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PROJECT TITLE:

Sustainable Biodegradable Green Nanocomposites From Bacterial Bioplastic For Automotive Applications

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Industrial Partners:

General Motors, Metabolix Inc and Nanocor

Environment

Giant Pollution Mass at Sea

When an oceanic garbage patch the size of Texas dumps some of its treasures along the West Coast this summer, By Marsha Walton -- **CNN**

YOU

'World Environment Week'

- To overcome the problems due to plastic wastes.
- To substitute non-degradable petroleum based polymers with biodegradable plastics.
- To introduce bioplastics from renewable resources into market.

Plastic ... Cleanup Costs Appro... Billion Dollars ...

...Moore/ Natural History v.112, n.9, Nov. 2003

HAWAII

NORTH PACIFIC GYRE

BIOPOLYMERS: CLASSIFICATION

Renewable Resource-based

- PLA Polymer (From Corn)
- Cellulosic plastics
- Soy-based plastics
- Starch plastics

Microbial synthesized

- Polyhydroxy alkanoates (PHAs)
- Polyhydoxybutyrate co-valerate (PHBV)

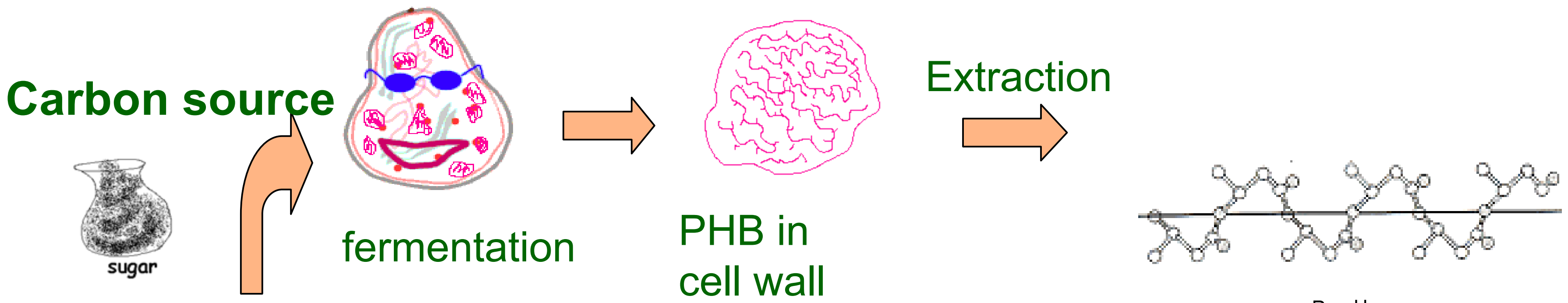
Petro-based synthetic

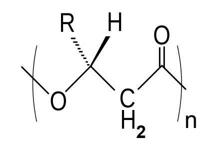
- Aliphatic polyester
- Aliphatic-aromatic polyesters
- Polyesteramides
- Polyvinyl alcohols

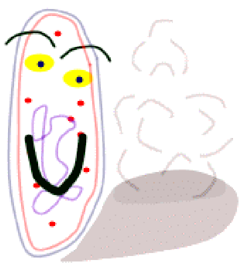
Petro-Bio (Mixed) Sources

- Sorona
- Biobased Polyurethane
- Biobased epoxy
- Blends etc

Polyhydroxybutyrate (PHB)





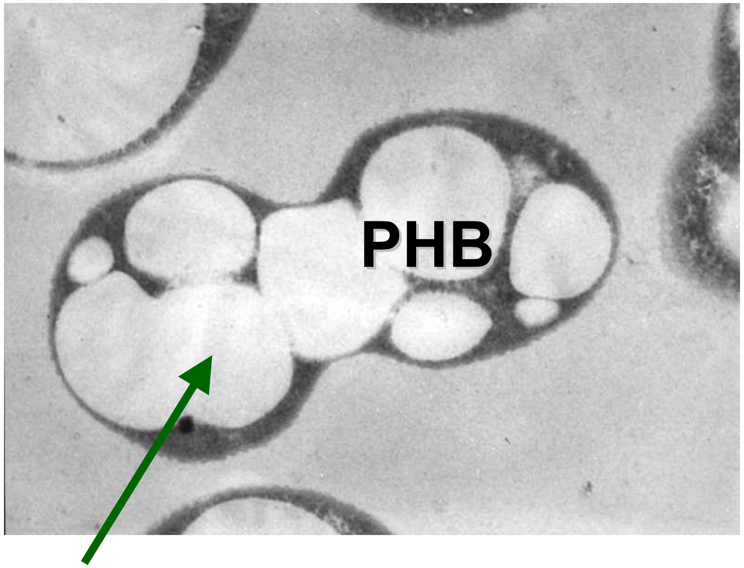


Bacteria

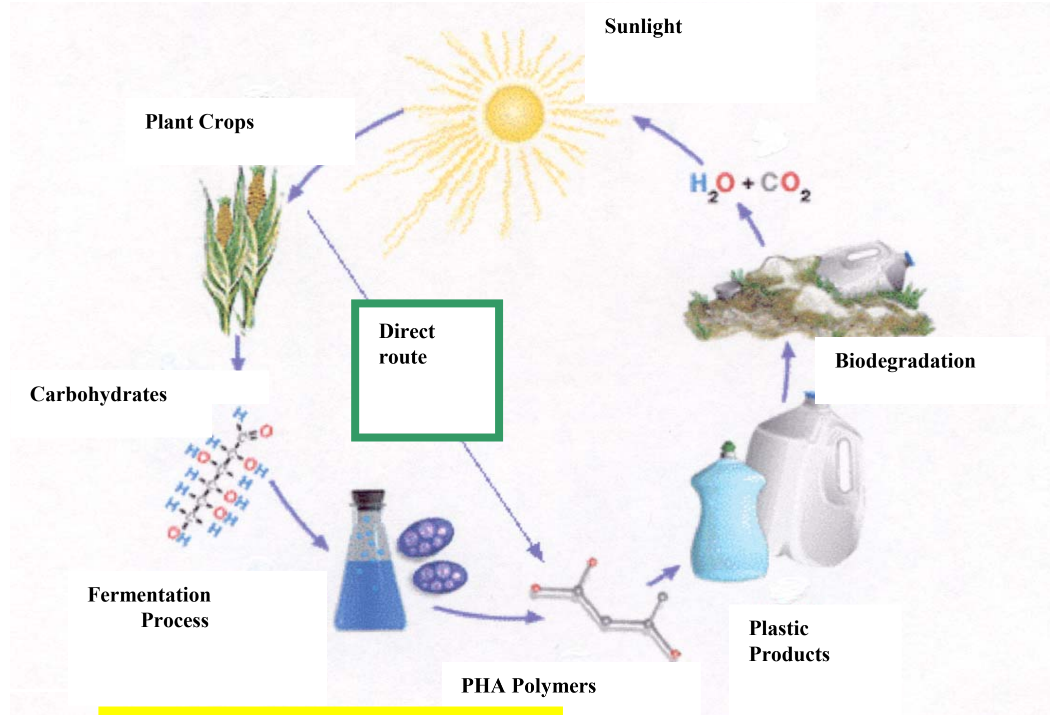
- Polyhydroxybutyrate (PHB) is a linear thermoplastic polyester produced by controlled bacterial fermentation process.
- Discovered by French microbiologist *Maurice Lemoigne* in 1923.
- Next generation PHB will come from Transgenic plants/micro-organisms
- Typical cost ranges from 1-2 $/lb

Ref: Marchessualt, R. H.; TRIP, 1994, **4**, 163

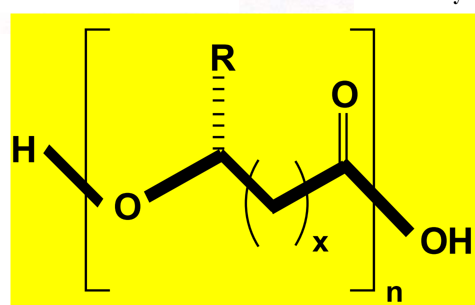
Bacterial Polyester Developments



White patches in microorganism



PHA	R
PHB	$-CH_3$
PHV	$-CH_2CH_3$
PHBV (Biopol®)	$-CH_3$ & CH_2CH_3
PHBHx	$-CH_3$ & $-CH_2CH_2CH_3$
PHBO	$-CH_3$ & $-(CH_2)_4CH_3$



PHA structure

R = Hydrocarbon (up to C13)

x = 1 to 3 or more

Courtesy: Metabolix & Biomer

BACTERIAL BIOPLASTIC

ADVANATAGES

- ▲ Biodegradable
- ▲ *Eco*-friendly synthesis
- ▲ Excellent processability
- ▲ From renewable resource
- ▲ Good mechanical properties

SHORTCOMINGS

- ▲ Poor interaction with fibers
- ▲ Narrow processing window
- ▲ Lack of reactive groups
- ▲ Thermal degradation
- ▲ Brittleness

OBJECTIVES

- ▲ To overcome some of the inherent material limitations of PHB/PHA bioplastics.
- ▲ To study the effect of PHB/PHAs modification on its Thermal and Morphological properties.
- ▲ To synthesize functionalized PHB/PHAs as a compatibilizer in PHB/PHAs based blends, and nanocomposites.

PART – I

“Functionalization and characterization of PHB and its derivatives via Solvent-free Reactive Extrusion”

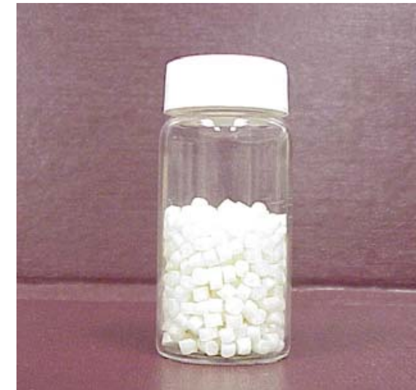
MATERIALS & PROCESSING

- **PHB-P226- from Biomer Germany**
- **Maleic Anhydride:MA**
- **Octadecenyl Succinic Anhydride: ODSA**
- **Trigonox 101 45B (2,5-dimethylhexane-2,5-ditertbutyl peroxide)**

EXPERIMENTAL SETUP

DSM MICRO 15, HOLLAND

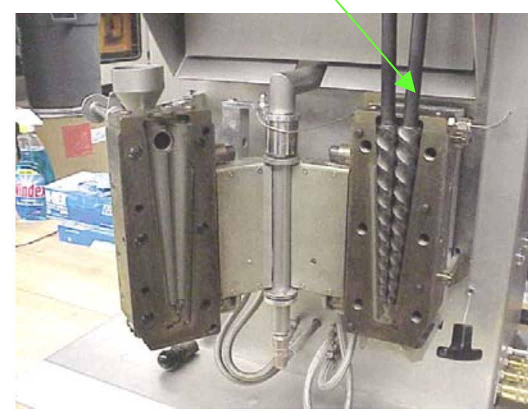
MA T 101



PHB P226

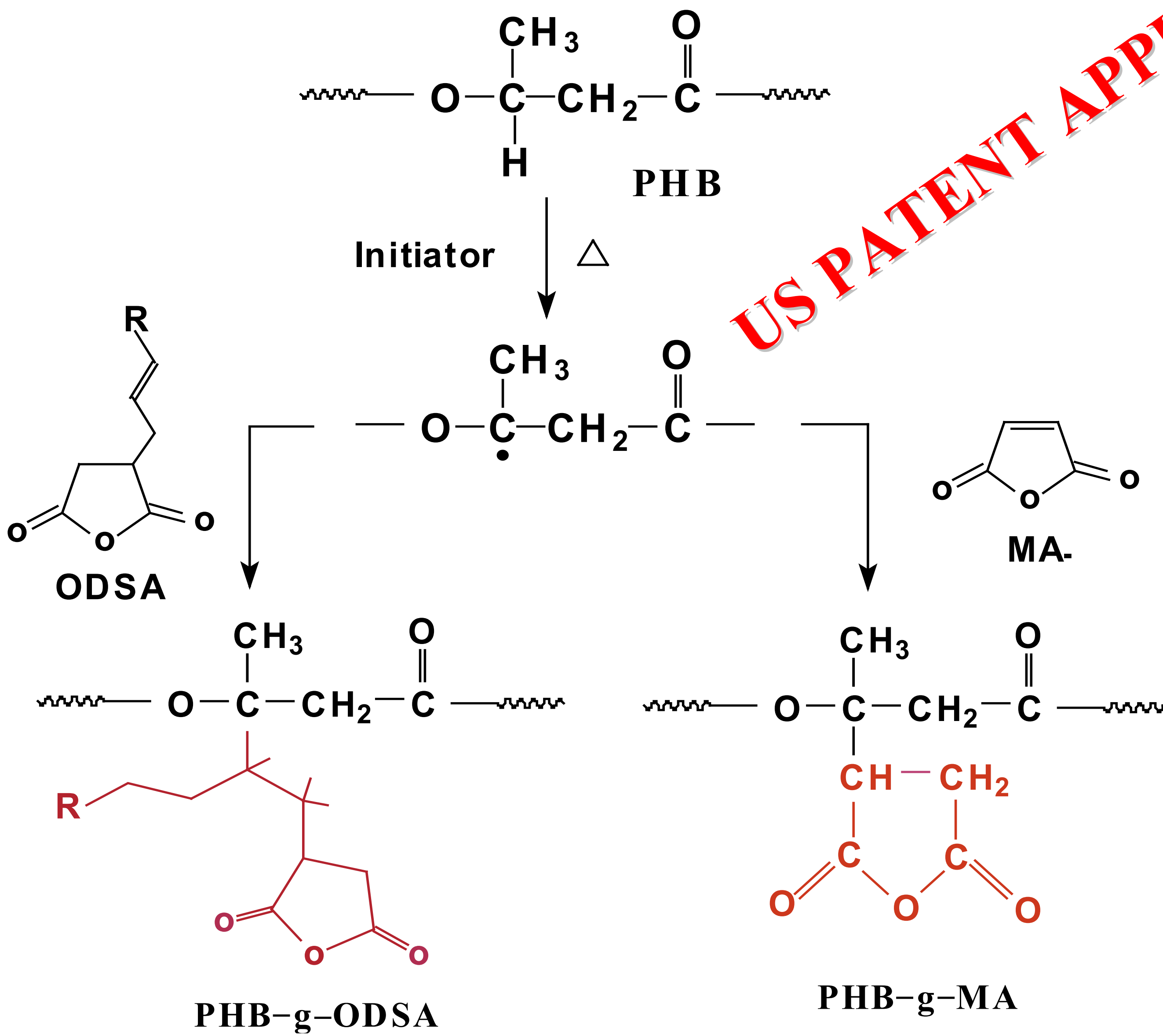
Feeder

Twin Screw Extruder



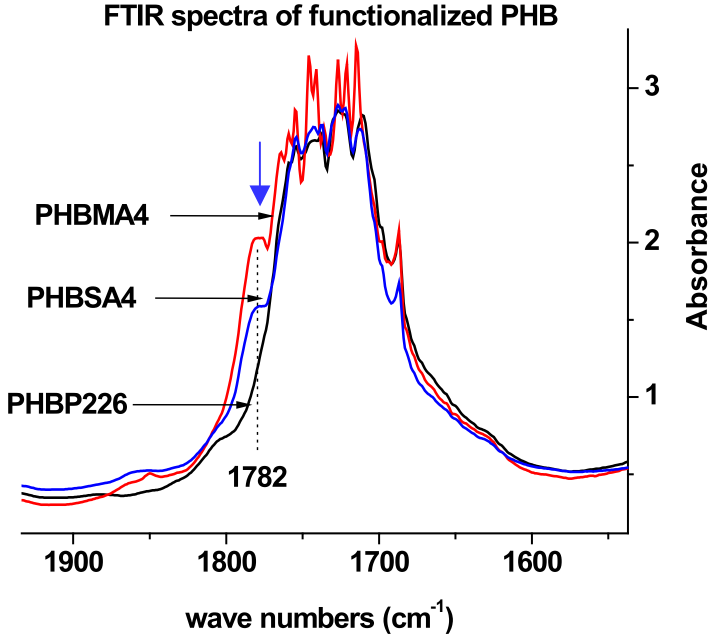
MECHANISM

US PATENT APPLIED

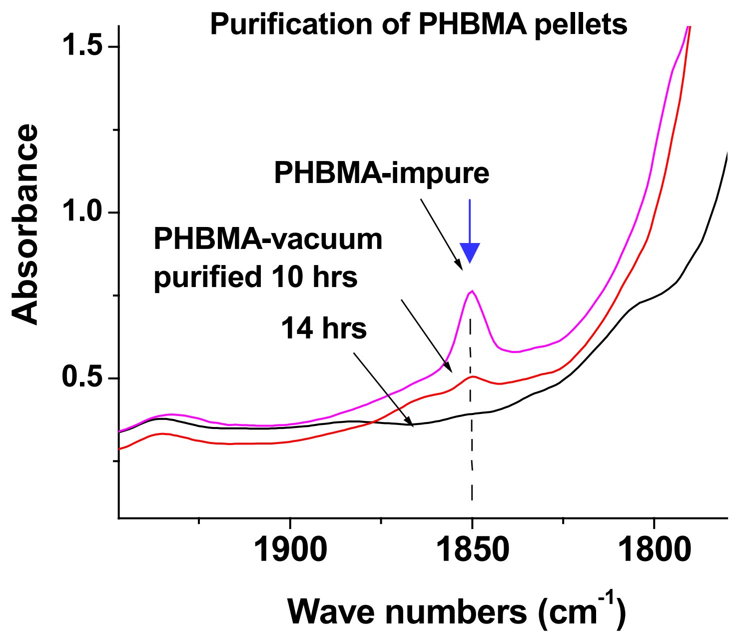


Free radical grafting of MA/ODSA onto PHB via reactive extrusion

FT-IR



▲ Peak at 1782 cm^{-1} indicates anhydride groups grafted onto PHB backbone.

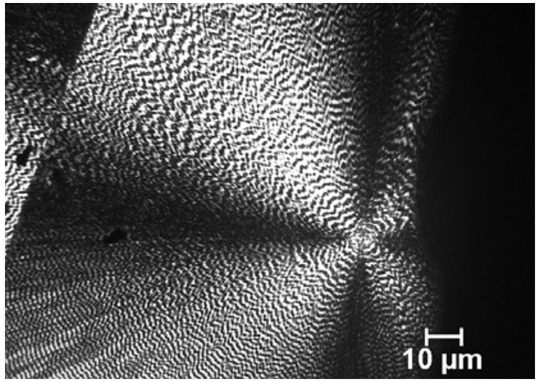


NAME	Initiator wt%	MA/ ODSA wt%	ACID No.	% AN
PHBMA4	1.8	4	23	2.0
PHBSA4	1.8	8	14	1.3

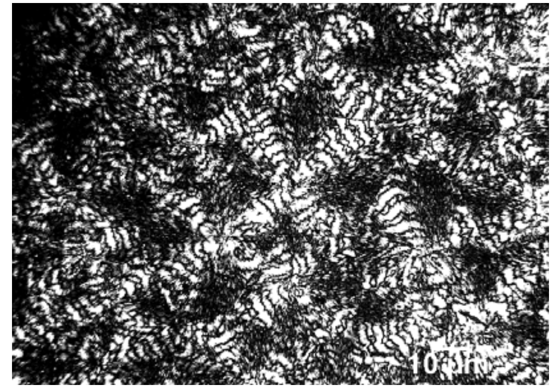
▲ Peak at 1850 cm^{-1} corresponds to unreacted MA in the PHB matrix.

▲ Vacuum drying of pellets at 80 ^{o}C for > 12 hrs ensures complete removal of unreacted MA.

OPTICAL MICROSCOPY

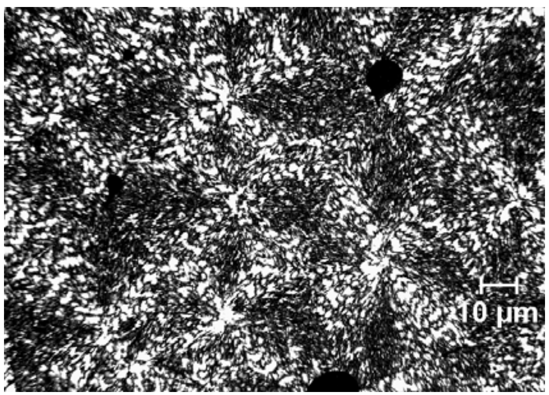


PHB



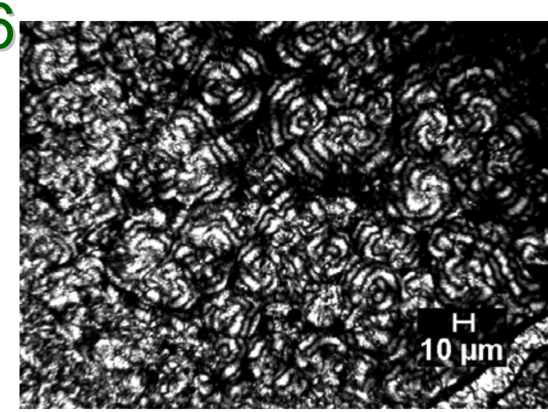
PHBP226

PHBMA4

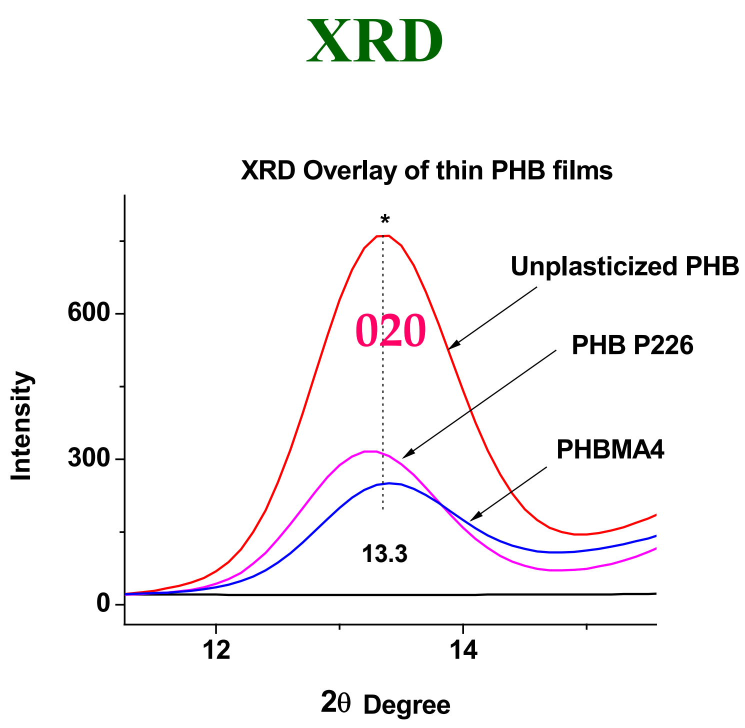


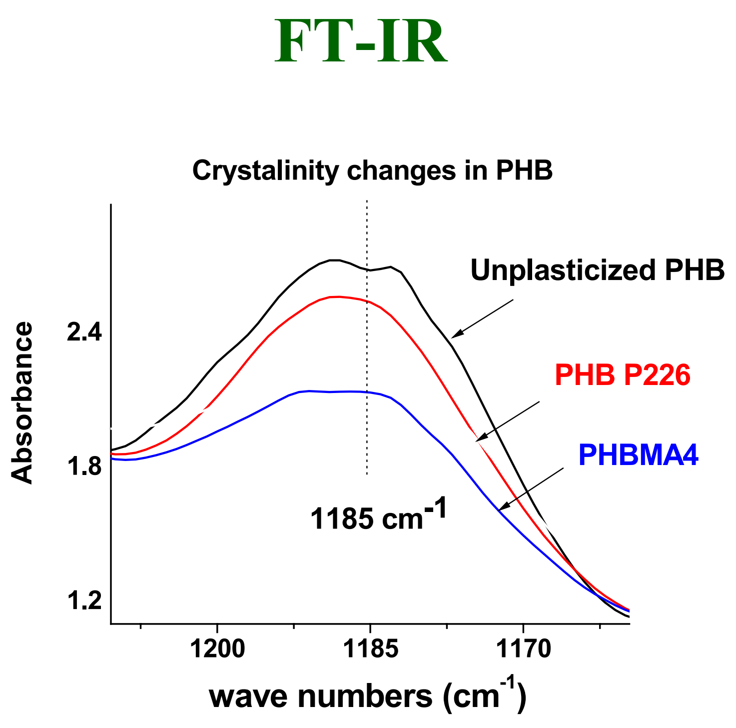
Thin (25 µ) films heated and cooled @ 20 °C/min

PHBSA4



- **Large spherulites with distinct maltase patterns and well defined boundaries are due to highly regular arrangement of pristine PHB chains**
- **Drastic decrease in spherulite size upon maleation results from hindered / irregular rearrangement of PHB chains bearing large anhydride groups**
- **Smaller spherulites size results in less brittle material**





- **XRD peak at 2θ =13.3° corresponding to crystalline region decreases upon maleation of PHB.**
- **Decrease in crystallinity of PHB upon maleation is evident from depletion of 1185 cm^{-1} peak intensity in FTIR spectral overlay.**
- **Intensity of crystalline peaks in both the graphs depend on % anhydride in the PHB backbone.**

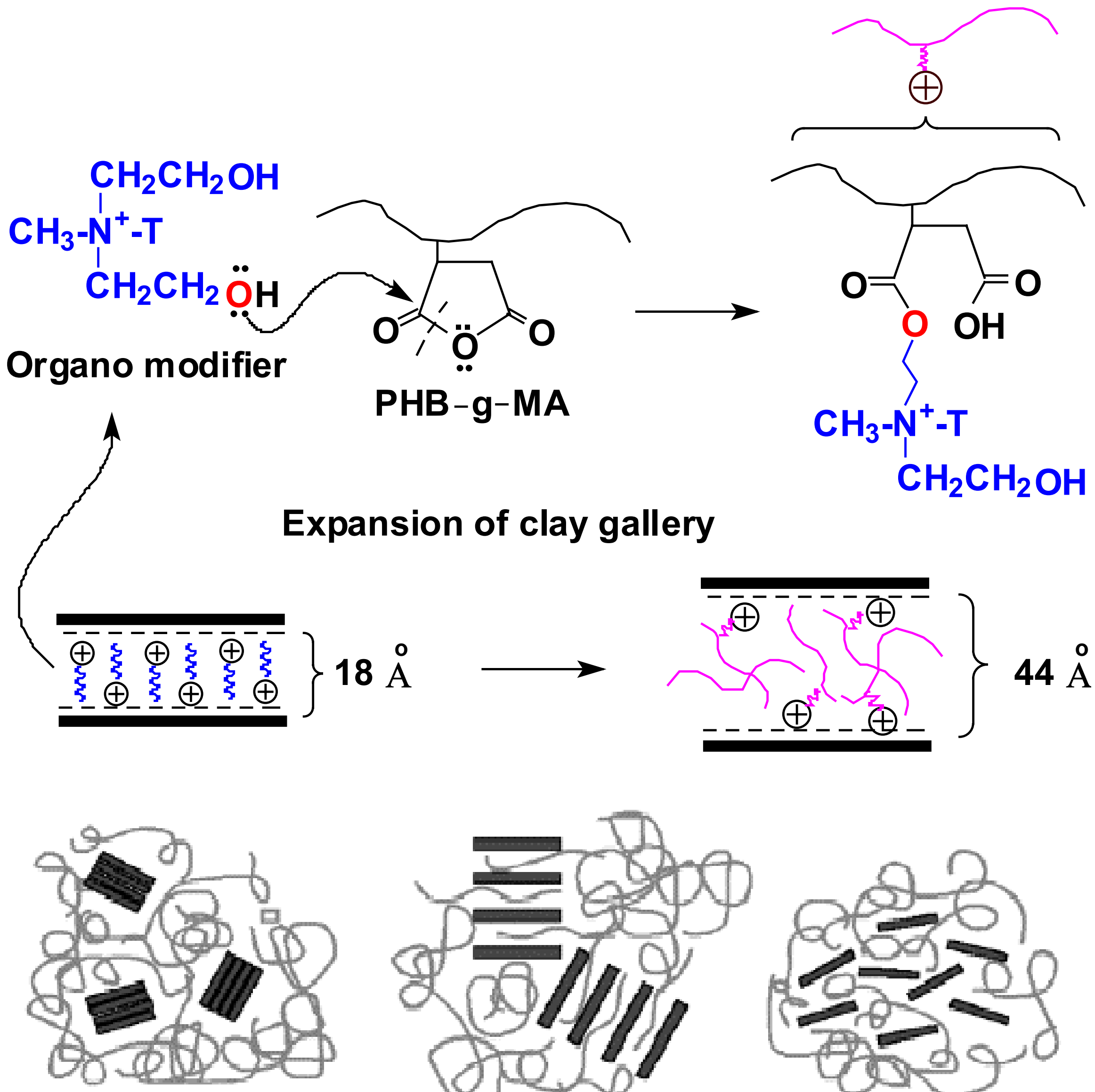
PART – I: CONCLUSIONS

- ✓ Reactive extrusion can be successfully employed for the grafting of functional groups onto PHB backbone by a solvent free process.
- ✓ Degree of grafting can be controlled by varying the reagent concentrations and residence time of melt in the extruder.
- ✓ Desired changes in the thermal and morphological properties of PHB can be achieved upon its functionalization.
- ✓ Decrease in PHB spherulite size with the grafting degree is due to the imperfect crystal formation and irregular rearrangement of PHB chains bearing bulky anhydride groups.
- ✓ Smaller crystal size leads to a less brittle material.

PART – II-A

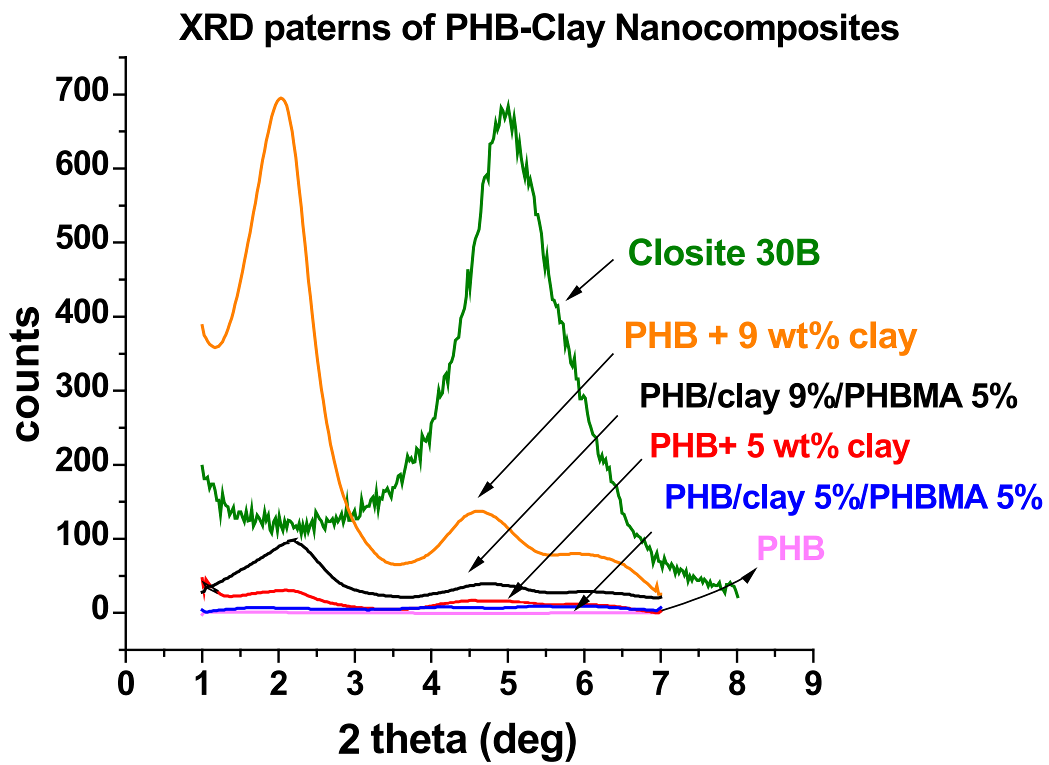
COMPTIBILIZED GREEN-NANOCOMPOSITES FROM PHB and NANOCLAY

MECHANISM



CH_2CH_2OH
CH_3-N^+-T
CH_2CH_2 OH
Organo modifier
O
O
O
PHB–g–MA
O
O
OH
CH_3-N^+-T
CH_2CH_2OH
Expansion of clay gallery
18 Å
44 Å

XRD ANALYSIS

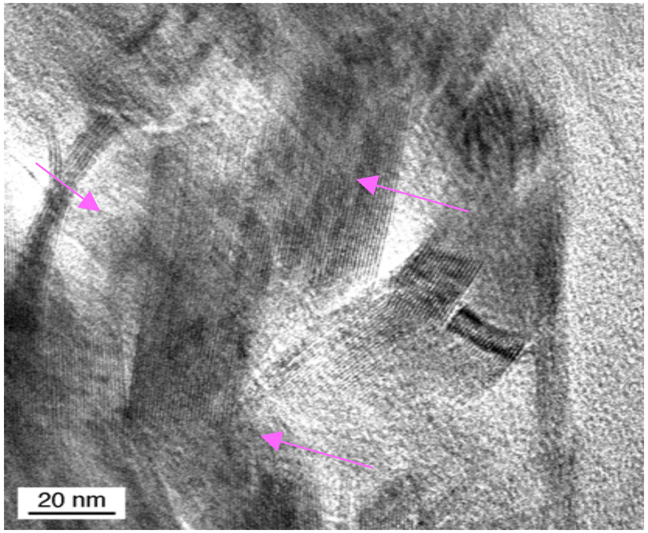


The d_{001} spacing in organo-clay sample *is 18 Å,* and that of the PHB/clay sample is *44 Å*.

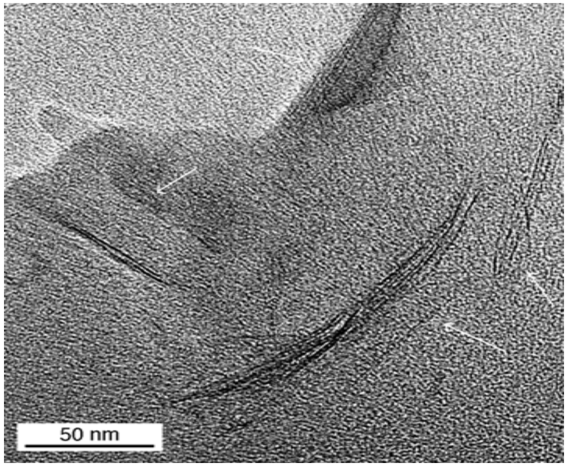
Upon intercalation, peak corresponding to clay crystallites shifts from 5° to 2° on 2θ axis

Decrease in the intensity of intercalation peak at 2θ = 2° indicates more number of exfoliated clay plates

TEM ANALYSIS



PHB + 9 wt% clay
(arrow indicates clay tactoid)



PHB + 9 wt% clay+ 5 wt% PHB-g-MA
(arrow indicates exfoliated clay)

Clay tends to remain as tactoids in the PHB matrix
Addition of small of amount of PHB-g-MA facilitates Clay exfoliation

PART – II-A : CONCLUSION

- ✓ PHB-MA is a good compatibilizer for PHB Nanocomposites

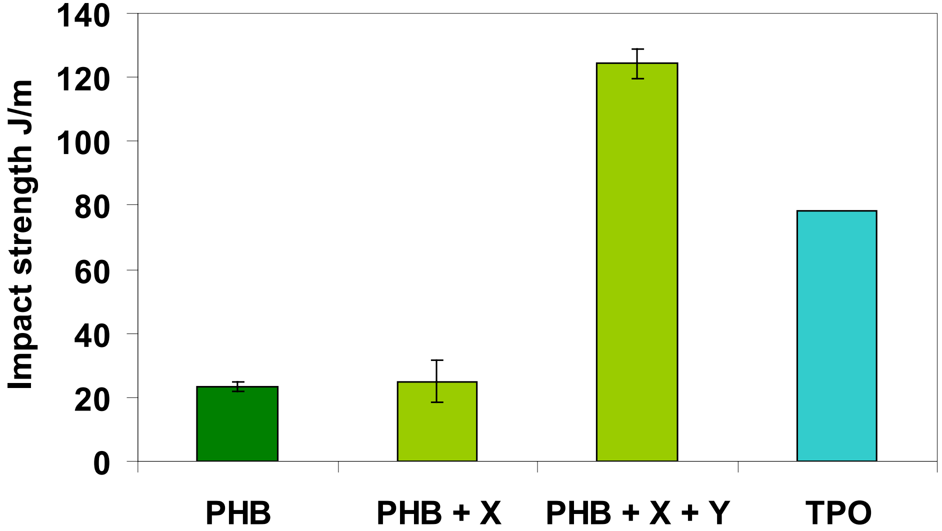
PART – IIB
Automotive application of nanocomposites

OBJECTIVES

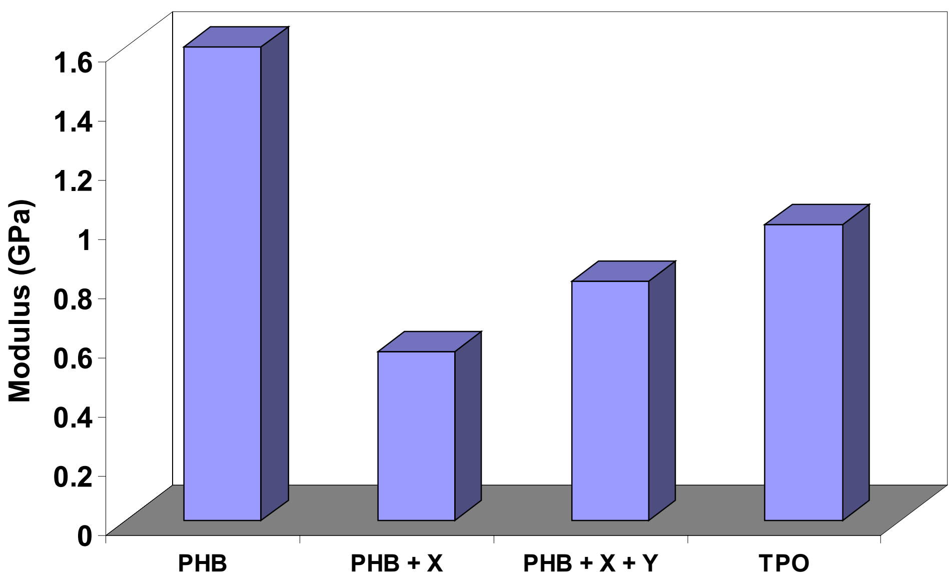
- PP's low impact strength led to the development of TPO but at the cost of flexural strength and scratch resistance.
- Clay-reinforced TPO has overcome these drawbacks and was the first instance of a nanocomposite being used for exterior automotive applications.
- However PP and subsequently TPO are both non-biodegradable and also petroleum-based.

- This project aims to replace these conventional petroleum-based clay-reinforced toughened polyolefin (TPO) materials with alternative 'Green' materials which will have comparable properties with TPO and also be biodegradable and recyclable.

Results (*Patent application on process*)



40% X does not affect the impact strength of PHB. But addition of 10 % additive Y improves the impact strength by 440% (50%more than TPO)



The modulus of PHB is reduced by only 50% when X and Y were added together and is only 20% lower than TPO.

Conclusions from Part II B:

Toughened Green-nanocomposites

- Toughening of PHB resulted in improvement in Impact properties with a loss in modulus.
- Nanoclay platelets were added to regain the stiffness to some degree.
- Optimum clay exfoliation and surface chemical modification produced nanocomposites with enhanced properties capable of competing with TPO.

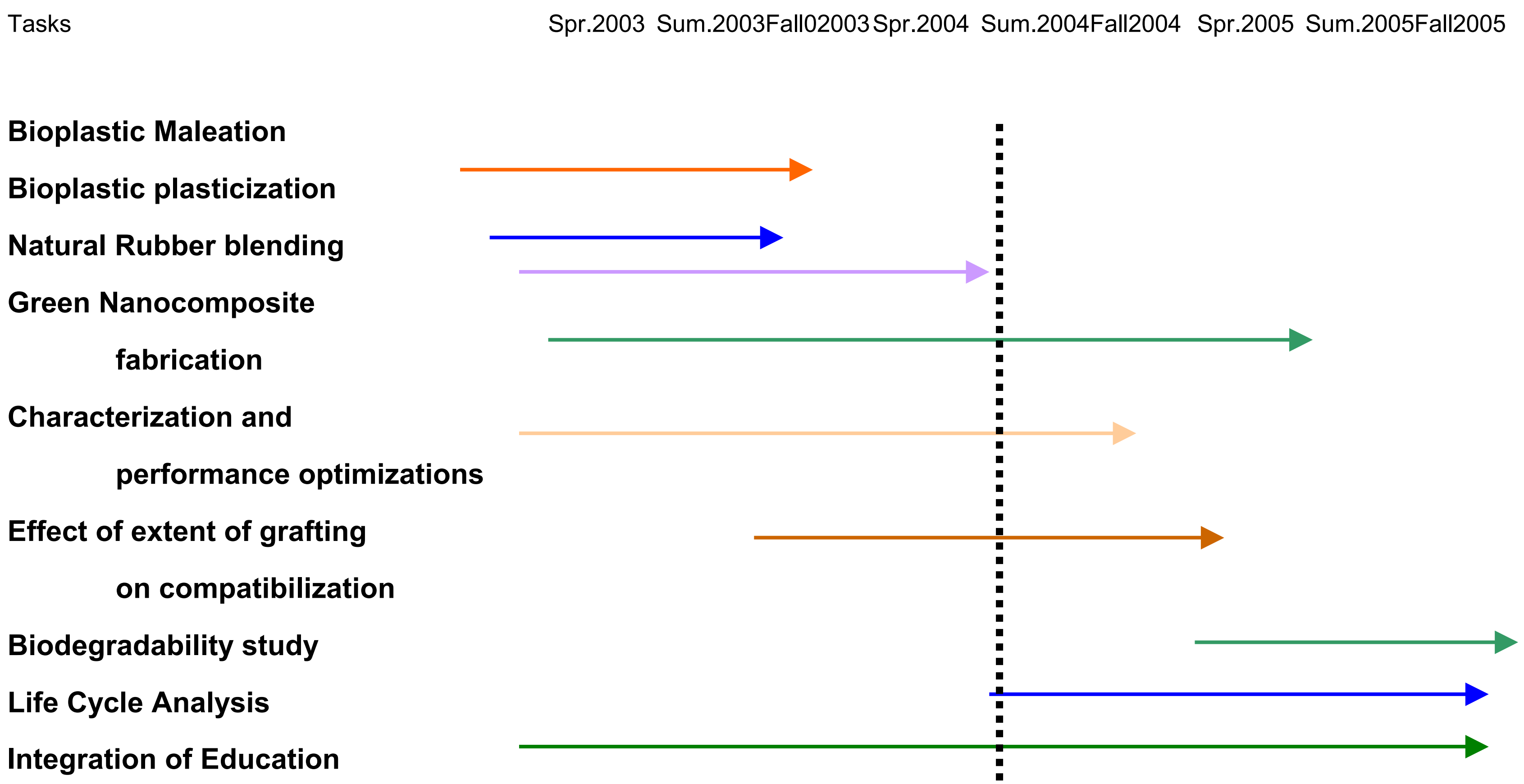
PART-III

(New Research Approach Underway)

Ionic liquids (ILs) to be used as:

- New plasticizer for PHA polymer matrix (replace phthalates)
- Exfoliating agent for layered silicates in ‘green nanocomposites’ preparation from PHAs

Project Schedule



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- FORD, GM, METABOLIX, EASTMAN & NANOCOR