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CORN STARCH BLEND BIODEGRADABLE POLYMERS

Dr. ANOMITRA CHAKRAVARTY

KPS CONSULTANTS & IMPEX PVT. LTD.

www.linkedin.com/in/anomitra-chakravarty-5a4b1414

Indian Institute of Chemical Engineers (NRC)

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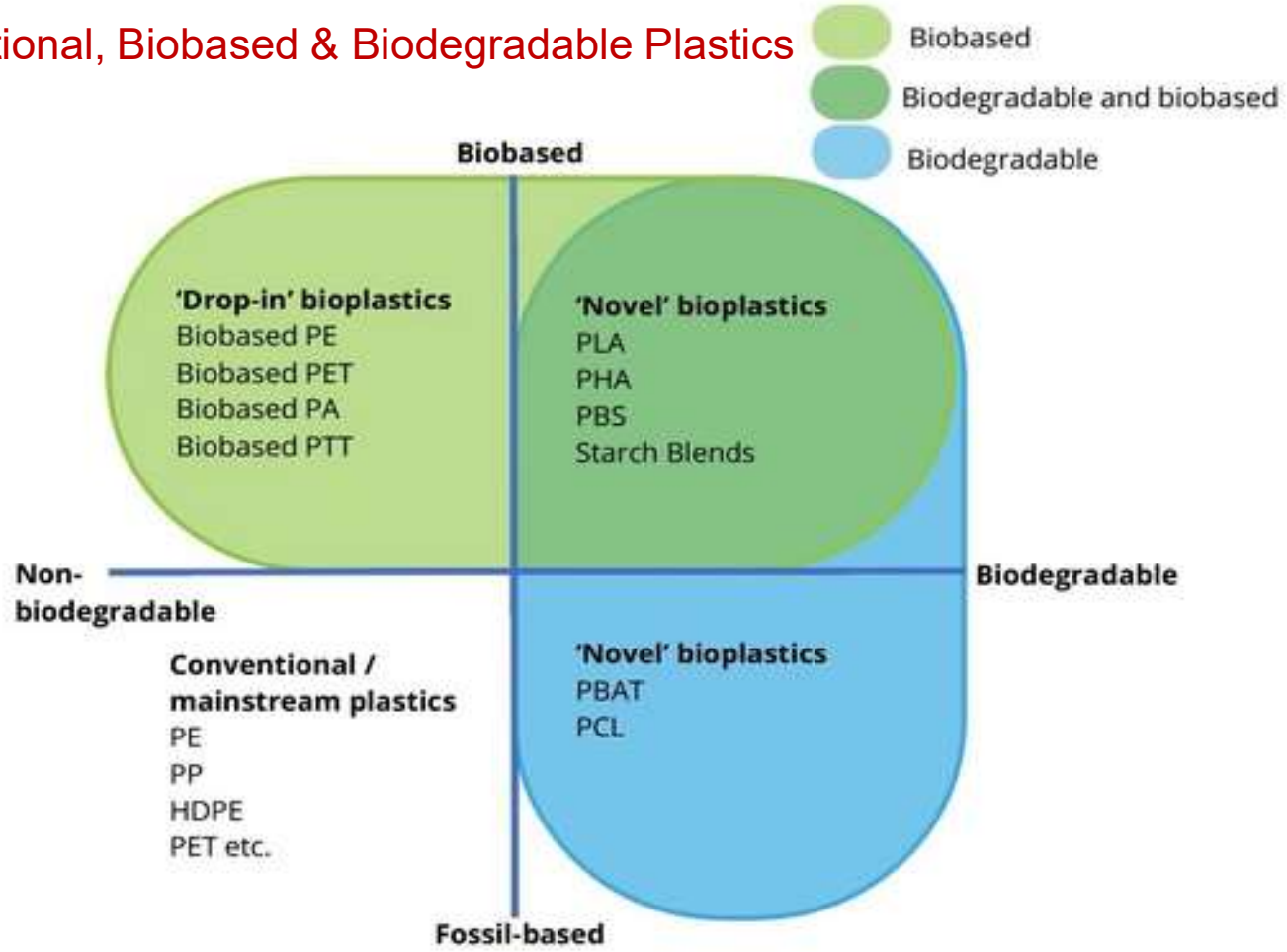
Conventional, Biobased & Biodegradable Plastics



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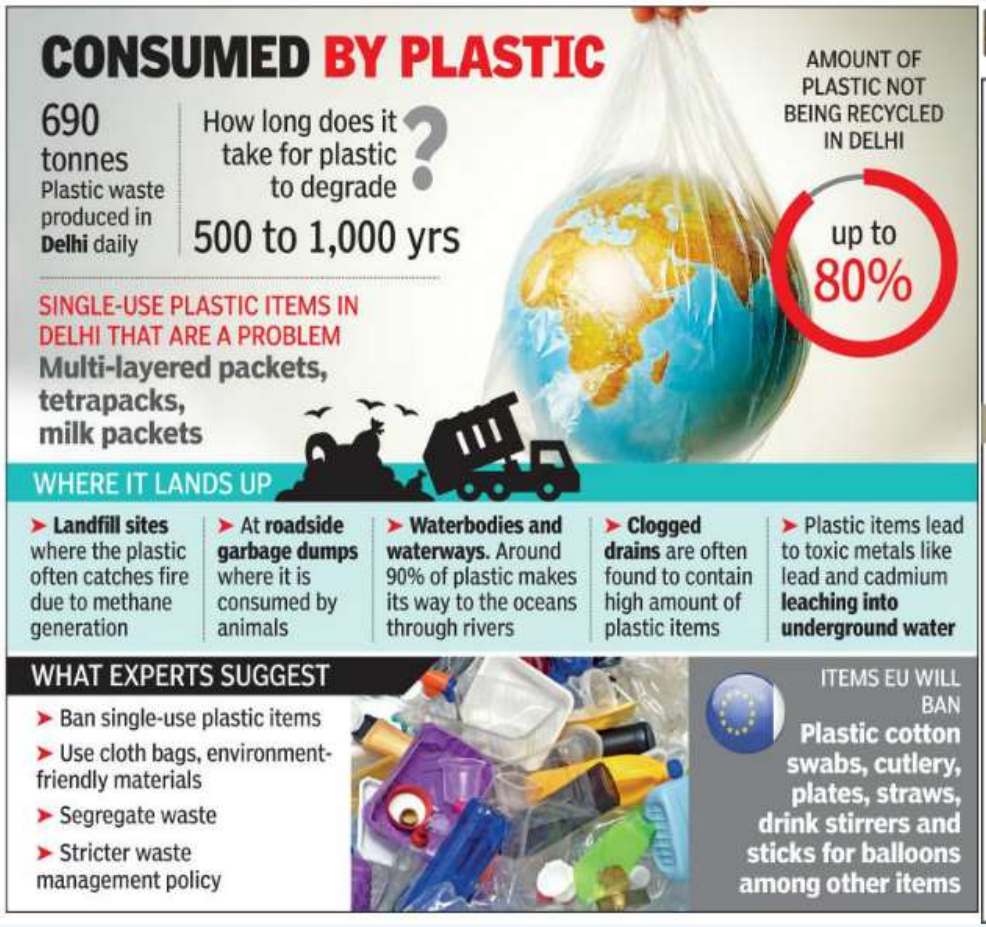
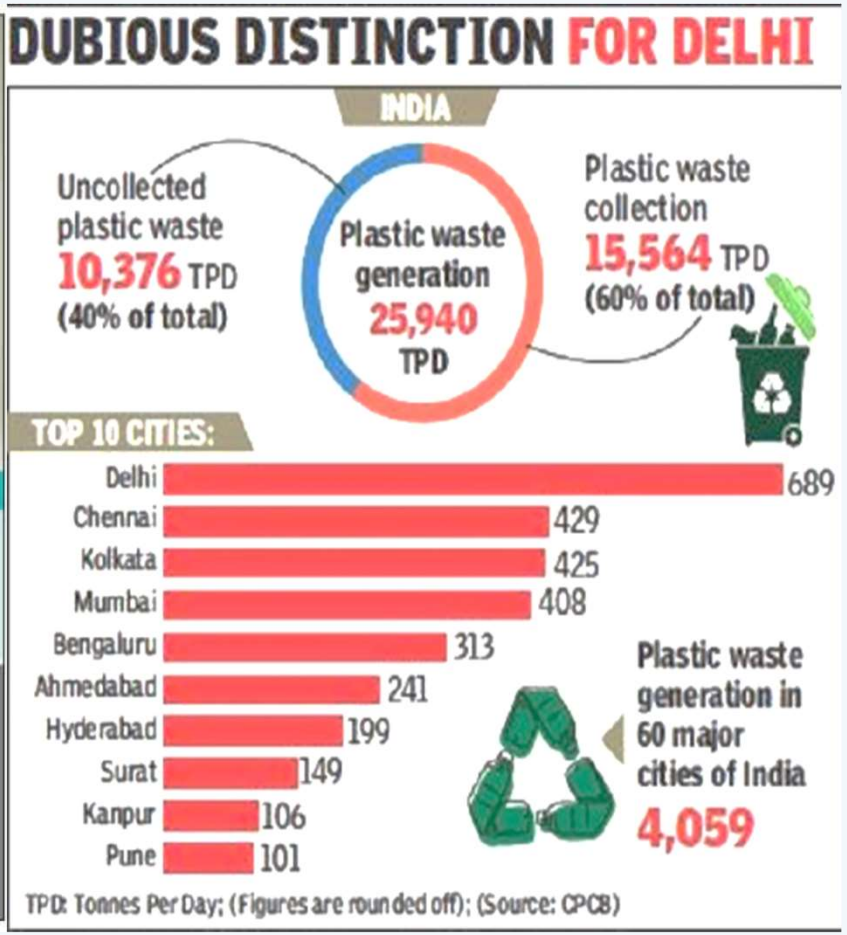
Why the need for biodegradable plastics?





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But almost 80% of all plastic remains in the environment

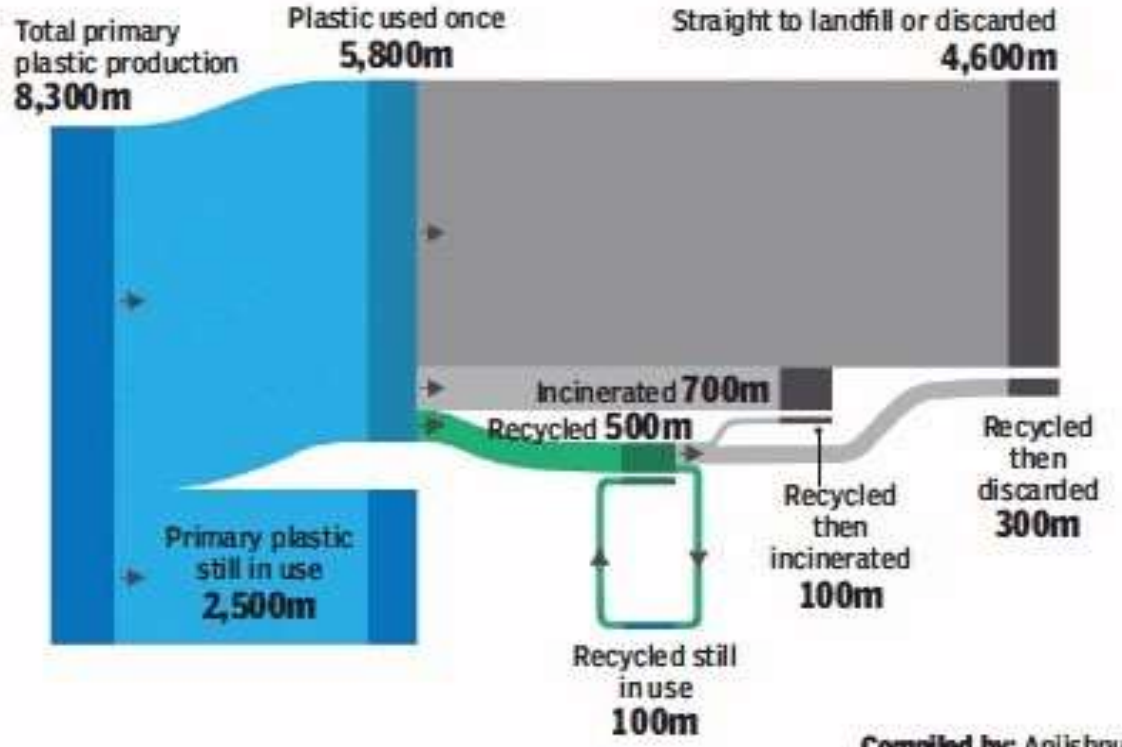
450 years to forever is how long plastic endures in the environment

40% Of plastic produced is packaging used once and then discarded

79% Of all plastic produced since 1950 is still in the environment

GLOBAL PLASTIC PRODUCTION AND ITS FATE (1950-2015)

(Measured in tonnes)



Compiled by: Anjishnu Da

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Changing Environment

Regulatory Clampdown and Societal Pressure

Ban on Single use Plastics (SUPs)

Plastic Bags, Cups, Plates, Drinking Straws, Stirrers, Small Bottles, Pouches, certain types of Sachets

Alternative materials ---- Paper, Textiles, Compostable Plastics, Bioplastics (e.g. PEF)

TPS blend biodegradable / compostable plastics – What are the Replacement targets?

Carry / Shopping / Grocery / Garbage bags, Apparel packing, Fruit & vegetable packing, Agricultural film

Consumer goods / FMCG / Hardware / Electronics / Industrial packaging (all non-food)

Extruded Sheet for thermoformed products like plates, thalis, bowls, cups, glass etc.

Coated paper board – disposable tableware, Drinking Straws, Stirrers

Difference between Biodegradable & Compostable Materials

- ASTM defines materials as compostable that undergo degradation by biological processes during composting to yield CO_2, water, inorganic compounds and biomass at a rate consistent with other compostable materials and leaves no toxic residue.
- While all compostable materials are biodegradable, not all biodegradable materials are compostable.
- Biodegradable materials return to nature and can disappear completely - they sometimes leave behind metal / toxic residue
- Compostable products are biodegradable, but with an added benefit - they break down, to release valuable nutrients into the soil, aiding the growth of trees and plants.
- Unlike compostable, certain biodegradable products can take several years to break down and, in some cases, even leave toxic waste behind.

IS / ISO 17088 (2008) – testing standard for industrially compostable plastics

Disintegration during composting

A plastic product is considered to have demonstrated satisfactory disintegration if, after 84 days in a controlled composting test, no more than 10 % of its original dry mass remains after sieving through a 2.0 mm sieve. The tests are carried out in accordance with ISO 16929, ISO 20200, ISO 14855-1 or ASTM D 5338 under thermophilic composting conditions without CO_2 trapping equipment.

Ultimate aerobic biodegradation

A plastic product is considered to have demonstrated a satisfactory rate and level of biodegradation if when tested in accordance with ISO 14855-1, ISO 14855-2 or ASTM D 5338, it achieves the ratio of conversion to carbon dioxide specified (90% of organic carbon in the polymer) within the time period specified (equal or less than 180 days)

No adverse effects on ability of compost to support plant growth

Concentrations of regulated metals and other toxic substances in the plastic product or material should be less than 50 % of those prescribed for sludges, fertilizers and composts in the country where the final product will be placed on the market.

The plastic product or material should contain a minimum of 50 % of volatile solids.

The seedling germination rate of the finished compost and the plant biomass in the compost should be not less than 90 % of that of corresponding blank composts to which test or reference material was added at the start of testing.

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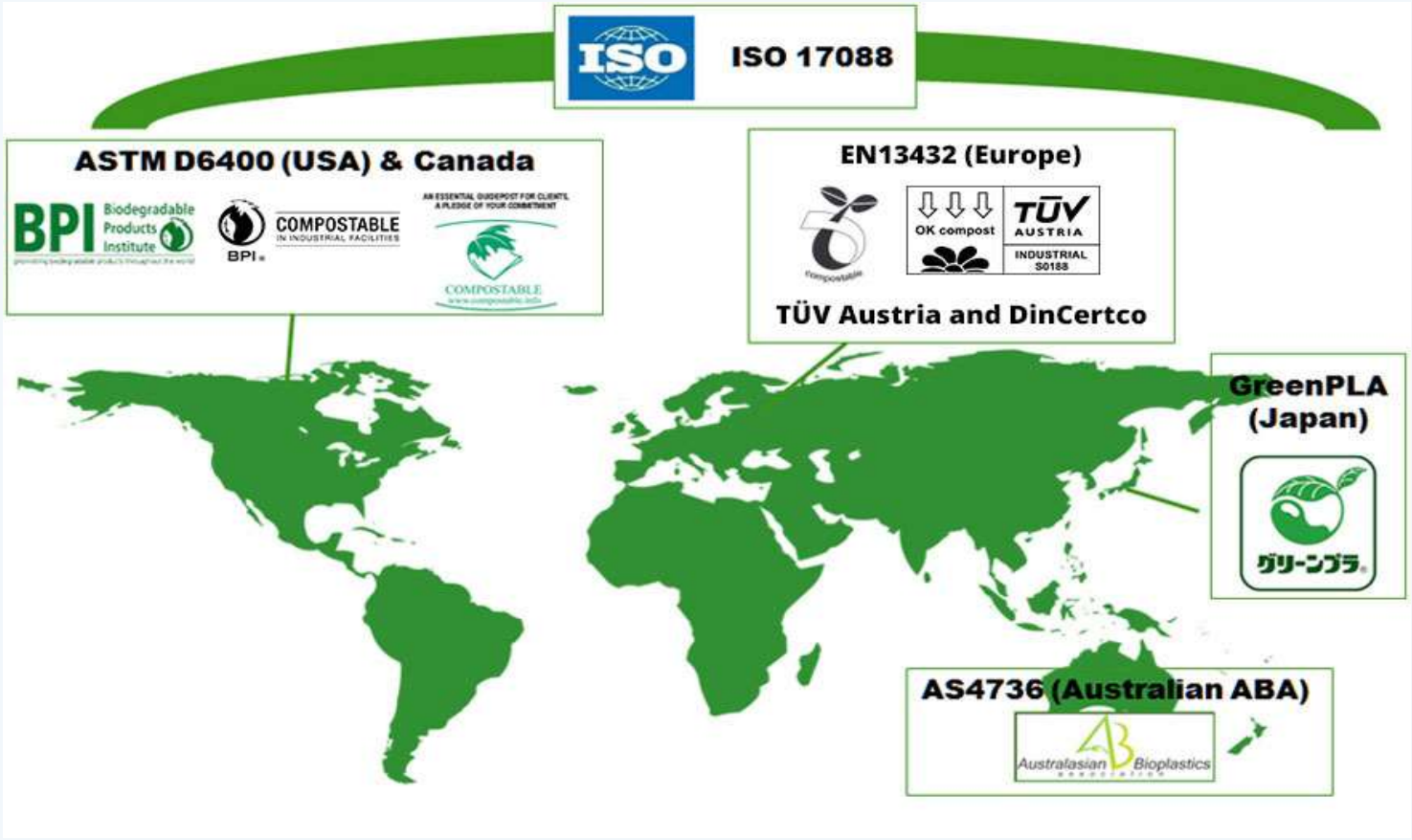
Global Compostability Testing Standards



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Types of biological waste treatment of biodegradable polymers

	Anaerobic Bacteria, no fungi	Aerobic Bacteria & fungi
50–60°C	Chemical pulp Starch PLA Starch/PCL PHA	Chemical pulp Mechanical pulp Starch PLA Starch/PCL PHA PBAT
≤35°C	Chemical pulp Starch Starch/PCL PHA	Chemical pulp Mechanical pulp Starch Starch/PCL PHA PBAT

Thermophilic digestion
Industrial composting
Mesophilic digestion
Home composting

Ref: M. Niaounakis, *Biopolymers: Reuse, Recycling, and Disposal*, William Andrew Publishing, 2013

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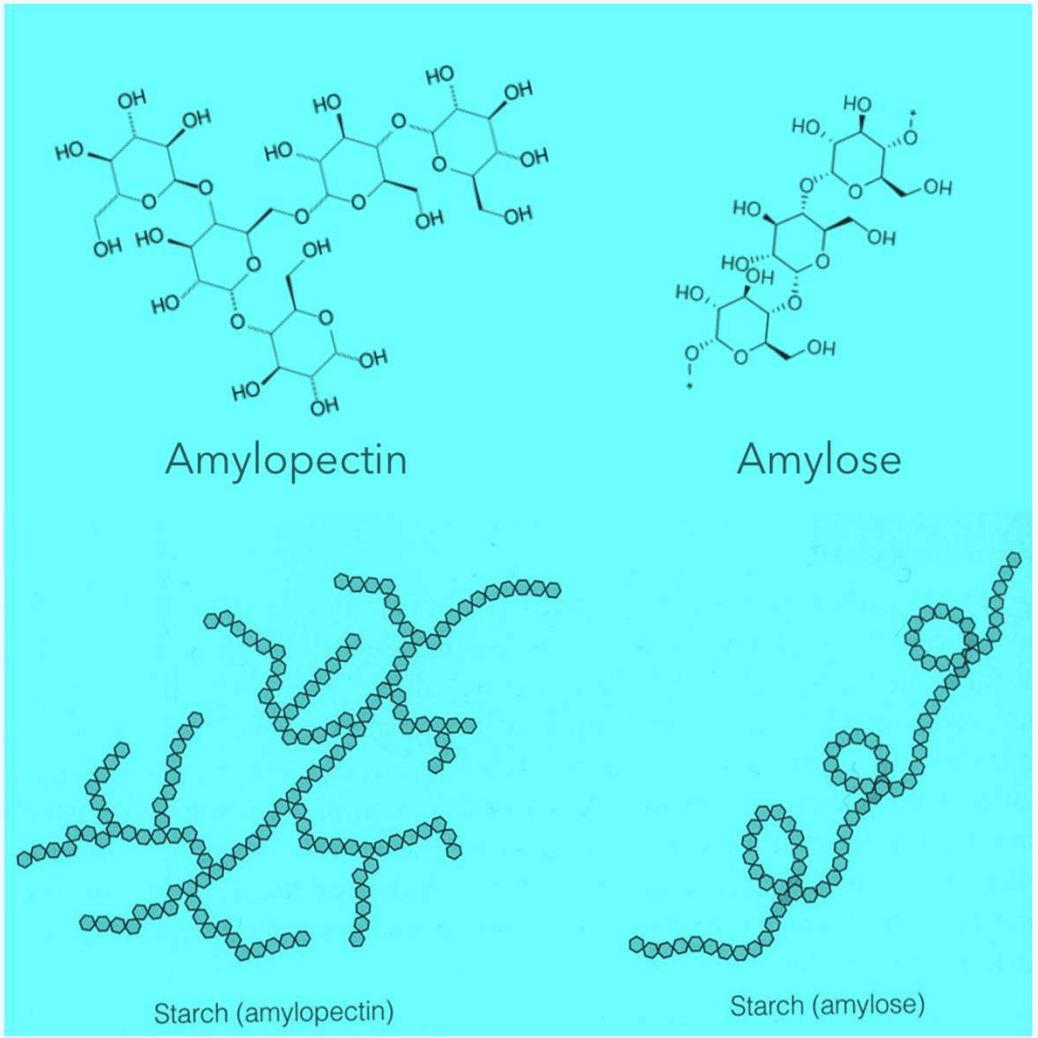
Composition of Corn Starch



Thermoplastic Starch

Native starch is converted into TPS by the action of heat and shear stress aided by action of plasticizers.

Macromolecular chains of amylose and amylopectin in native starch are linked by strong intermolecular and intramolecular hydrogen bonding. The plasticiser at high temperatures (90 to 180°C) converts starch granules to thermoplastic starch, dissolving starch granules and lowering its melting temperature, enabling it to be extruded.

Breaking up the starch granules results in an increase of macromolecular chain mobility and consequently the material softens and becomes less brittle. The semi-crystalline granules are converted into a homogeneous and amorphous material, which is known as the plasticization of starch.

An effective plasticiser needs to be polar, hydrophilic and small enough to fit between the starch chains. Additionally, the boiling point of the plasticiser should be higher than manufacturing conditions so that it does not evaporate during processing.
E.g. Glycerol, sorbitol, urea, formamide, ethylene bisformamide, EG, PG, PEG

Plasticisers have hydroxyl groups allowing compatibility with starch granules and they plasticise starch by breaking internal hydrogen bonding between glucose rings in starch.

TPS has low strength and is affected by moisture / water.

Recrystallization of starch molecules (retrogradation) which promotes migration of plasticizer to the surface of the pellets. Chemically modified starch - hydroxy-propylated starch, acetylated starch. Using plasticisers in combination. Cellulosic fillers etc.

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Why Corn Starch?

- While more than 60 per cent of the domestic maize output goes towards poultry and feed segment, 20-25 per cent is set aside as industrial corn starch
- Corn starch is used in fast-moving consumer goods (FMCG), juices, pharmaceutical, textile, paper, packaging, and adhesives, among other sectors.
- Domestic production of corn starch around 400,000 MT / Yr
- Not a staple crop like rice or wheat. Easy availability & low cost.
  Tapioca starch, Potato starch, Rice starch, Wheat starch, Cassava starch
- Agricultural renewable crop (biobased), Low Cost, Fast Rate of Compostability
  (Polysaccharides – amylose & amylopectin)

Biodegradable / Compostable Polymers blended with TPS

Polybutylene Adipate Co- terephthalate (PBAT) is a Co-polyester of adipic acid, 1,4 butanediol and terephthalic acid. PBAT is a biodegradable alternative to LDPE, having similar properties including high flexibility and toughness, used for various packaging applications.

Polylactide (PLA) is based on lactic acid monomers obtained from the fermentation of sugars obtained from renewable sources such as sugar cane / corn starch. PLA has high strength and stiffness, however it is has low ductility (brittle) and impact strength, low thermal stability & gas barrier properties.

Polyvinyl alcohol (PVOH) is a water-soluble and biodegradable polymer (when dissolved in water in certain types of sludges). PVOH has excellent film forming properties and is also resistant to oil, grease and solvents. PVOH has high tensile strength and flexibility, as well as high oxygen and aroma barrier properties.

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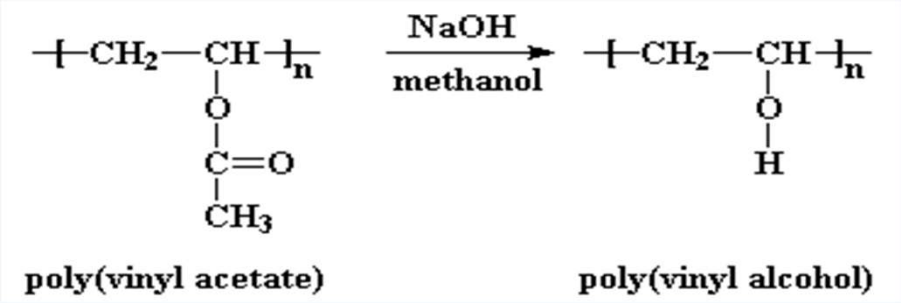
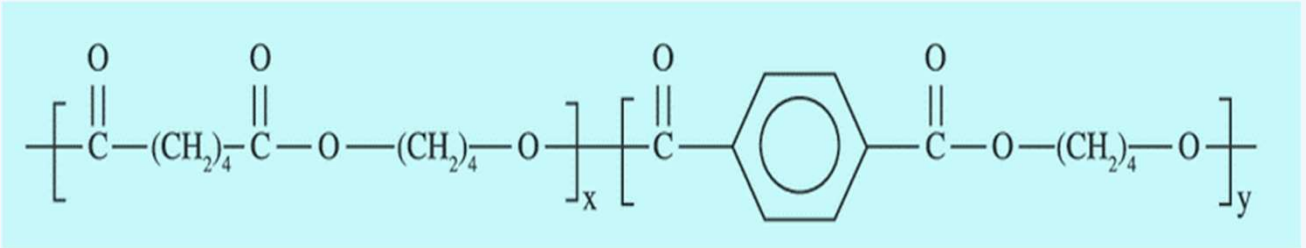
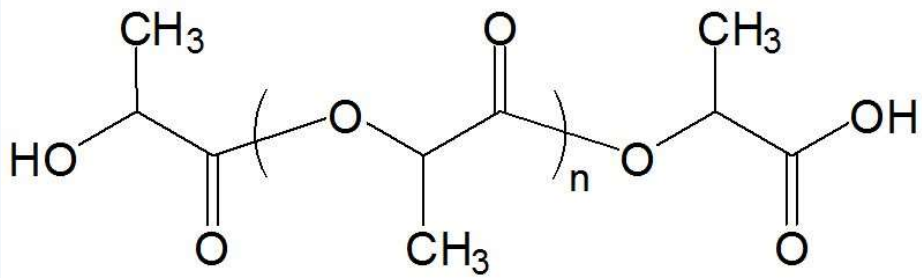
PVOH



PBAT



PLA



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Comparative Mechanical Properties

REVIEW WILEYONLINELIBRARY.COM/APP Applied Polymer SCIENCE

Table I. Summary of Tensile Properties (Tensile Strength, Tensile Modulus, and Strain at Break) of Some Biodegradable Polymer Matrices

Polymer category	Polymer	Tensile strength (MPa)	Young's modulus (GPa)	Strain at break (%)	References
Polyesters	PCL	19-21	0.21-0.33	300-897	4,50
	PBAT	>84	0.04	>200	102
	PBSA (Bionolle)	20	0.44	20	106
	PLA	21	0.35	3	4
	PHBV	40	3.5	5	4
Protein	Wheat gluten[a]	1.86	0.004	58	103
Polysaccharides	Starch	5	0.13	31	4
	Cellulose	12-13	1.41-1.50	4-5	104
	Chitosan[b]	27-39	-	11-33	105

[a] Measured at 25°C and 70% RH.
[b] Measured at 25°C and 50% RH.

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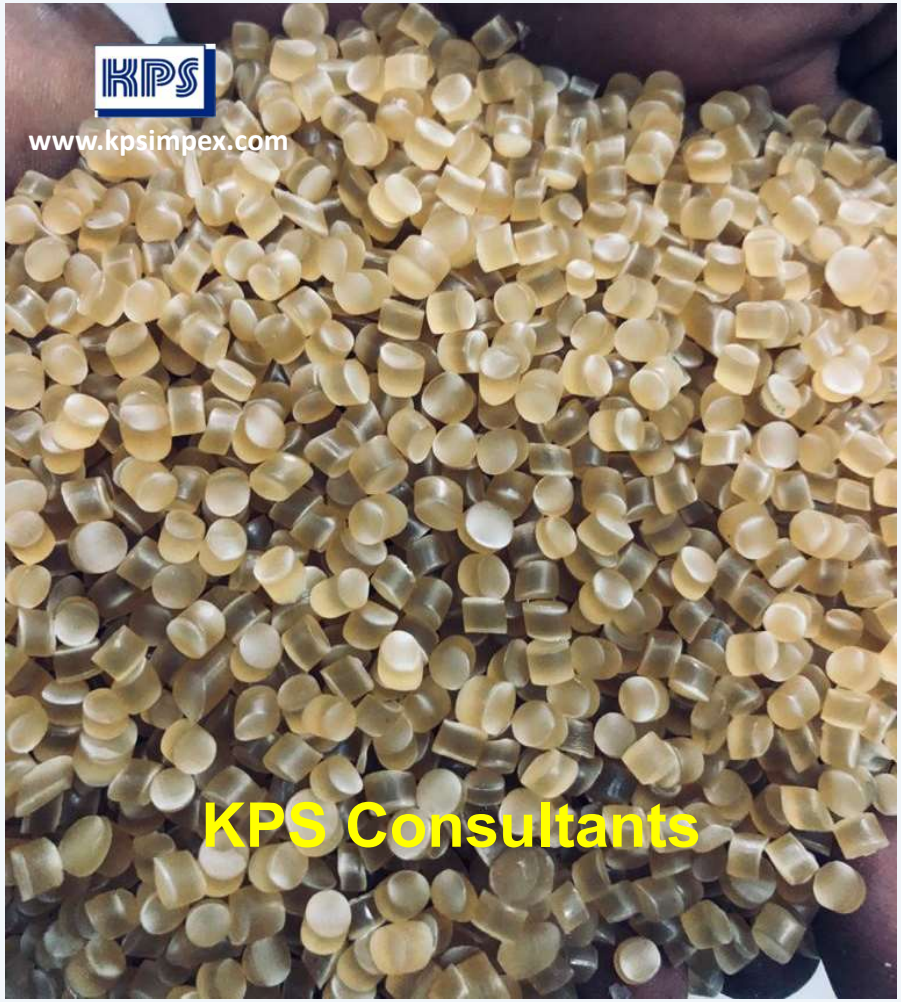
Thermoplastic Starch Pellets



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PBAT + TPS blend compound pellets

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Biodegradable Plastic

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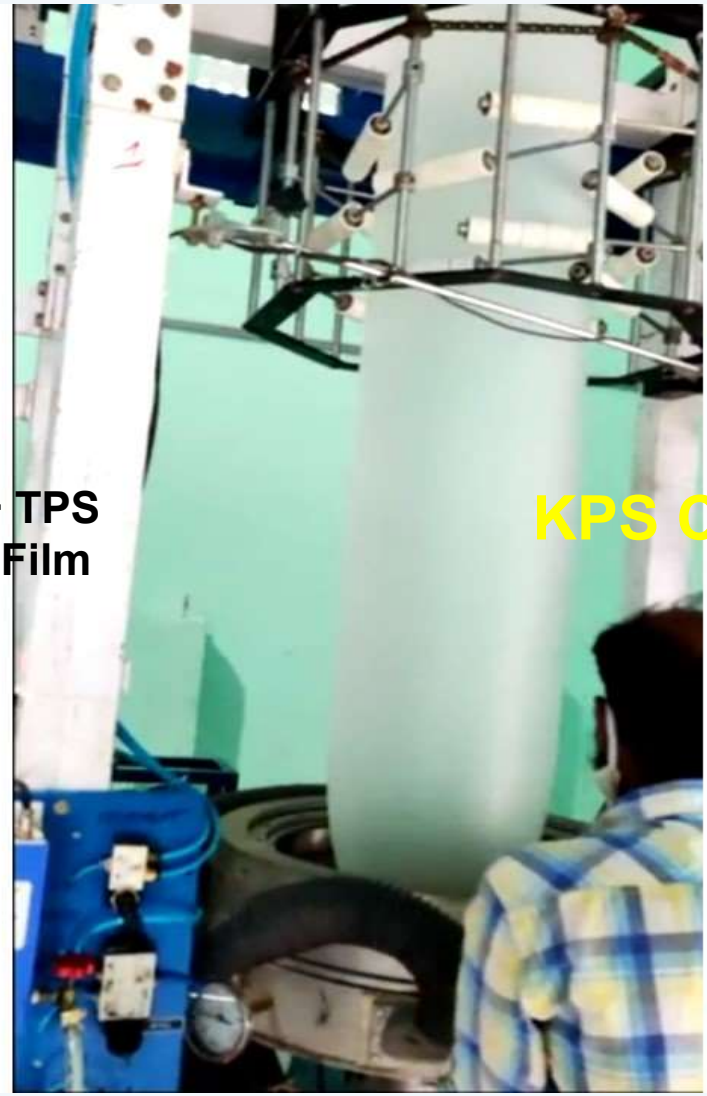
PBAT + TPS
Blown Film



Biodegradable Plastic

Extrusion Blown film from compound based on PBAT 70% & TPS 30%

- Tensile Strength (machine direction) ---- 25 MPa
- Elongation at Break (machine direction) ---- 350%
- Density ---- 1.3 g / cm^3
- MFI ---- 9.0 g / 10 minutes (190 ºC at 2.16 kg)
- Melting Temperature (DSC) ---- 119 ºC & 126 ºC
- Thickness 30 micron film

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TPS + PBAT Base compound pellets

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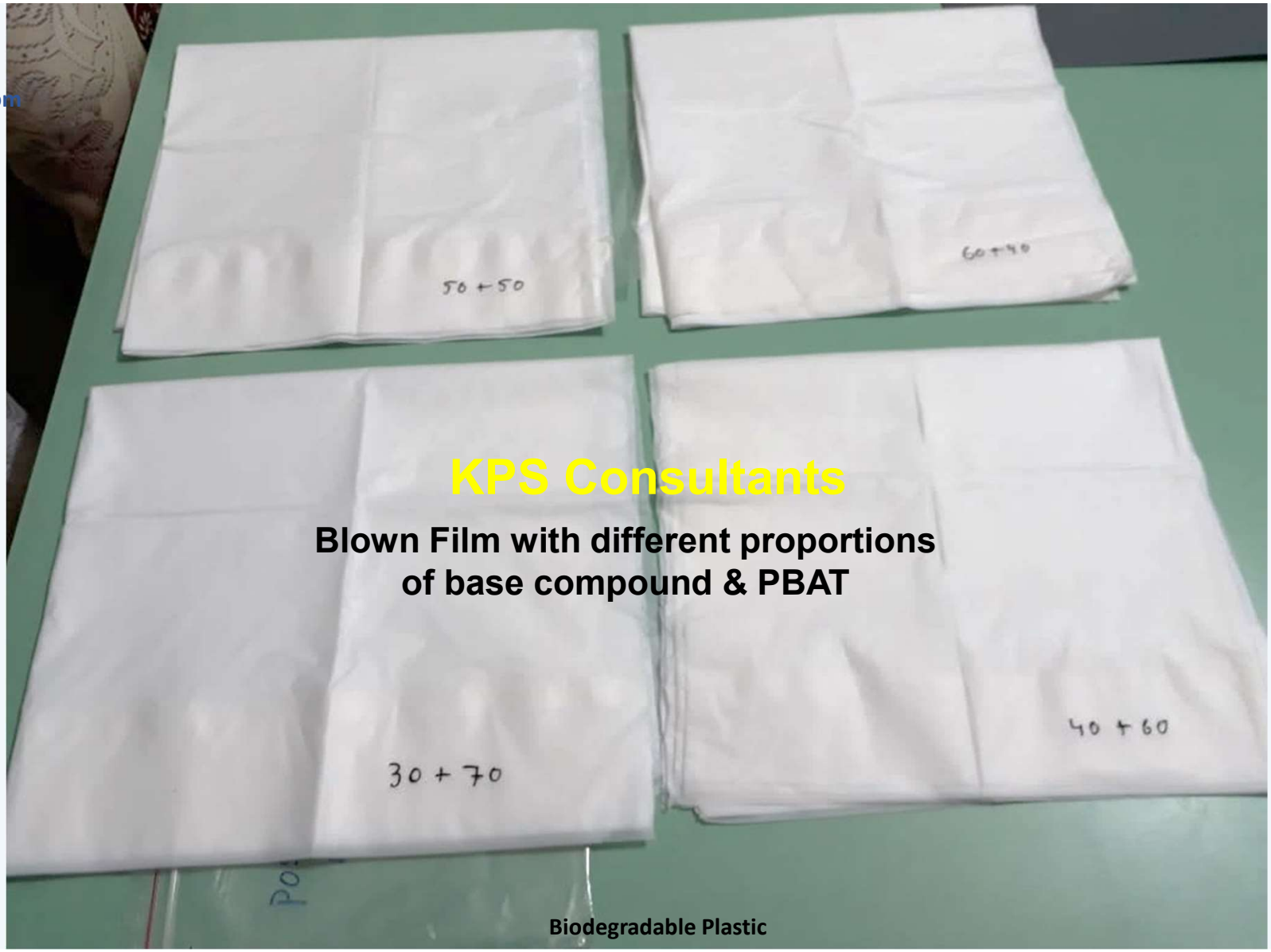

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Blown Film with different proportions of base compound & PBAT

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Extrusion Blown Films

- Base compound (70 TPS + 30 PBAT) 40% + PBAT 60%
- Base compound 40% + PBAT 57% + PLA (LX 175) 3%
- Base compound 50% + PBAT 50%
- Base compound 50% + PBAT 45% + PLA (LX 175) 5%
- Base compound 60% + PBAT 40%
- Base compound 60% + PBAT 35% + PLA (LX 175) 5%
- Base compound 60% + PBAT 32% + PLA (LX 175) 8%
- Manual dry blending, one can add 10 to 20% filler MB, Colour MB
- All blown films are processed at temperatures between 130 and 150 ºC
- Blow up ratio 2 to 2.5
- Monolayer or Three Layer ABA / ABC type

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Blown film - dry blending Base compound 60% + 40% PBAT

- Tensile Strength (machine direction) ---- 19 MPa
- Elongation at Break (machine direction) ---- 200%
- Density ---- 1.26 g / cm^3
- MFI ---- 8.0 g / 10 minutes (190 ºC at 2.16 kg)
- Melting Temperature (DSC) ---- 111 ºC & 120 ºC
- Thickness 30 - 35 micron film

Blown film - dry blending Base compound 80% + 20% PBAT

- Tensile Strength (machine direction) ---- 14 MPa
- Elongation at Break (machine direction) ---- 350%
- Density ---- 1.3 g / cm^3
- MFI ---- 18.0 g / 10 minutes (190 ºC at 2.16 kg)
- Melting Temperature (DSC) ---- 117 ºC
- Thickness 30 - 35 micron film


Thermoplastic Starch + Polyvinyl Alcohol compound pellets
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TPS + PVOH Blown Film
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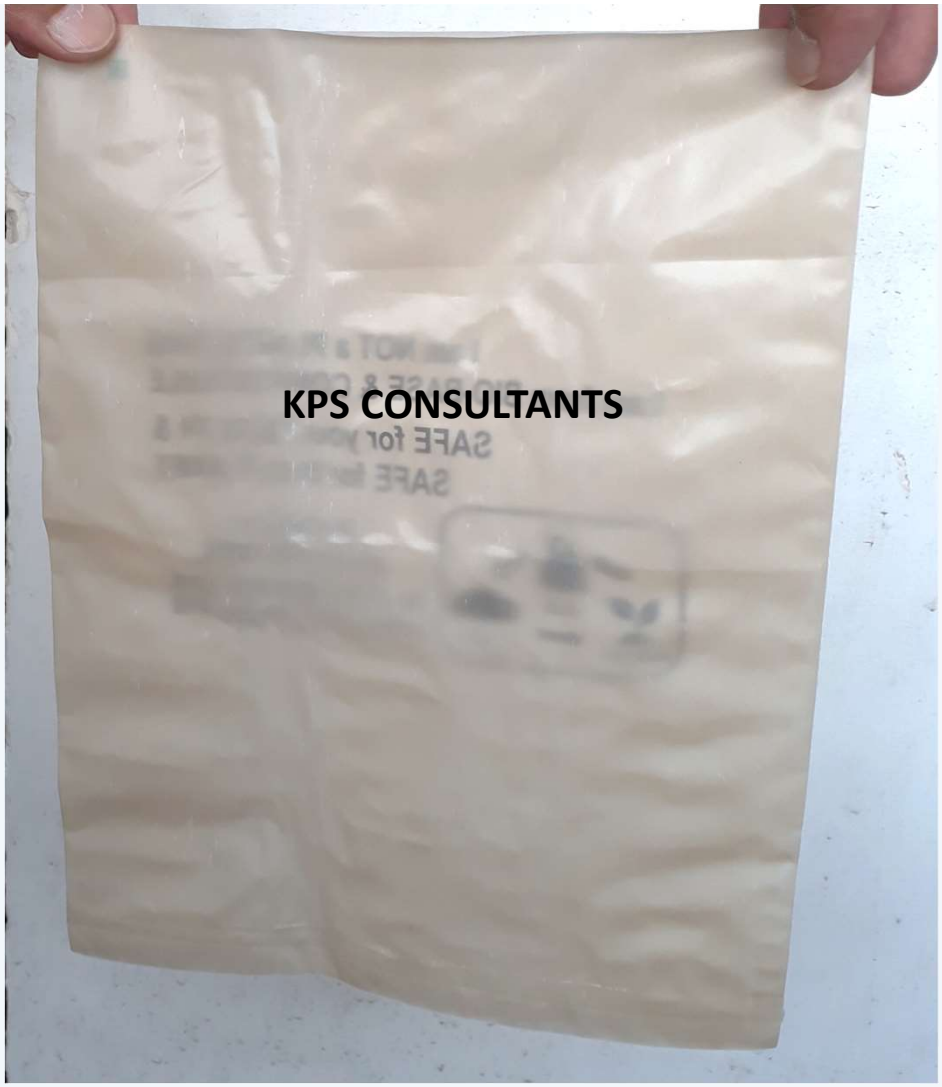
TPS + PVOH Pouch



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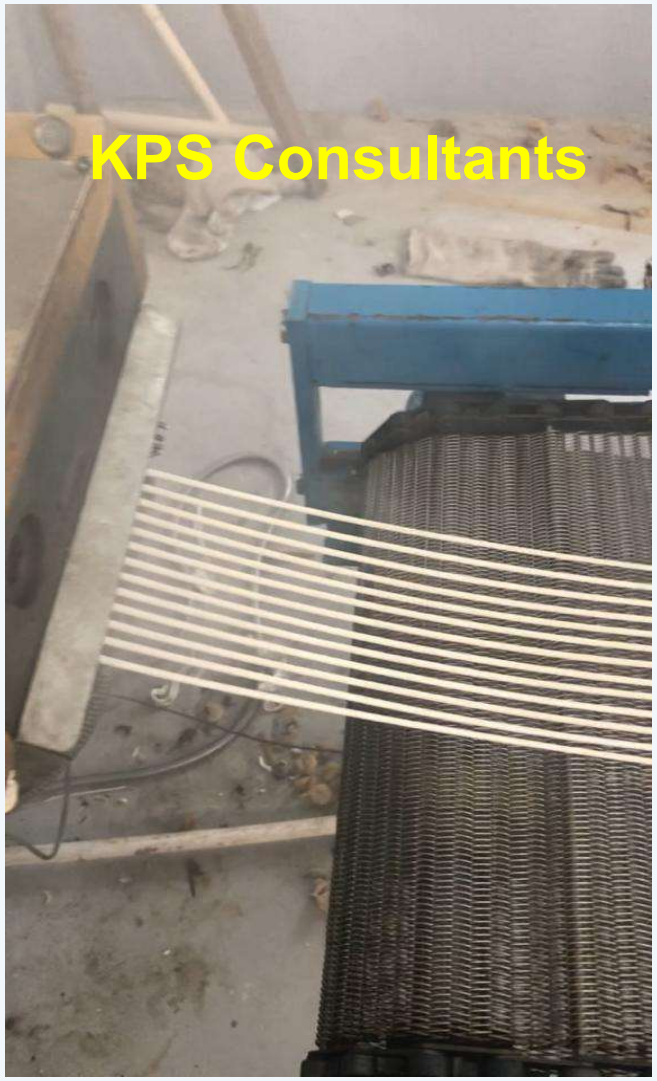
PBAT + TPS Compound Extrusion



PBAT + TPS Blown Film

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PBAT + TPS Blown Film

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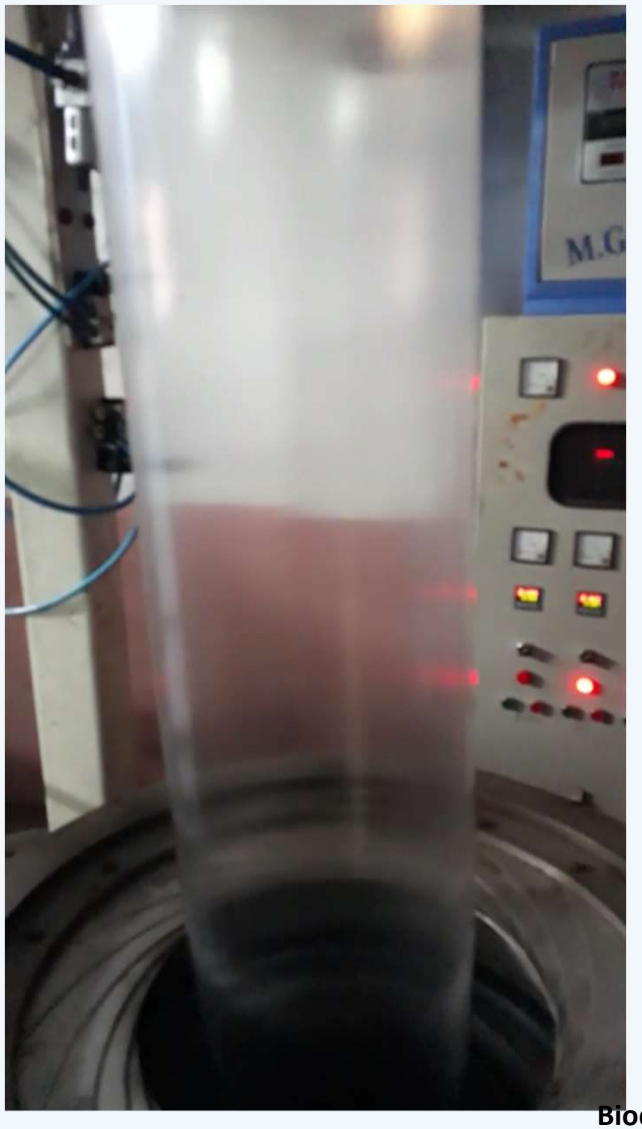
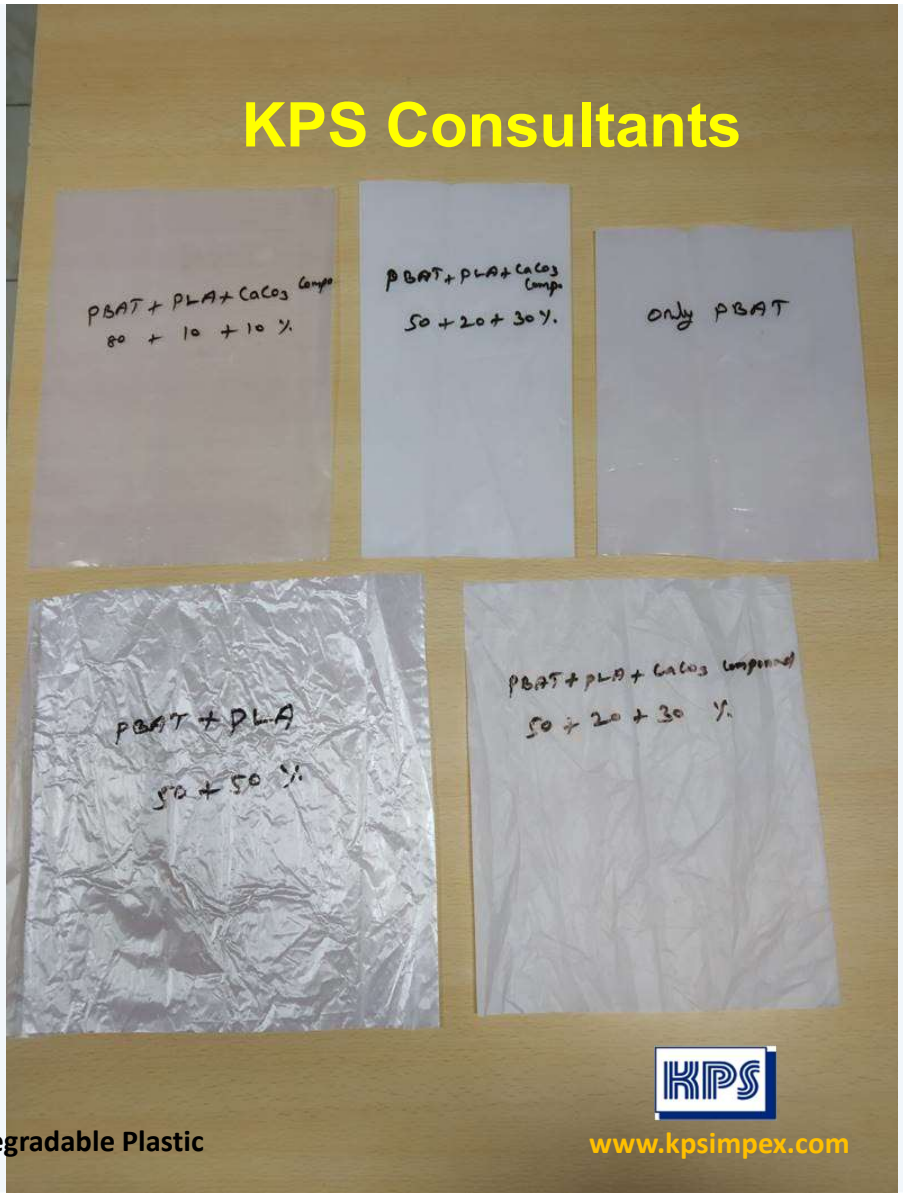
PBAT + PLA Blown Film





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High Speed Heating & Cooling Mixer

Biodegradable Plastic

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Parallel Co-rotating Twin Screw Extruder

Modular Screw elements mounted on a splined shaft

Extruder Configuration – different types of screw elements in each zone

Extruder zones - Intake, Melting, Venting, Mixing, Vacuum venting, Metering

L/D = 48 : 1, 12 barrel zones, venting & vacuum degassing, liquid injection

Source: Steer

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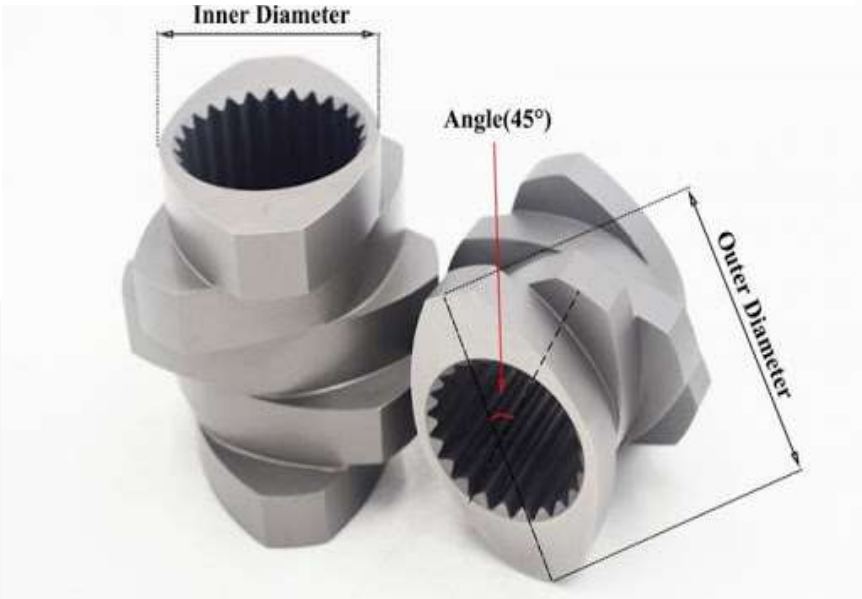
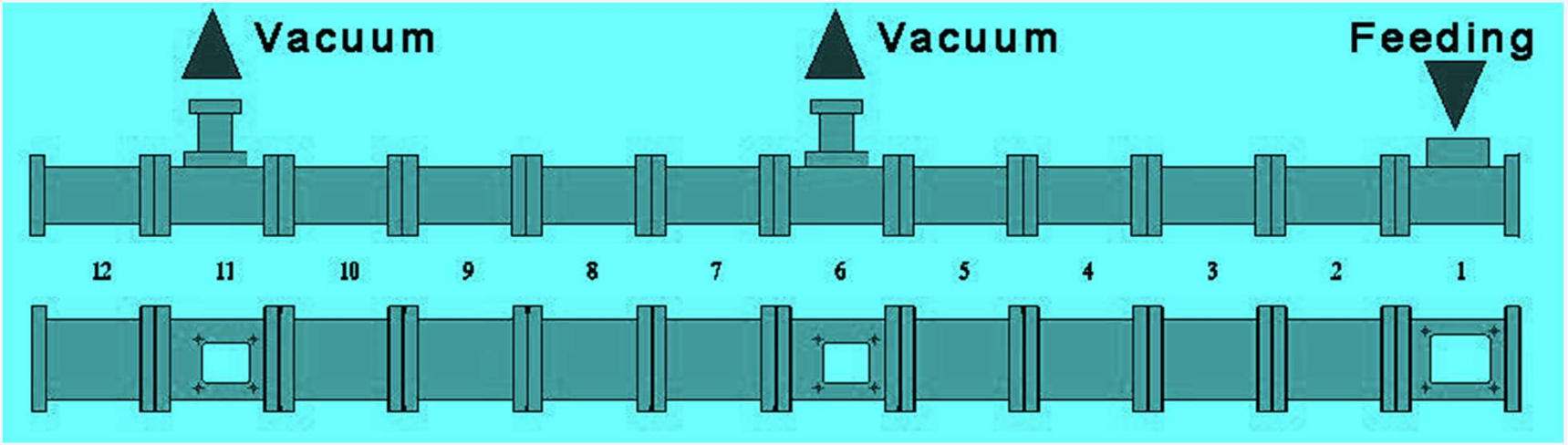


Vacuum Degassing System



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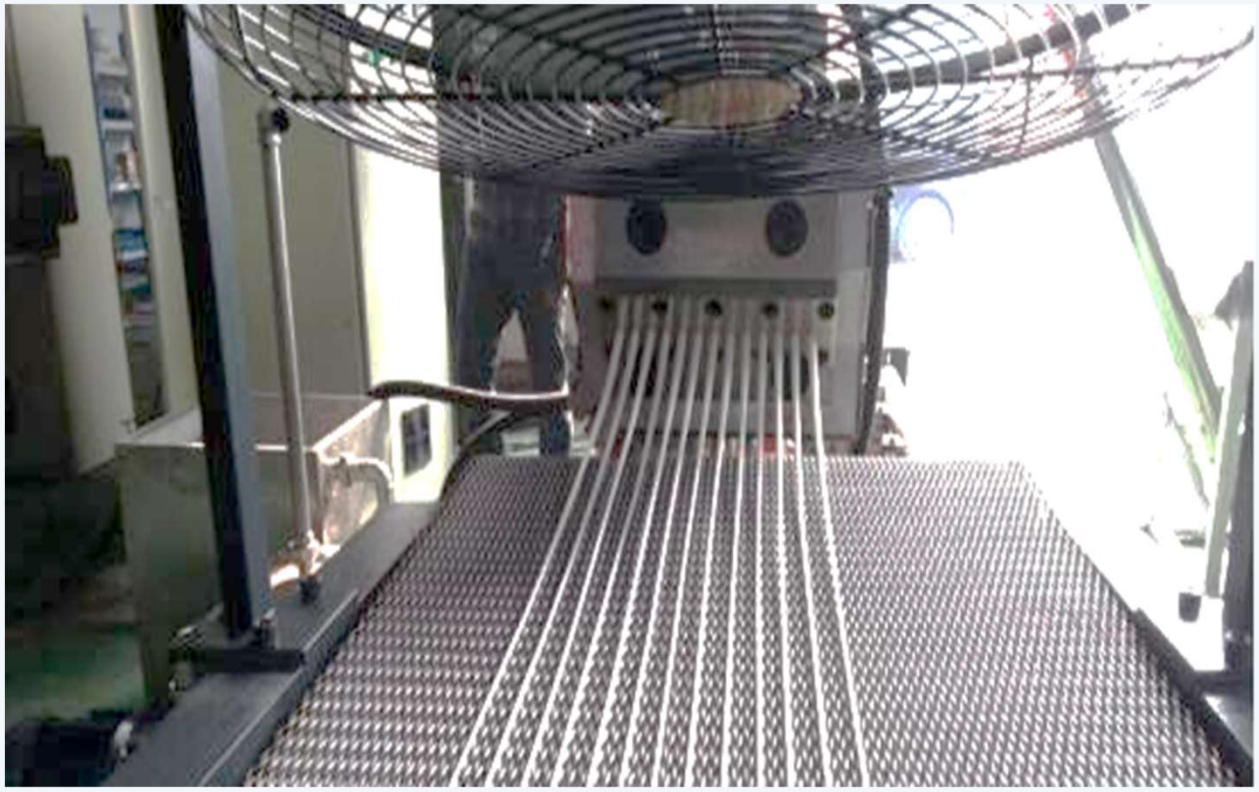
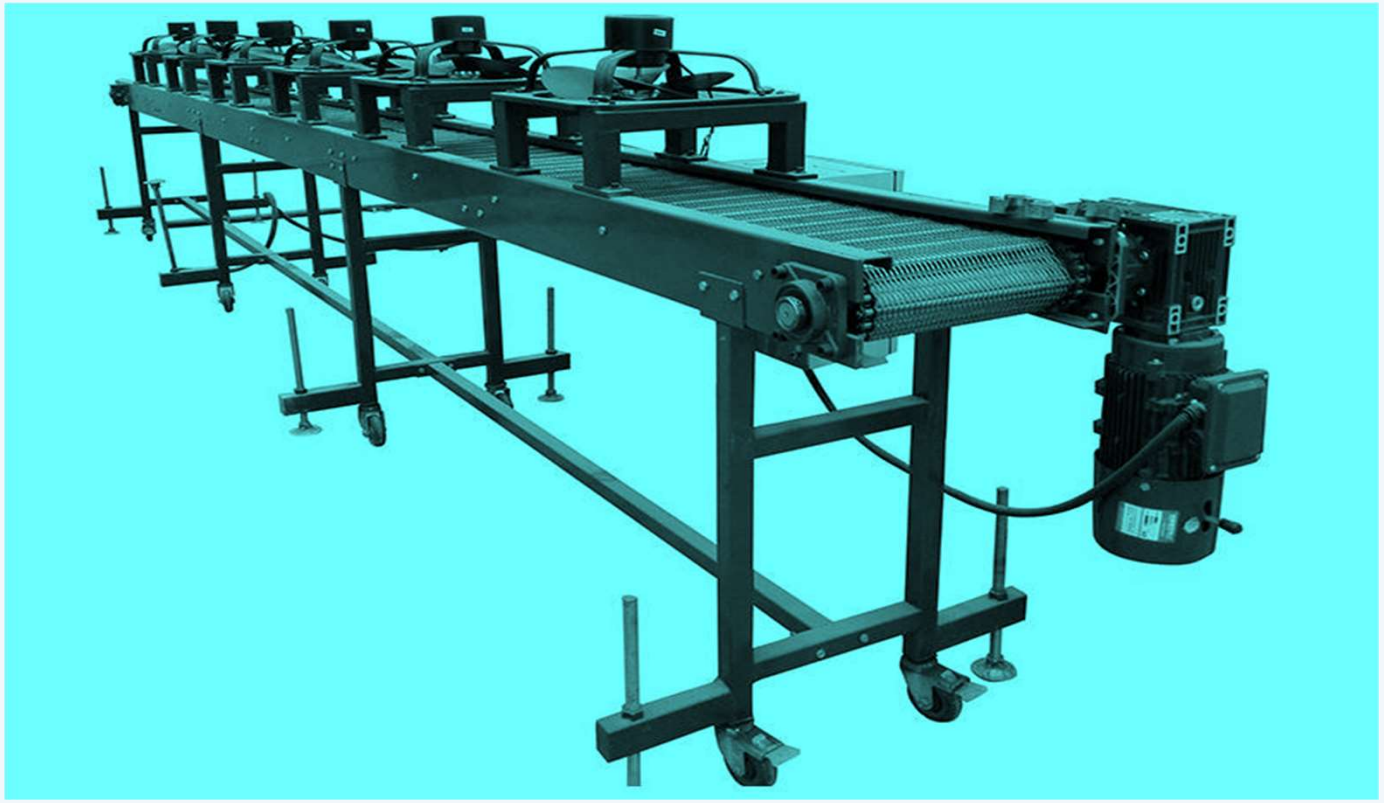
Plasticizer Injection

Hydraulic Screen Changer and Strand Extruder Die



Air Cooling Conveyor Belt



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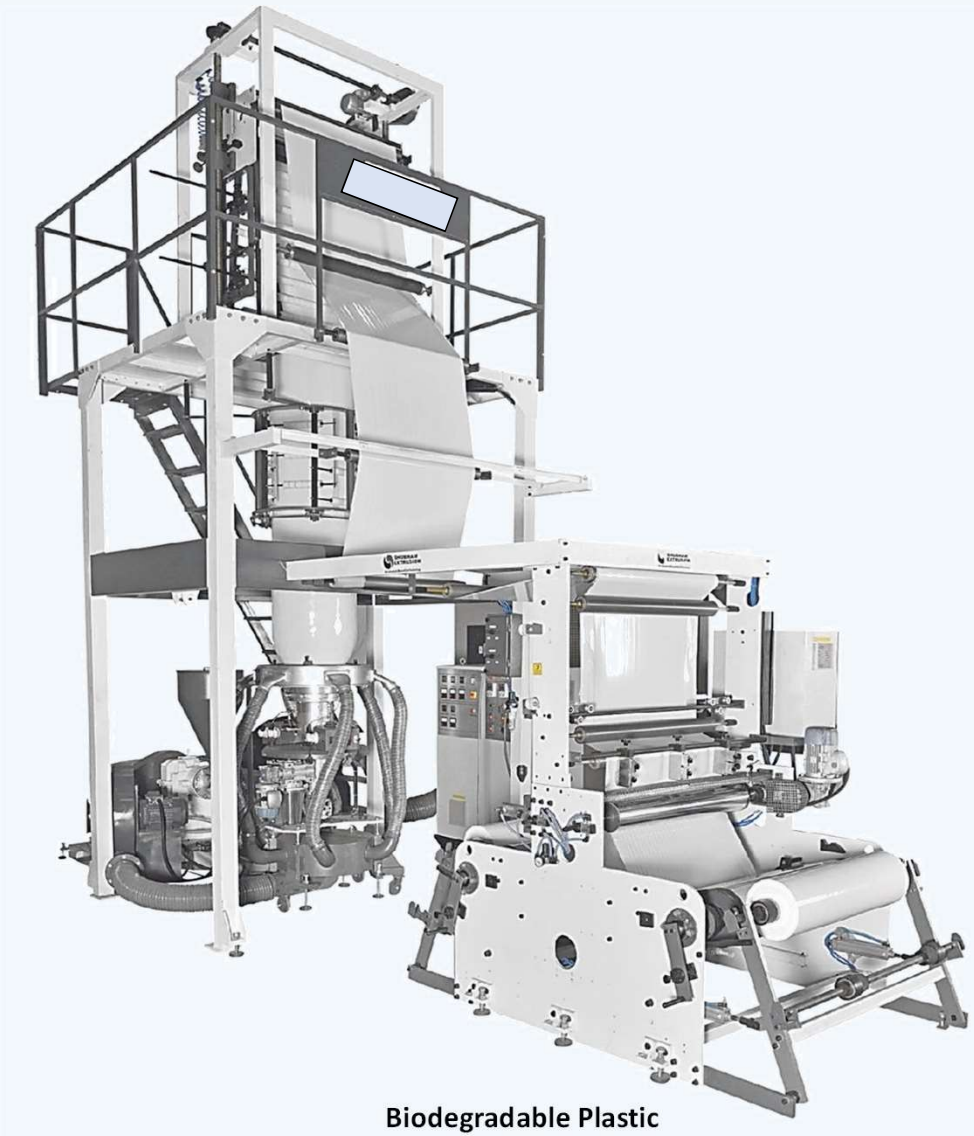
Monolayer Film Extrusion Blowing Line



Biodegradable Plastic

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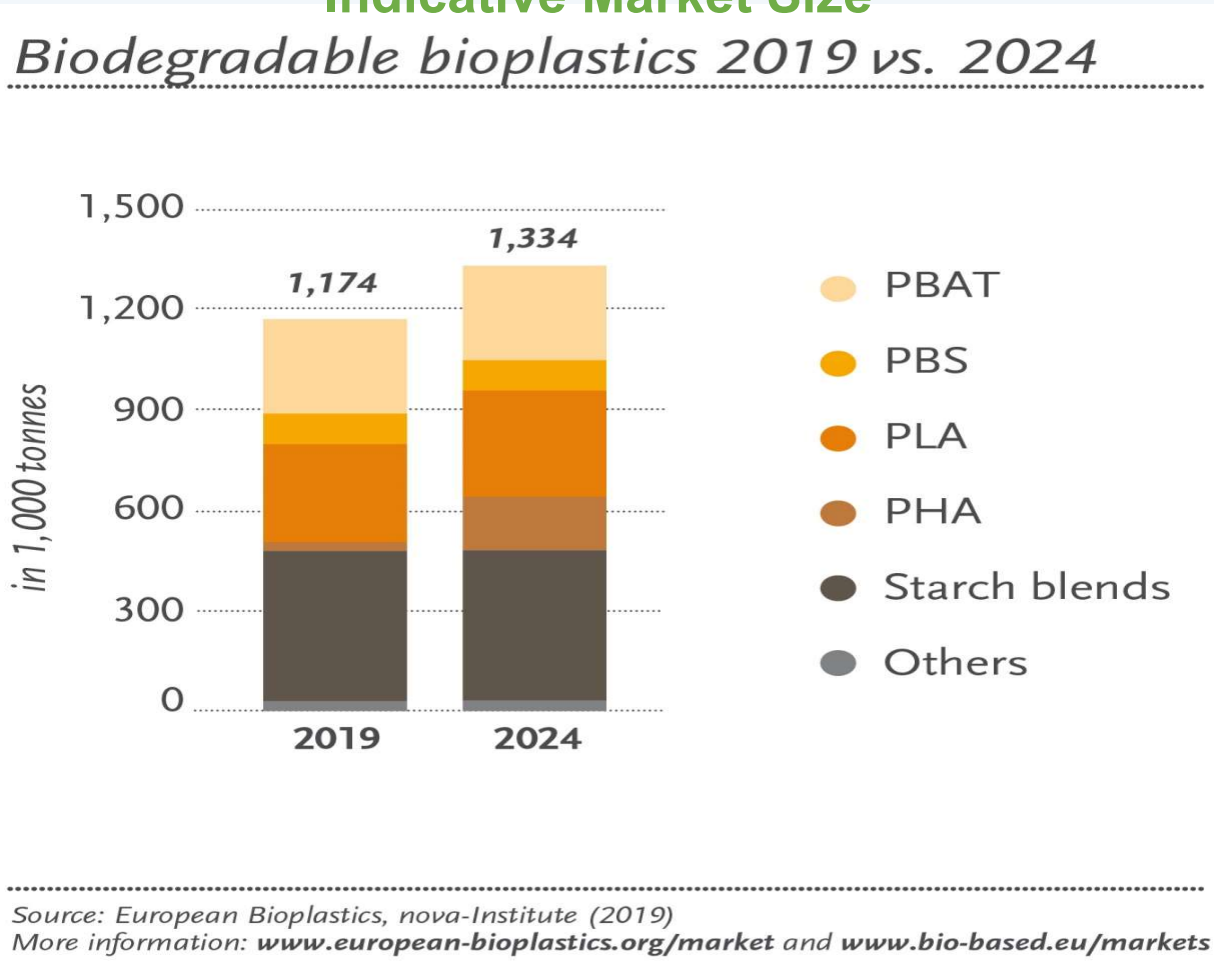
Indicative Market Size



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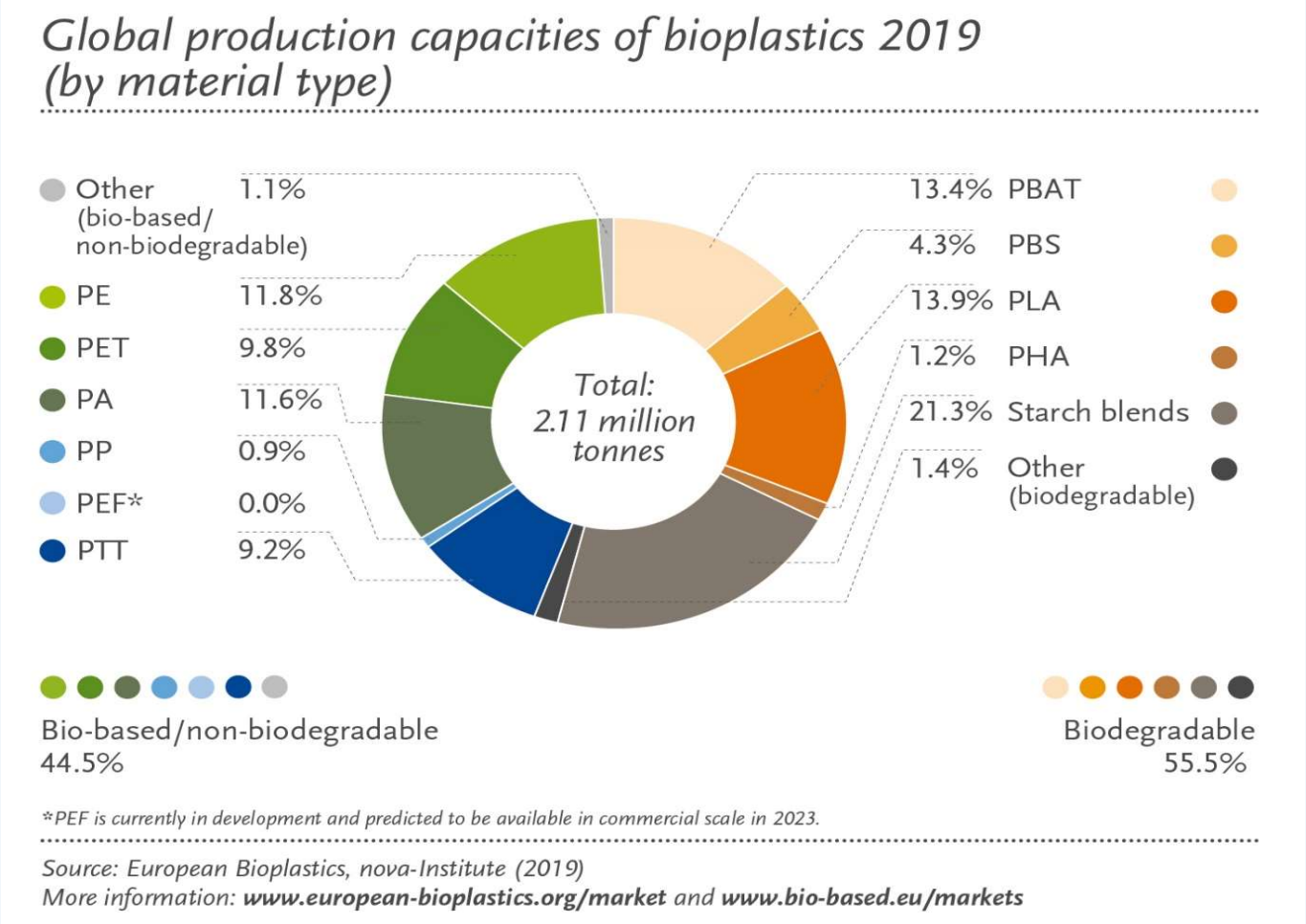

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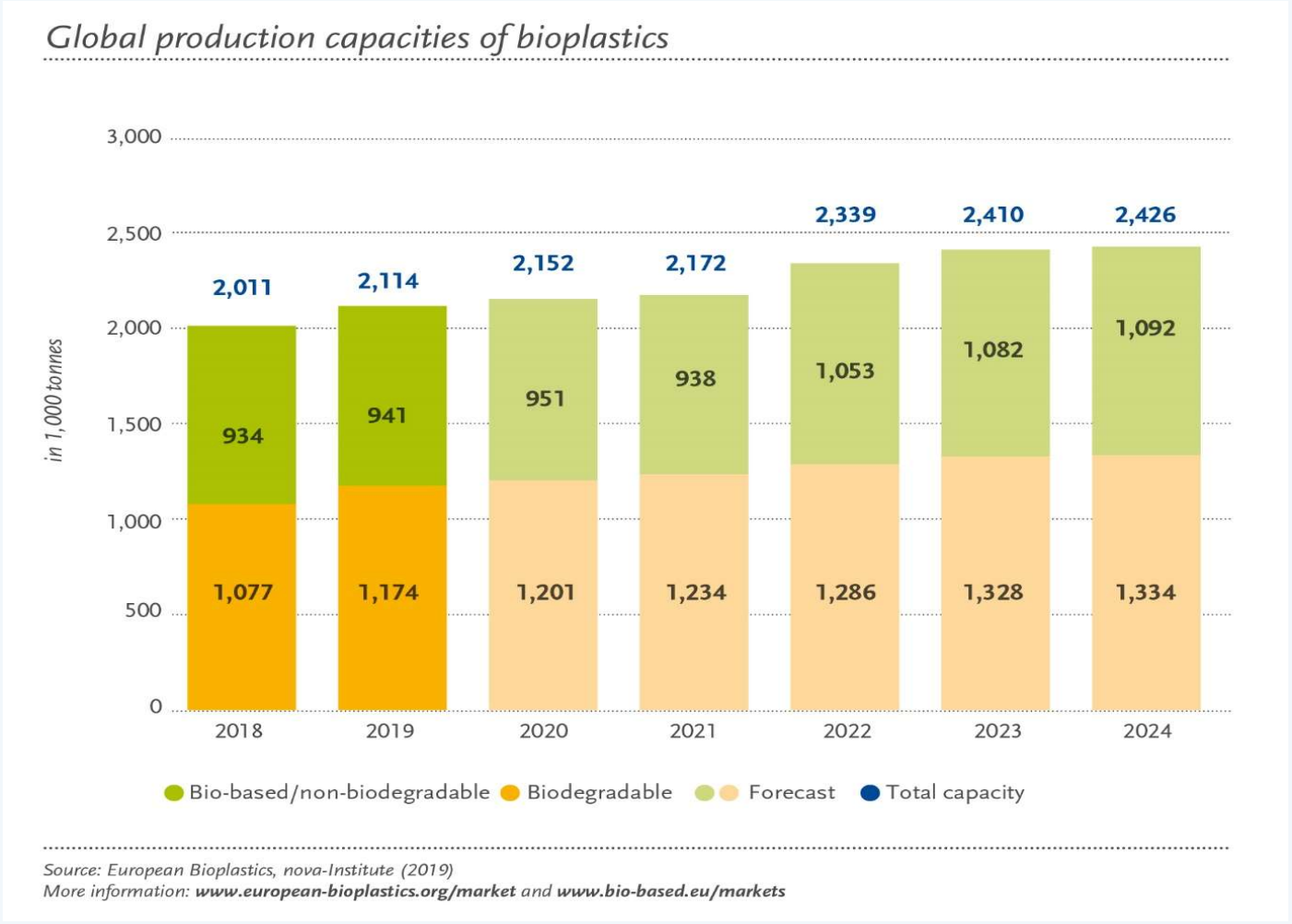

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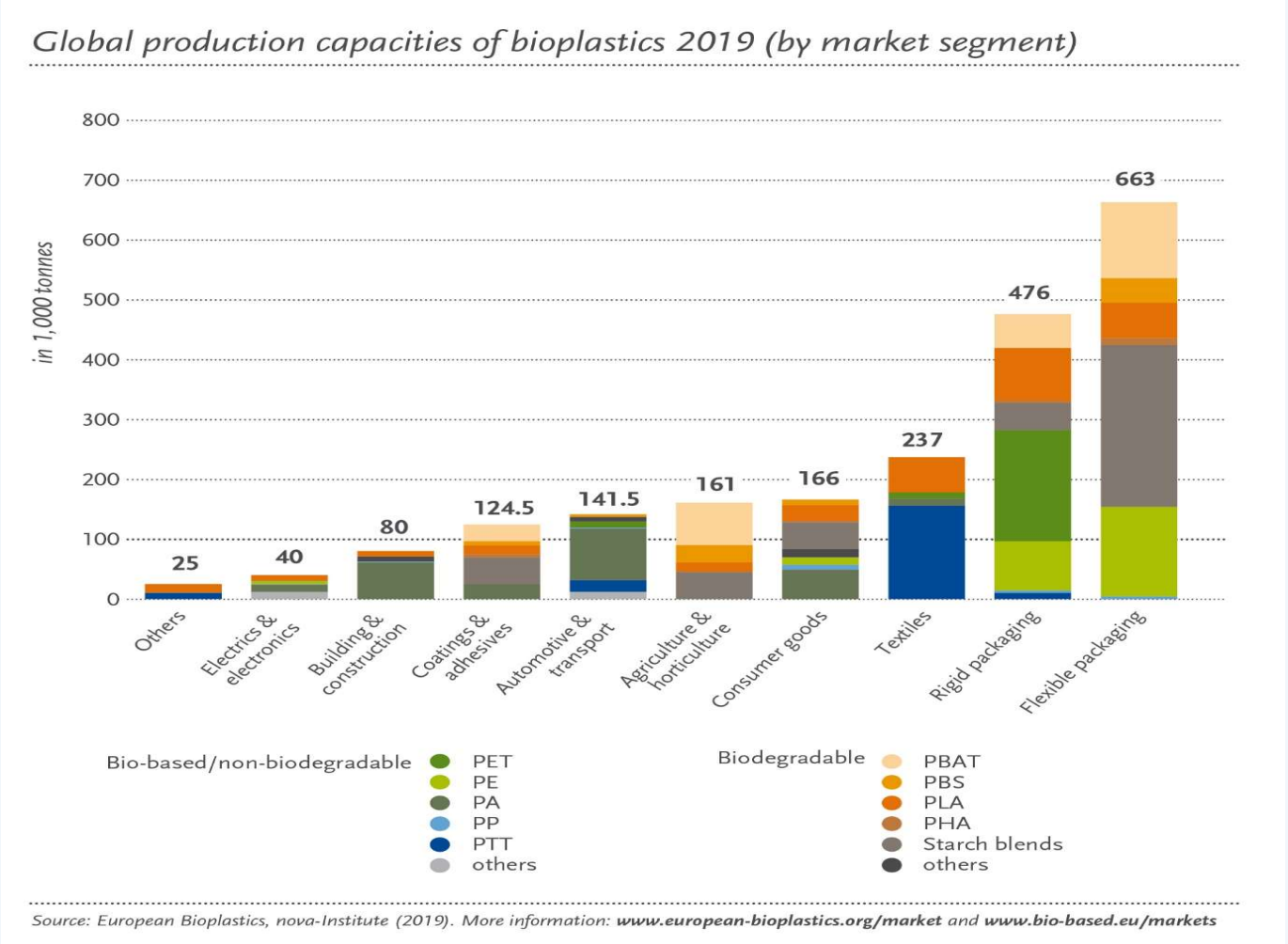
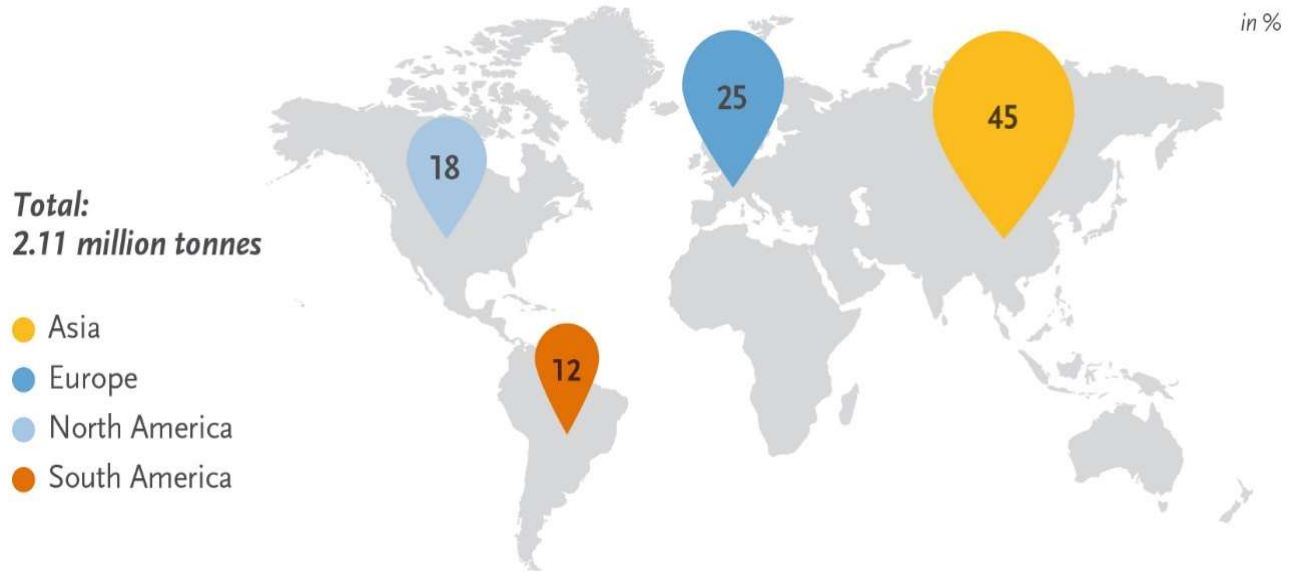


Biodegradable Plastic

Global production capacities of bioplastics in 2019 (by region)



Source: European Bioplastics, nova-Institute (2019)
More information: **www.european-bioplastics.org/market** and **www.bio-based.eu/markets**

Examples of some well known TPS blend compound manufacturers

Agrana Starch (Austria) -------- AMITROPLAST® with 100% biobased content.
AGENACOMP® (TPS + PBAT) is home compostable as well as industrial compostable.

Novamont SpA (Italy) ---- TPS blended with PBAT, PLA & Cellulosic fillers. MaterBi® compounds are used for extrusion blowing of films, extrusion of sheet for thermoformed products and injection moulding

Cardia Bioplastics (Australia) ---- compostable resin based on blend of TPS, biodegradable polyesters and natural plasticizers known as Cardia Compostable B-F®.

Plantic Kuraray (Japan, Australia, China) ---- hydroxypropylated, high amylose starch forms the base of all Plantic Technology products, and its use in packaging applications.

Biome Bioplastics Ltd. (UK) --- BiomeEP1® is a potato-starch based resin & BiomeEP2® is a corn starch based polymer resin

Biotec (Germany) ---- BIOPLAST GF 106/02® TPS from natural potato starch blended with biodegradable polyesters. BIOPLAST GS 2189 is a plasticizer-free thermoplastic material that has biobased content of around 69%.

Kingfa Science & Technology Co. Ltd. (China) --- ECOPOND®. Their compound Ecopond Flex 162 is based on TPS and is used for extrusion blowing of films

BioLogiQ (USA) - NuPlastiQ® BioPolymer is a thermoplastic resin made with a process that converts high crystalline starch powder into a low crystalline (mostly amorphous) plastic resin. Bioblend BC produced by the company is a blend of TPS with biodegradable polyesters.

Enso Plastic LLC (USA) produces Enso Renew RTP® a TPS compound from corn starch blended with biodegradable polyesters.

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Source: Agrana Starch GmbH

Biodegradable Plastic

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Bio-degradable / Compostable Plastics – Market Segments

Market Segment 1 – Extrusion Blown Films

- Largest in volume and sales
- Materials – PBAT + PLA, TPS + PVA, PBAT + TPS, PBAT + PLA + TPS, PLA + TPS
- Conventional uses - Carry bags, Shopping bags, Grocery bags, Apparel packing, Fruit & vegetable packing, Garbage bags, Agricultural film
- Specialized uses – Consumer goods / FMCG / Hardware / Electronics / Industrial packaging (all non-food)
- Other Specialized uses – e.g. PLA + PHA packaging for potato chips, tea bags etc.
- New materials – PHAs, PBS, PCL, PBSA, PBST (low availability and high cost)

Market Segment 2 – Extruded products

- Limited but emerging market in India
- Materials – PLA compounds and blends with PBS / PCL / TPS / PBSA / PBST / PHAs etc.
- Extruded Sheet (0.3 to 1.0 mm thickness) for thermoformed products like plates, thalis, bowls, cups, glass etc.

Market Segment 2 – Extruded products (Cont.)

- Extruded Drinking Straws (cold & hot drinks), stirrers, coffee cup lids, cold drink glass lids etc.
- Extrusion lamination on paper for cups, plates, thalis, glass etc.
- High temperature resistant compound for extrusion lamination on paper for hot beverage glass, hot food plates & bowls
- 3D printing filament compound
- PLA fiber and non-woven fabrics, cigarette filter buts

Market Segment 3 – Injection Moulded products

- Tiny and niche market in India
- Materials – PLA compounds and blends with other bio-degradable plastics
- Injection moulded cutlery (fork, spoon, knife), small containers / bottles (toiletries)
- Injection moulded small containers / bottles for pharmaceutical usage, syringe, vials etc.
- Injection moulded consumer goods – pens, stationary, food boxes etc.
- Crystalized PLA (opaque) for higher mechanical properties and higher temperature resistance

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Brief Project Profile

- Plant & Machinery (compound pellets) – Rs. 60 to 100 Lacs
- Plant & Machinery (blown film) – Rs. 50 to 100 Lacs (no. of units)
- Production capacity - 250 to 500 kg per hour
- Factory building 800 sq. meters (40 X 20 m)
- Total Connected Power – 300 to 500 kW (running power 60%)
- Technical manpower – 5 nos. per shift
- Finished product – compound pellets and / or film in roll form
- Project Payback Period < 2 years
- EBDIT – 25 to 30%

Products Being Developed

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Compression moulded TPS + Bagasse Fiber

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Compression moulded TPS with hydrophobic coating layer

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Biodegradable Plastic

Figure 3 Starch loose-fills used as a cushioning material for protecting valuable goods in the packing box

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Lamination on paper board

Extruded sheet for thermoforming

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Dr. Anomitra Chakravarty

KPS CONSULTANTS & IMPEX. PVT. LTD.

812, Devika Tower, 6 Nehru Place, New Delhi 110019

+ 91 98993 59661, 011 26213885, 41616899

kpspltd@gmail.com / www.kpsimpex.com

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