한국화학공학회 2025년도 봄 총회 및 학술대회
April 23-25, 2025 Dague, Exhibition & Convention Center (EXCO), Korea

부산대학교 PUSAN NATIONAL UNIVERSITY

Polyamide 6,6 Polymerization Through High Efficiency Catalytic Reaction And Process Pressure Control

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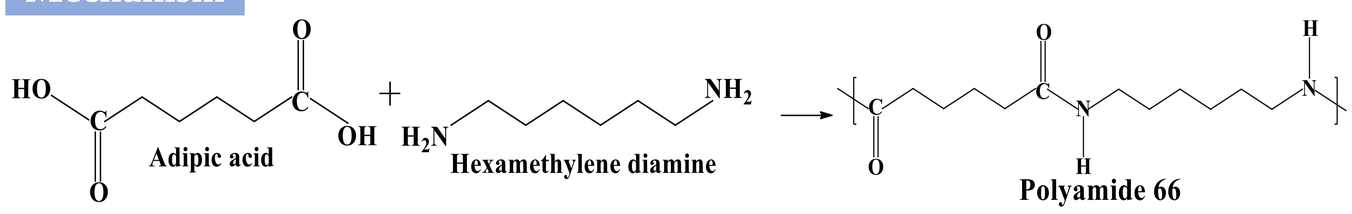
Abstract

Polyamide 6,6 (PA66) was synthesized through a polymerization process utilizing a vacuum reactor. Adipic acid and hexamethylenediamine were used as monomers for condensation polymerization, under a pressure range of 300–50 Torr. Additionally, the polymerization of PA66 synthesized using sodium hypophosphite and phosphoric acid as catalysts was compared. Gel permeation chromatography (GPC) was used to measure molecular weight, while viscosity analysis were used to evaluate the degree of polymerization (DP) and processability. PA66 synthesized under low pressure conditions was analyzed the molecular structure and chemical composition through nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FTIR) respetivlely. Moisture generated during the PA66 polymerization process interferes with polymerization, a vacuum process is important to effectively remove water. As a result, successfully polymerized PA66 by optimizing conditions of low pressure and catalyst type. Polymerizing PA66 under low pressure conditions is more efficient than high pressure

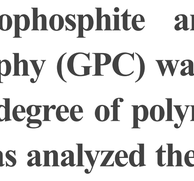
Experimental

Mechanism

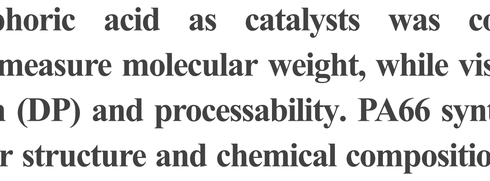


Catalysts

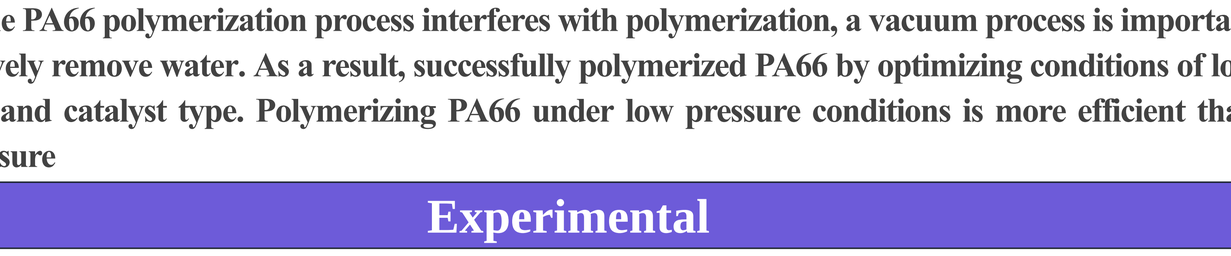
Case1. Phosphorous catalyst



Case2. Phophrous + Citric acid



Case3. Phosphorous + DES



Step 1 Formation of a transparent aqueous solution of nylon salt

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Step 2 Preparation the system for polycondensation

↓

Step 3 Polymerization

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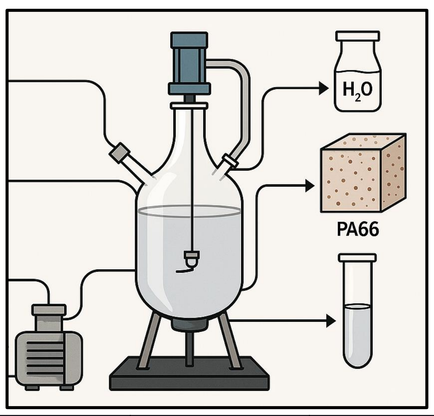
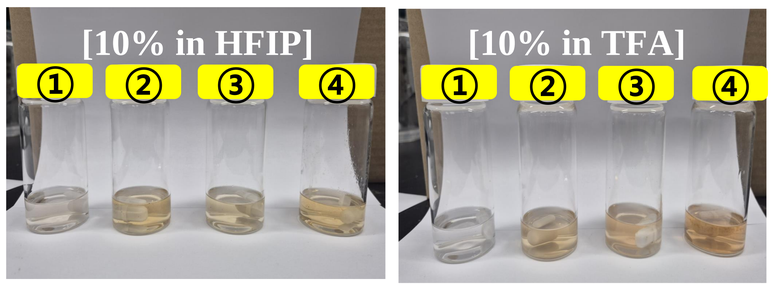
Step 4 Cooling and Solidification



Category	Substance	Amount
Monomers	HMDA AA	116.2 g 146.1 g
Solvent	Distilled Water	300 mL
Catalyst	Phosphate Citric acid	0.5-1.0 g

Figure1. PA66 polymerization reduced pressure reduction process design

Relative Viscosity

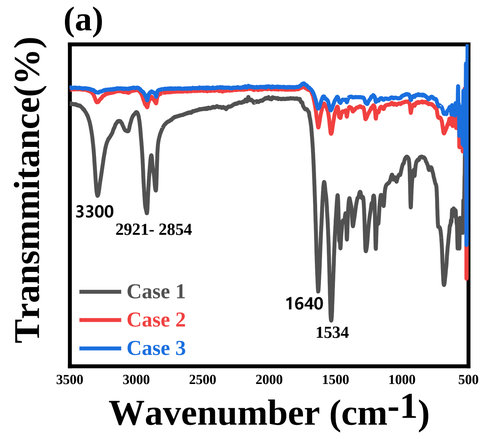


	10% in HFIP	10% in TFA
① Neat PA	1.70	1.40
② Phosphorous	1.50	1.25
③ + Citric acid	1.60	1.30
④ + DES	1.75	1.45

Figure 2. Relative viscosity comparison analysis of neat pa66 and case 1,2,3

Result & Discussion

FT-IR

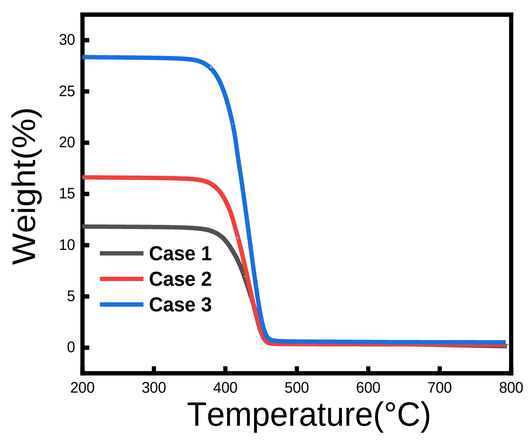


Wave number (cm^{-1})	Assignment	Interpretation
~ 3300	N–H stretching	Indicates the presence of amide N-H bonds
~ 2910–2854	C–H stretching (CH_2)	Corresponds to methylene (-CH_2-) groups
~ 1640	Amide I (C=O stretching)	Confirms amide bond formation (C=O double bond)
~ 1534	Amide II (N–H bending)	Characteristic of amide structure (N-H deformation)

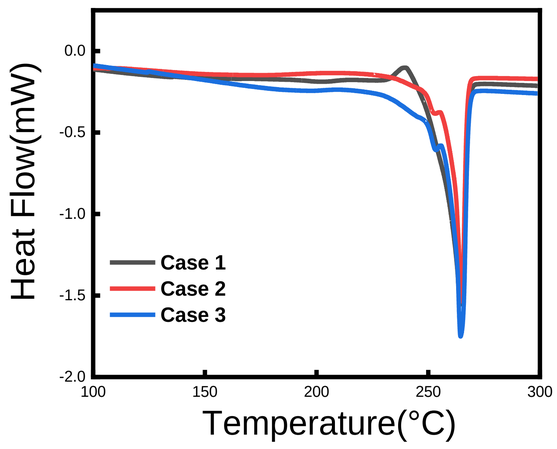
Wave number (cm^{-1})	Assignment	Interpretation
~ 3300	N–H stretching	Confirming amide bond presence
~ 1640	Amide I (C=O stretching)	Indicates amide structure (-CONH-)
~ 1534	Amide II (N–H bending)	Typical amide signal

Figure 3. FTIR analysis of (a) case 1,2,3 and (b) PA66 Condensed water

TGA



DSC



Sample	Phosphorous catalyst	Phosphorous + Citric acid	Phosphorous + DES
T_g (°C)	53	53	53
T_m (°C)	252	255	258
T_d (°C)	425	435	445
Residue (%)	12	16	29

Figure 4. TGA,DSC analysis of Case 1,2,3

Conclusion

- ✓ Polymerization reaction using a catalyst on neat PA66 for Bio PA66 production
- ✓ Samples with DES or organic acid additives showed higher relative viscosity and enhanced thermal stability, confirming the high efficiency of the catalytic system
- ✓ Structural characterization by FT-IR and ^{1}H NMR confirmed that all PA66 samples exhibit highly similar peak positions → the reaction occurred successfully and the structure was well formed
- ✓ The pH measurement results showed that only a small amount of HMDA (0.133%) was present in the condensed water, and the FTIR results showed that the peak positions of the condensed water and distilled water were almost the same → This means that the product is virtually free of other impurities or reaction by-products

Acknowledgement

This work was supported by the Korea Institute of Industrial Technology Evaluation and Planning (KEIT) in 2025 (00433823, Production technology development of bio polyamide66 advanced materialproduct based on starch(sugar) byproducts for future transport internal & external components/modules).

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