Contract R&D for Polymer

DJK One Stop Satellite Laboratories.

Key Themes in Polymer R&D… "Conservation" & "Sustainable Economy"

Challenges	Solutions	Actions
Dependence on fossil resources	-Transition fuels and chemical feedstocks to renewable biomass resources -Harness natural polymers	-Biomass-derived polymer materials -Biomass composites (CNF-reinforced, wood flour-filled) -Bio-based polymers from plants and microbes (NR, farnesene)
Environmental impact (pollution & degradation)	-Use the following materials & promote CO_2 fixation /Biodegradable polymers for waste plastics & marine litter /Materials free from hazardous substances /Low-impact materials throughout production to disposal	-Development and use of biodegradable polymers from biomass -Substitution with safer raw materials -Review of material structures and manufacturing processes -Development of polymer synthesis from CO_2 (carbonyl source)
Saving resources & energy (efficient use)	-Effective utilization of underused resources -Recycling (reuse, raw material/monomer recovery) -Durable materials -Energy & loss reduction in production	-Valorization of unused biomass (waste, woody, biomass) -Development of easily recyclable materials -Improvement of durability in use conditions -Milder production methods & fewer processing steps

Bio-Plastics Synthesis

Bio-process / Chemical-process

Biomass → Monomers Chemicals → Polymer (DJK's Field)

• Example of Target Monomer

Fluoroglutaric acid, Succinic acid, Lactic acid, Glycolic acid, Sebacic acid, 2-Pyrone-4,6-dicarboxylic acid, 3-Methoxy-4-acetoxystyrene, Isosorbide, 1,3-Propanediol, 1,5-Pentanediamine, 2-Pyrrolidone, Ferulic acid

• Considering process

- Monomer Synthesis & Purification
- Screening of Polymerization Catalysts
- polymerization Condition Optimization (reaction conditions, concentration)
- Polymer Purification (residual monomer removal)
- Molding Evaluation
- Property Evaluation
- Feedback to Poly. Formulation

DJK's resource: Synthesis & Polymerization; Molding & Property Eval.

Synthesis of Recyclable Elastomers (TPE)

Synthesis of TPE in DJK

Type (Abbr.)	Hard Segment	Soft Segment	Polymer Structure	Synthesis Method
TPV (Olefin)	PP crystal phase (Tm: 165 °C)	EPDM, EPR	Multi-phase Polymer Blends	Dynamic vulcanization
TPU (Urethane)	Urethane (H-bond, crystal)	Polyester, Polyether	Multi-block polymer	Step-growth polymerization
TPEE (Ester)	Polyester crystalline phase (Tm: 225 °C)	Polyester, Polyether	Multi-block polymer	Polymerization, Ring-opening polymerization
TPAE (Amide)	Polyamide (H-bond, crystal)	Polyester, Polyether	Multi-block polymer	Polymerization, Ring-opening polymerization

• Items for Investigation

- Small-scale synthesis of raw materials (polymers and oligomers)
- Examination of composition and polymerization conditions
- Small-scale trial production
- Evaluation of moldability and physical properties

• Case 1: Bio-based Polyester (PEF)

Biomass (Glucose) → Dehydration → 5-Hydroxymethylfurfural (HMF) → Oxidation → Furan dicarboxylic acid (FDCA) → Polymerization (HO-R-OH) → Bio-based Polyester

Case of R=C_2H_4

Transesterification (DMF, $HO-(CH_2)_2-OH$) → Melt polymerization → Polyethylene Furanoate (PEF)

Property	PET	PFE
Density (g/cm³)	1.36	1.43
O_2 Barrie	1	X10
CO_2 Barrier[1]	1	X40
H_2O Vapor Barrier	1	X2
Glass Transition Temp (℃)	76	88
Melting Point (℃)	250-270	210-230
Crystalline Elastic Modulus (GPa)	108	117

- **PEF's property…** tighter packing and a more rigid structure, which restricts molecular mobility.
- **Compare to PET…**
  - Higher Tg by approx. 10 ℃
  - Higher elastic modules
  - **Excellent Gas barrier property**
  - Slower crystallization rate

• Case 2: Biodegradable Polymer(Polylactic acid : PLA)

- **PLA Production Methods**
1) **Direct polymerization –** Simple, but hard to get high-molecular-weight polymer → Room for improvement
2) **Lactide Method (ROP) –** High-molecular-weight polymer achievable → Main PLA synthesis method

【Synthesis of PLA via Lactide Method】

Biomass (Glucose) → Fermentation → L-Lactic Acid → Dehydration condensation → Depolymerization & Dimerization → L,L-Lactide → ROP → PLLA

• To gain high molecular weight polymer PLA
* High-purity lactic acid monomers
* Suppress racemization in synthesis
* Remove meso-lactide in purification
* Minimize lactide moisture

Bio-mass 1 kg
→PLA yield approx. 0.4 kg

PLLA's property

項目	代表値
Crystalline Density(g/cm³)	1.29
Tg (℃)	57
Melt point (℃)	176
Molecular weight (Mw)	0.1-0.3 million

• PLA's property

The ester linkage contains only one methine carbon, resulting in poor chain segment mobility. Therefore, as an aliphatic polyester, it exhibits high heat resistance, high crystallinity, and excellent mechanical properties. On the other hand, it is stiff and brittle, with a slow crystallization rate.

• Case 3:Thermoplastic Polyurethane (TPU)

Segment	Performance	Property	e.g.
Soft- segment (SS)	Exhibiting **Rubber Elasticity (Entropy Elasticity)**	Polymer glycols with Tg less than RT	Polyester, Polyether, PC, Aliphatic (Mn=1000~4000)
Hard-Segment (HS)	Aggregating and functioning as **physical crosslinking points.**	Diisocyanate–chain extender product (high Tg, high Mp)	MDI, low-molecular-weight diols (1,4-BD), diamines

【Methods】

Prepolymer method: Polymer glycol and isocyanate are reacted to form an NCO-terminated prepolymer, followed by chain extension with a low-molecular-weight diol.

One-shot method: Polymer glycol, short-chain glycol, and diisocyanate are polymerized simultaneously (single-step process).

• Case 4:Dynamically crosslinked thermoplastic elastomer (TPV)

Thermoplastic Resin + Rubber Elastomer → Compatibilizer / Melt compounding → Rubber–Resin Blend → Cross-linker / Dynamic Crosslink → Thermoplastic Elastomer(TPV)

Thermoplastic Resin–Rubber Combinations[1)]

Resin \ Rubber	EPDM	IIR Rubber[2)]	Acrylic Rubber[3)]	H-NBR	NR	ENR[4)]	SR
PA		●	●	●		●	●
PBT		●	●	●			
PLA					●		
PP	●		●				
EVOH		●					

1) ●⇒Automotive glass run channel, door seals, interior materials, ●⇒Gas barrier applications, ●⇒Other, ●⇒Oil, heat, fatigue resistance, compression set resistance.
2) Butyl Rubber (IIR), Brominated Butyl Rubber (BIIR), Brominated isobutylene-co-para-methylstyrene Rubber (BIMS),
3) ACM, ANM,
4) Epoxidized Natural Rubber

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