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

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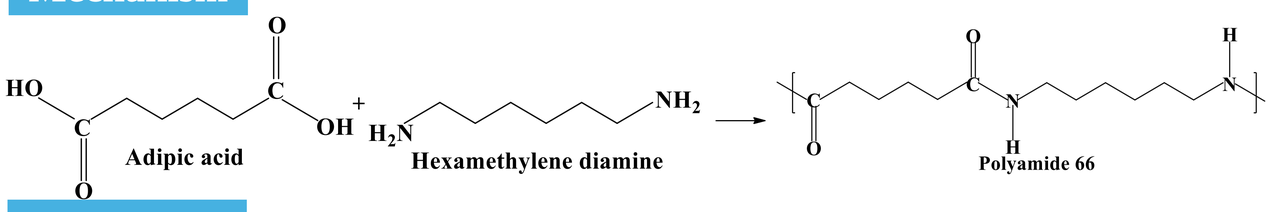
Abstract

Polyamide 6,6 (PA66) was successfully polymerized under vacuum conditions. Adipic acid and hexamethylenediamine were used as monomers for condensation polymerization, and the reaction was performed in the vacuum range of 300–50 Torr. In addition, the polymerization of PA66 synthesized by mixing a conventional phosphorus catalyst and a phosphorus catalyst with choline chloride : urea was compared. The molecular weight change of the synthesized PA66 was confirmed using gel permeation chromatography (GPC) and viscosity measurement. The structural characteristics were confirmed using nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopy. Since water generated during the polymerization of PA66 causes defects in the experiment, a vacuum process is essential to remove the water. As a result, PA66 was successfully synthesized by controlling the pressure and catalyst. PA66 synthesized under vacuum offers the potential for high-efficiency production from an industrial perspective.

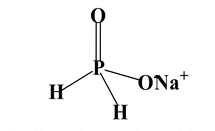
Experimental

Mechanism

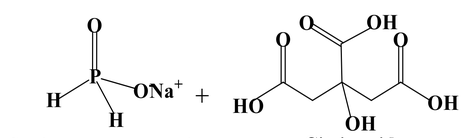


Catalysts

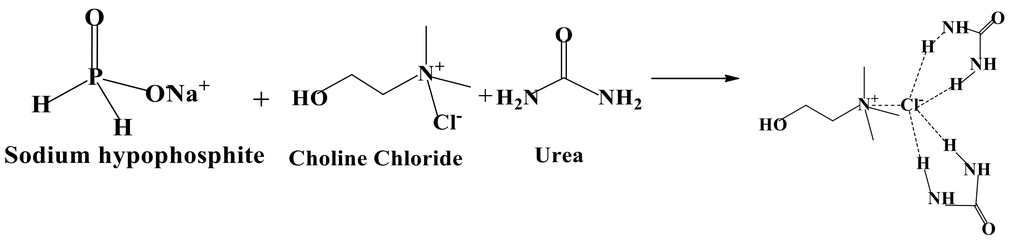
Case1. Phosphorous catalyst



Case2. Phophrous + Citric acid



Case3. Phosphorous + DES



Step 1 Formation of a transparent aqueous solution of nylon salt

↓

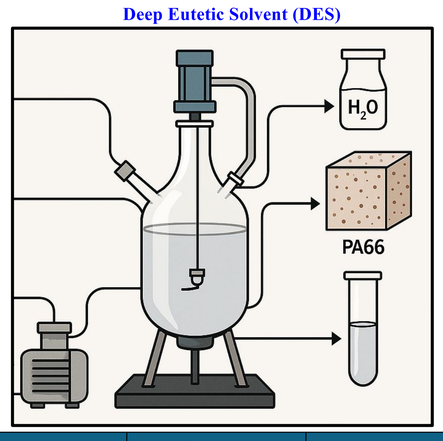
Step 2 Preparation the system for polycondensation

↓

Step 3 Polymerization

↓

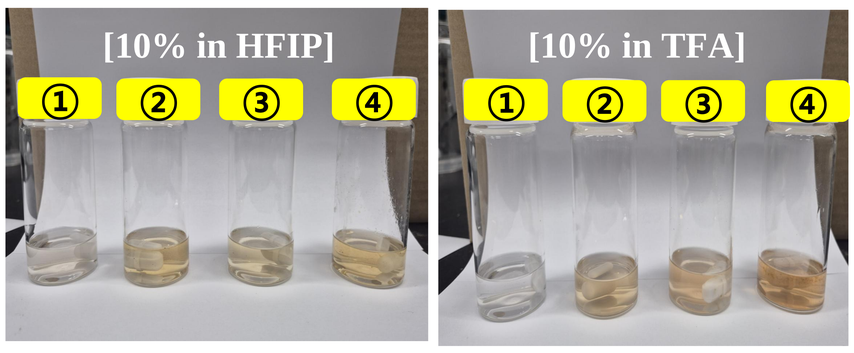
Step 4 Cooling and Solidification



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

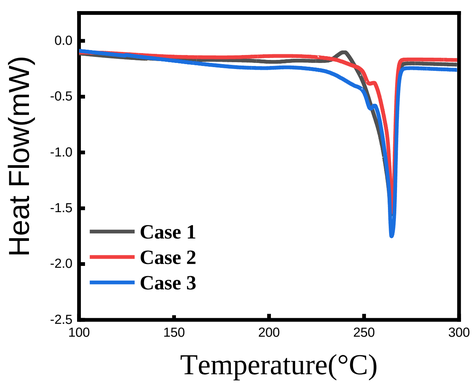


	10% in HFIP	10% in TFA
① Neat PA	1.70	1.40
② Phosphorous	1.50	1.25
③ + Citric acid	1.60	1.30
④ + DES	1.75	1.45

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

Result & Discussion

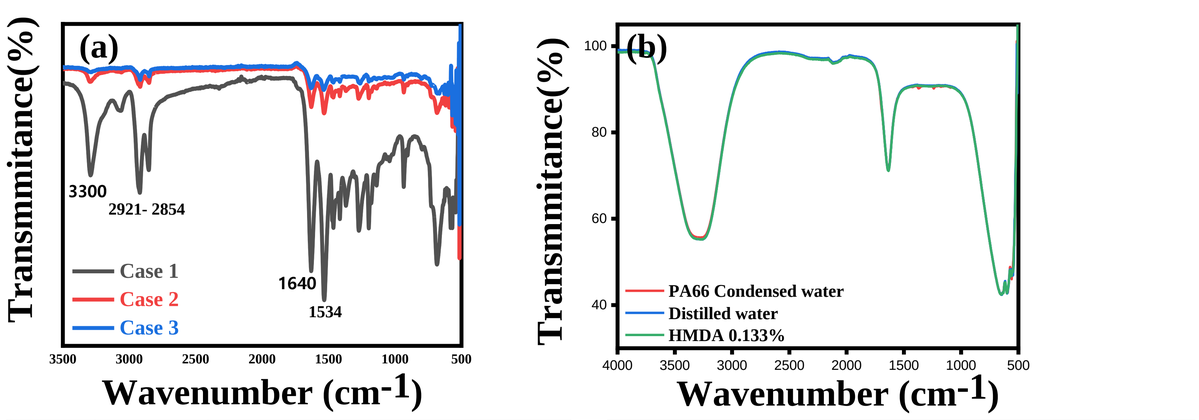
DSC



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 3. DSC analysis of Case 1,2,3

FT-IR

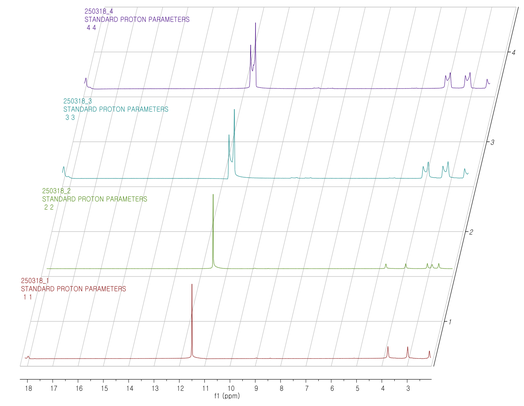


Wave number (cm^{-1})	Assignment Cas 1e	Interpretation
~ 3300	N–H stretching	Indicates the presence of amide N-H bonds
~ 2910–2854	C–H stretching (CH_2)	Corresponds to methylene (-CH_2-) groups
~ 1640	Amide I (C=O stretching)	Confirms amide bond formation (C=O double bond)
~ 1534	Amide II (N–H bending)	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 4. FTIR analysis of (a) case 1,2,3 and (b) PA66 Condensed water

1H NMR



δ (ppm)	Proton Type / Structure	Interpretation
~8.0	-NH (Amide proton)	Proton in the amide group (N-H of –CONH-)
~3.0-3.5	-CH_2-NH (α-Methylene)	Methylene protons adjacent to amine groups
~1.5-2.0	Internal -CH_2 (CH_2- CH_2-)	Methylene units in the polymer backbone

Figure 5. 1H NMR analysis results of case 1,2,3 and Neat PA66

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

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