

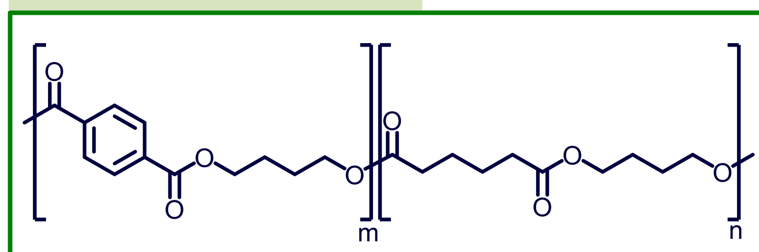
### Materials

**Commercial PLLA**



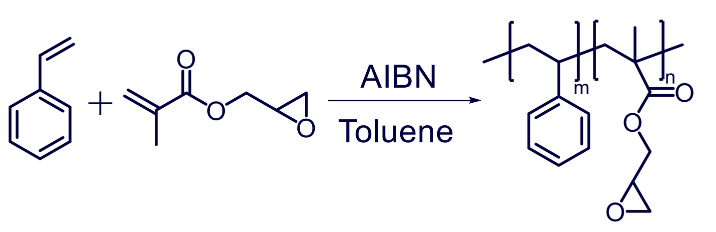
- $M_w$ (kg/mol) : 127 (PDI : 1.27)
- Specific Gravity : 1.24
- Nature Works LLC (Ingeo™ 4060D)

**Commercial PBAT**



- $M_n$ (kg/mol) : 50
- PDI : 2.0
- Specific Gravity : 1.26
- Wango A400

**Poly(styrene-*co*-GMA) (PS-*co*-GMA)**

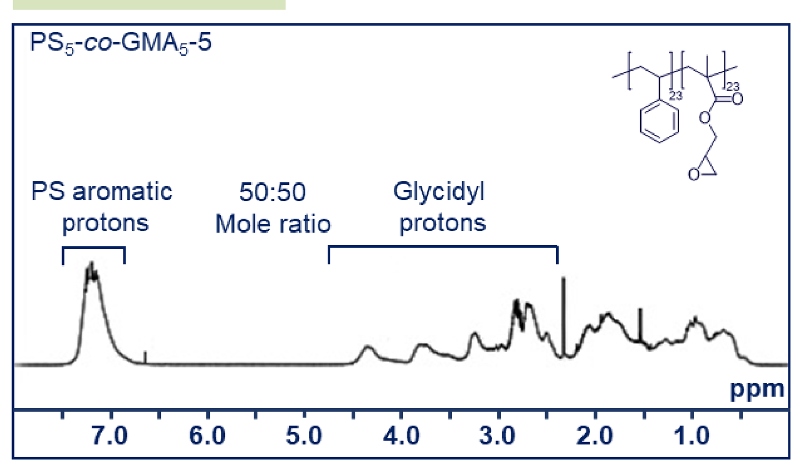



- $M_n$ (kg/mol) : 4.6-17.1
- PDI : 1.5-1.7
- Epoxy eq.: 178-621

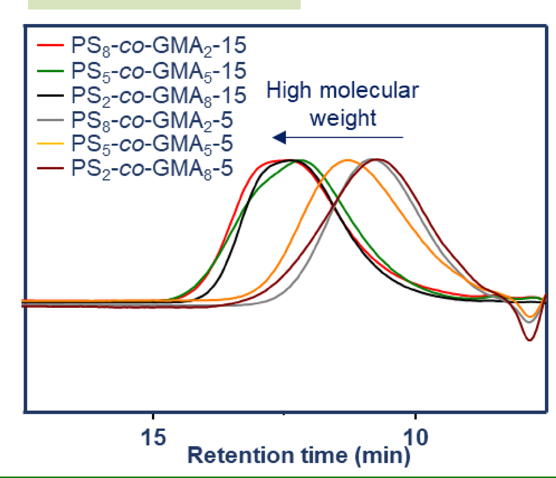
### Physical properties of synthetic poly(styrene-co-GMA) copolymers

| Copolymers | S/G ratio theoretical | S/G ratio experimental | Epoxy eq. | Styrene conv. (%) | GMA conv. (%) | Yield (%) | $M_{n,SEC}$ (kg mol$^{-1}$) | PDI | $T_g$ (°C) | $T_{d,5\%}$ (°C) |
|---|---|---|---|---|---|---|---|---|---|---|
| $PS_8$-*co*-$GMA_2$-15 | 80/20 | 77/23 | 621.2 | 75.9 | 91.4 | 92.6 | 15.1 | 1.7 | 88.2 | 339 |
| $PS_5$-*co*-$GMA_5$-15 | 45/55 | 51/49 | 261.3 | 92.1 | 94.0 | 86.2 | 17.1 | 1.6 | 52.5 | 318 |
| $PS_2$-*co*-$GMA_8$-15 | 20/80 | 29/75 | 186.7 | 99.9 | 98.0 | 83.5 | 15.6 | 1.5 | 49.4 | 284 |
| $PS_8$-*co*-$GMA_2$-5 | 80/20 | 80/20 | 558.2 | 93.1 | 97.8 | 71.5 | 4.6 | 1.5 | 55.7 | 306 |
| $PS_5$-*co*-$GMA_5$-5 | 45/55 | 50/50 | 267.4 | 99.9 | 98.2 | 89.6 | 5.7 | 1.7 | 53.8 | 294 |
| $PS_2$-*co*-$GMA_8$-5 | 20/80 | 24/76 | 178.4 | 99.9 | 97.9 | 77.5 | 4.8 | 1.6 | 48.3 | 256 |
| BASF ADR | | | 301.7 | | | | 4.7 | 1.7 | 60.6 | 308 |

**$^1$H-NMR**




**SEC analysis**



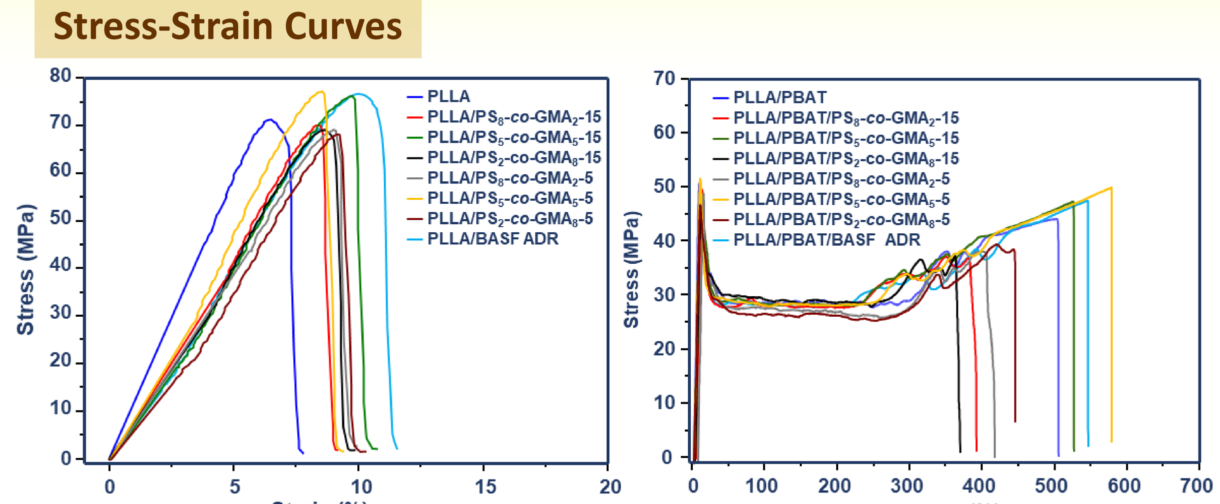

### Testing and Characterization

- *$^1$H-NMR : Bruker DRX-500 sprectrometer (500 MHz)*
- *SEC : Agilent 1260 Infinity LC system equipped with a refractive index detector*
- *Impact Strength : Tinus Olsen Izod Impact Tester; Notched Izod Impact Tests (ISO 180 method)*
- *Tensile Strength and Elongation : UTM QRS-S11H, ASTM D1708; Modulus, Stress, Strain and Tensile Toughness*
- *Differential Scanning Calorimetry (DSC) : TA Q-1000 DSC; $T_g$ & $T_m$*
- *Scanning Electron Microscope (SEM) : SEM XL30 ESEM FEG; FEI Co. ; Fractured Surfaces after Tensile Test*

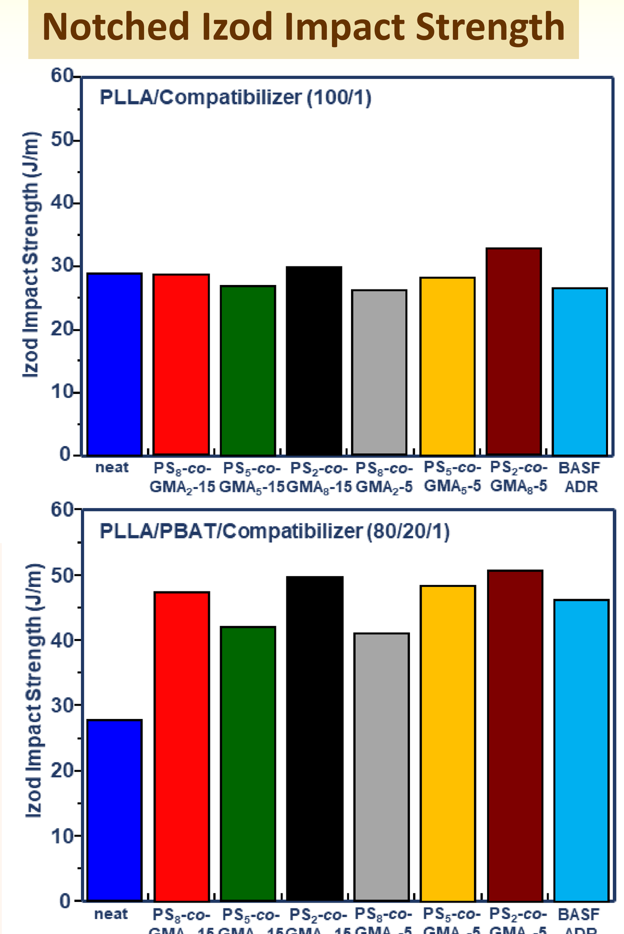
## Results and Discussion

### Tensile and Impact Properties

**Stress-Strain Curves**




**Notched Izod Impact Strength**



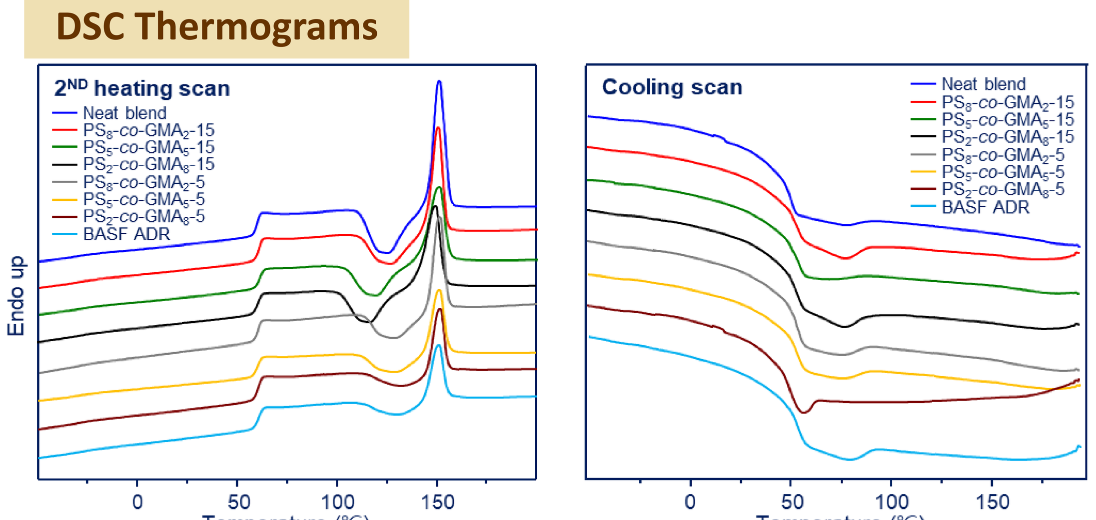

- Binary composites blended with PLLA and compatibilizers exhibited improved properties in yield stress, but had no significant effects on strain and impact properties.
- In the composites blended with PLLA, PBAT and compatibilizer of $PS_5$-*co*-$GMA_5$-15 and $PS_5$-*co*-$GMA_5$-5, the strain and impact strength properties were improved compared to the properties of the other composites, which was more dependent on the composition of styrene and epoxy groups than molecular weight.
- In particular, in the composites using the compatibilizer, the impact strength were improved by more than twice that of the PLLA/PBAT composite without compatibilizer, which is believed to be due to the reaction of the terminal carboxylic acid group with the epoxy group contained in the compatibilizer.

**Mechanical Properties of Blends**

| Blends | Young's modulus (GPa) | Yield stress (MPa) | Strain at break (MPa) | Izod impact strength (J m$^{-1}$) |
|---|---|---|---|---|
| PLLA (100) | 1127 ± 117 | 68 ± 6 | 8 ± 1 | 29.0 |
| PLLA/$PS_8$-*co*-$GMA_2$-15 (100/1) | 882 ± 30 | 68 ± 3 | 10 ± 1 | 28.5 |
| PLLA/$PS_5$-*co*-$GMA_5$-15 (100/1) | 888 ± 45 | 76 ± 7 | 12 ± 2 | 27.1 |
| PLLA/$PS_2$-*co*-$GMA_8$-15 (100/1) | 830 ± 21 | 69 ± 4 | 10 ± 1 | 29.9 |
| PLLA/$PS_8$-*co*-$GMA_2$-5 (100/1) | 871 ± 71 | 68 ± 8 | 9 ± 1 | 26.1 |
| PLLA/$PS_5$-*co*-$GMA_5$-5 (100/1) | 944 ± 66 | 74 ± 6 | 9 ± 1 | 28.2 |
| PLLA/$PS_2$-*co*-$GMA_8$-5 (100/1) | 752 ± 20 | 67 ± 6 | 11 ± 1 | 32.8 |
| PLLA/BASF ADR (100/1) | 836 ± 44 | 75 ± 3 | 12 ± 1 | 26.6 |
| PLLA/PBAT (80/20) | 839 ± 33 | 51 ± 1 | 509 ± 26 | 27.8 |
| PLLA/PBAT/$PS_8$-*co*-$GMA_2$-15 (80/20/1) | 728 ± 16 | 55 ± 9 | 439 ± 122 | 47.6 |
| PLLA/PBAT/$PS_5$-*co*-$GMA_5$-15 (80/20/1) | 695 ± 32 | 54 ± 9 | 541 ± 22 | 42.0 |
| PLLA/PBAT/$PS_2$-*co*-$GMA_8$-15 (80/20/1) | 683 ± 9 | 52 ± 9 | 347 ± 277 | 49.7 |
| PLLA/PBAT/$PS_8$-*co*-$GMA_2$-5 (80/20/1) | 716 ± 9 | 49 ± 9 | 421 ± 218 | 40.9 |
| PLLA/PBAT/$PS_5$-*co*-$GMA_5$-5 (80/20/1) | 684 ± 44 | 56 ± 7 | 572 ± 39 | 48.6 |
| PLLA/PBAT/$PS_2$-*co*-$GMA_8$-5 (80/20/1) | 640 ± 2 | 47 ± 2 | 305 ± 217 | 50.9 |
| PLLA/PBAT/BASF ADR (80/20/1) | 635 ± 2 | 50 ± 2 | 530 ± 33 | 46.2 |

### Thermal and Crystallization Behaviors

**DSC Thermograms**

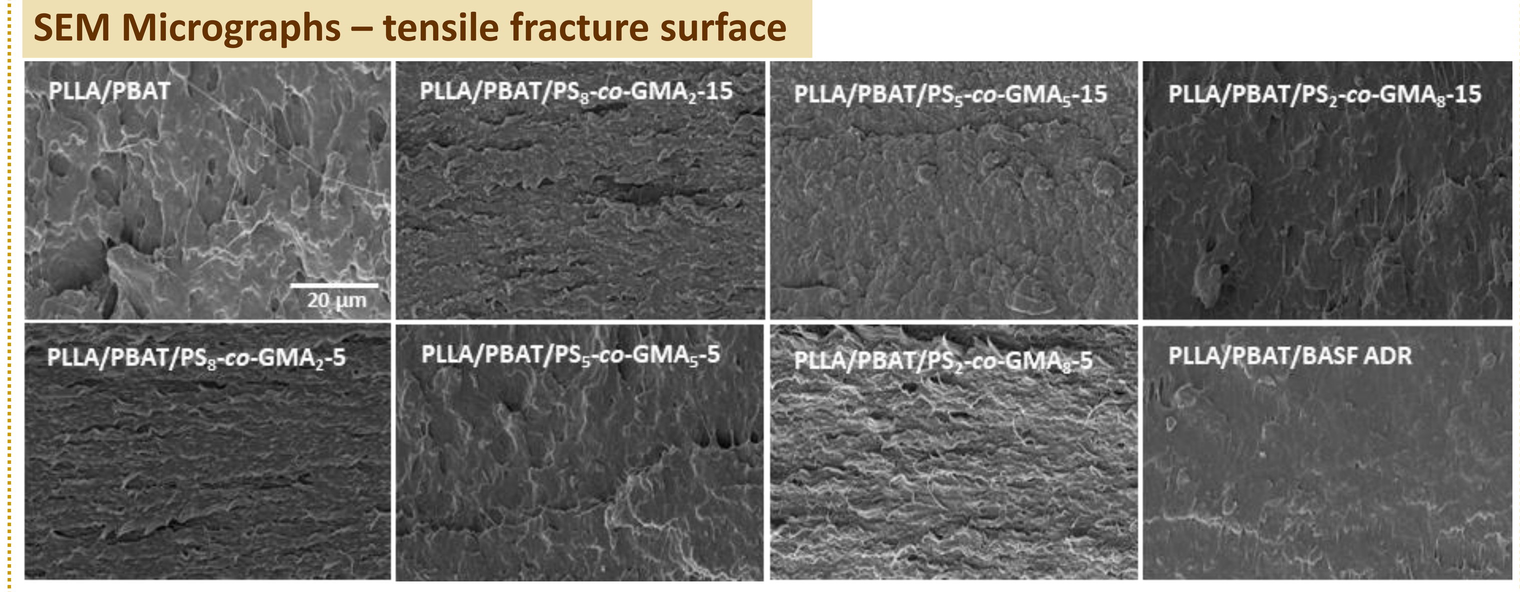



| PLLA/PBAT/ compatibilizer blend (80/20/1) | $T_{g,PBAT,PLLA}$ (℃) | $T_{m,PLLA}$ (℃) | $T_c$ (℃) | $\Delta H_{f\ PLLA}$ (J g$^{-1}$) | $X_{polymer}$ (%,DSC) | $T_{d,5\%}$ (℃) |
|---|---|---|---|---|---|---|
| Neat | -29.6 | 151 | 80 | 22 | 10 | 326 |
| $PS_5$-*co*-$GMA_5$-15 | -31.6 | 150 | 79 | 16 | 8 | 330 |
| $PS_8$-*co*-$GMA_2$-15 | -30.6 | 150 | | 16 | 8 | 320 |
| $PS_2$-*co*-$GMA_8$-15 | -30.6 | 149 | 80 | 17 | 8 | 329 |
| $PS_8$-*co*-$GMA_2$-5 | -30.6 | 151 | 80 | 10 | 5 | 327 |
| $PS_5$-*co*-$GMA_5$-5 | -30.6 | 151 | 79 | 11 | 5 | 328 |
| $PS_2$-*co*-$GMA_8$-5 | -30.6 | 151 | | 13 | 6 | 328 |
| BASF ADR | -30.6 | 151 | 82 | 10 | 5 | 335 |

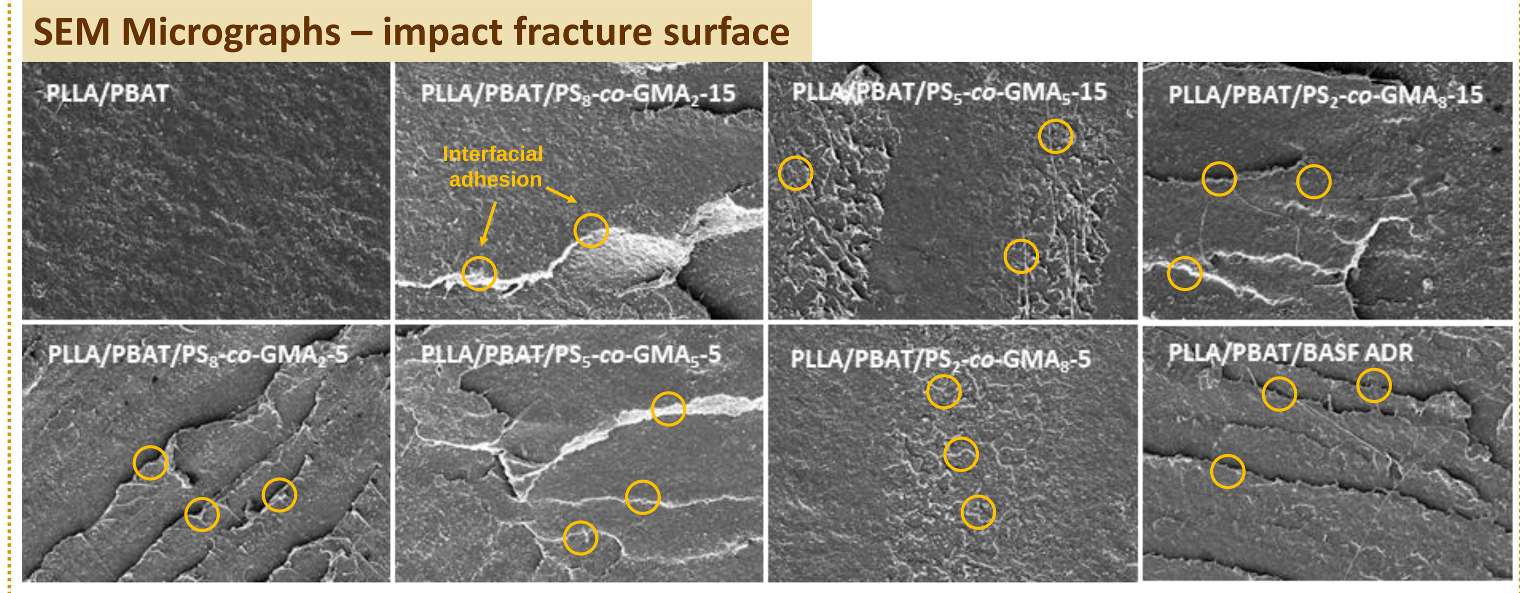
- In the PLLA/PBAT composites, $T_g$ and $T_m$ of PBAT and PLLA did not change regardless of the compatibilizer, and showed a great influence on the degree of crystallinity (calculated by 100% crystallinity of PLLA, $\Delta H_f^\circ = 213.0$ J g$^{-1}$).
- That is, the smaller the molecular weight of the compatibilizer, the lower the crystallinity of PLLA by inhibiting the crystallization rate of PLLA.

### Fractured Surface Morphology

**SEM Micrographs – tensile fracture surface**

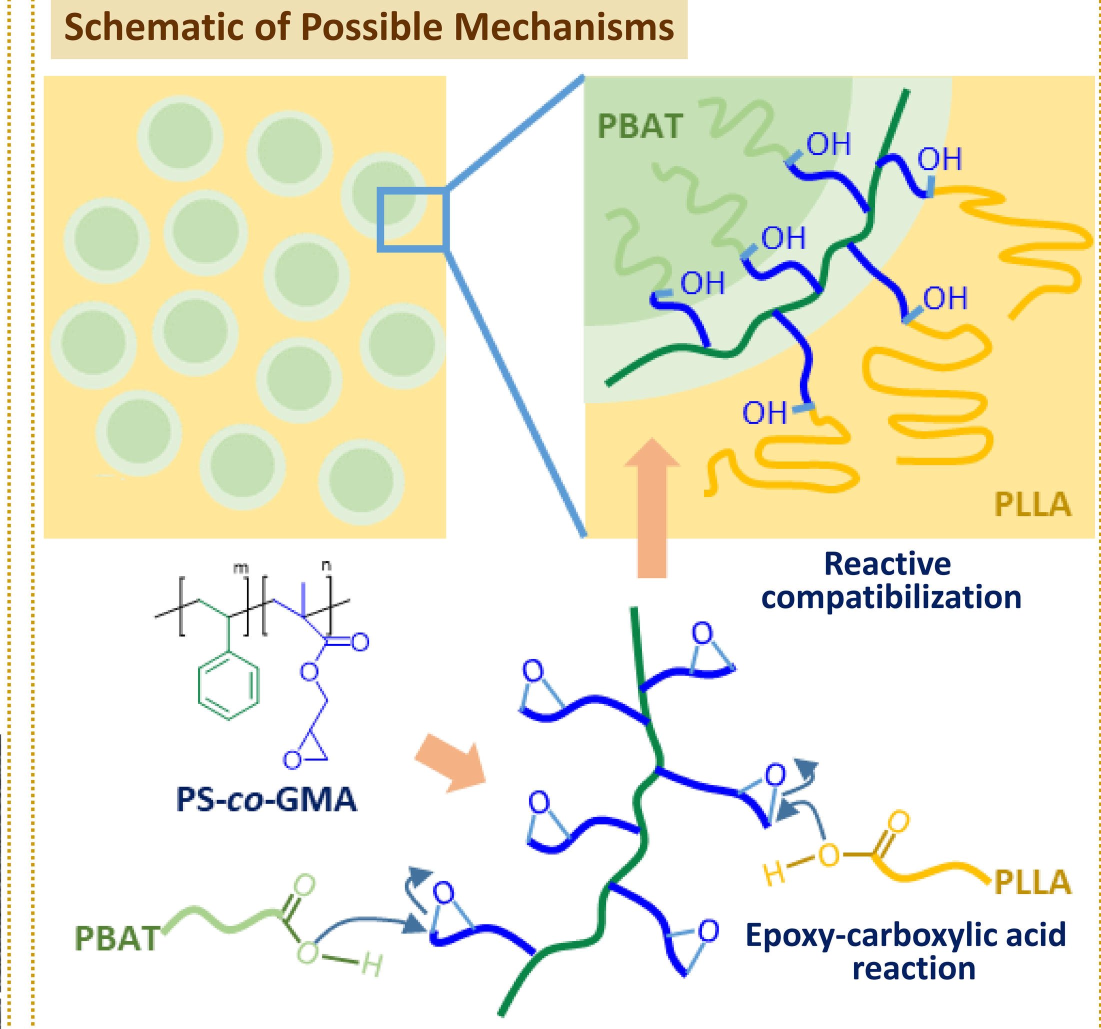



**SEM Micrographs – impact fracture surface**




### Toughening Mechanisms

**Schematic of Possible Mechanisms**




### Acknowledgments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