

## 불용성 방향족 폴리이미드의 구조개질 및 소결특성

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## Structure Modification and Sintering Behaviors of Infusible Aromatic Polyimide

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**요 약 :** 불용성 폴리이미드의 소결 성형거동을 조사하기 위하여 폴리이미드 미세분말을 다양한 방법으로 제조하였다. 제조조건 및 공중합구조 도입에 의해 결정구조 및 분말입자형태의 변화가 수반되었으며 소결시편의 제반 특성과 파단 조직을 비교 검토하여 본 결과, 소결시편의 역학적 강도의 발현과 분말의 성형성은 분말 입자간의 접합성과 밀접히 연계된 폴리이미드 분말의 미세성과 결정화도에 크게 기인함을 확인하였다. 본 연구의 몇몇 시편의 경우 용매 캐스팅 방법으로 제조된 폴리이미드 필름의 인장강도 대비 60~70%에 해당하는 역학적 강도의 도달이 가능하였다.

**Abstract :** Fine powders of polyimides were prepared via various methods in order to examine the sintering behaviors of infusible aromatic polyimides. Significant changes of crystallinity and particle structure were observed when comonomers and different preparation methods were applied on particle formation. As a result from related characteristics and fracture textures of sintered samples, it may be concluded that mechanical strength performance and moldability of polyimide powder are closely related with the degree of fineness and the crystallinity of polyimide powders, which facilitate binding of particles. In this work, some sintered bulk samples could reach the 60-70% of the tensile strength given by solvent-casted polyimide films.

**Keywords :** polyimide, sintering, crystallinity, particle size, moldability.

### Introduction

Aromatic polyimides are well known as extremely high-melting polymers, which do not flow at the applied temperatures for molding. The polyimide from PMDA-ODA has  $T_g$  about 385°C and a theoretical melting point of 592°C.<sup>1</sup> It does not show fluidity at the temperatures up to its theoretical melting point but decomposes

thermally before reaching its theoretical melting point. The technical problems in preparing bulk moldings from polyimides has been partially facilitated by modifying the physical or chemical structures of polyimides to improve moldability. The chemically modified polyimides such as 'LaRC-TPI, Ultem, PI2080, Torlon, etc' have improved moldability by lowering  $T_g$  or  $T_m$  through the incorporation of flexible units in the

polymer main chain. Though these classes of polyimides still present good thermal stabilities, considerable sacrifice of the thermal properties in comparison with those of the full aromatic polyimides could not be avoidable.

Vespe<sup>2</sup>, which is useful over a wide range of temperature and suitable for continuous service at 315°C, has the PMDA-ODA structure, and has known to be prepared by high temperature sintering of polyimide powders. However, the adhesion and binding mechanism of the infusible polyimides powders during sintering has not well defined.

## Experimental

**Materials.** Pyromellitic dianhydride(PMDA) and benzophenone tetracarboxylic dianhydride (BTDA) were purified by recrystallization in dioxane and acetic anhydride solution. 4,4'-oxydianiline(4,4'-ODA), m-phenylene diamine (m-PDA), 4,4'-diaminodiphenyl sulfone(DDSO) were used after recrystallization in the mixed solvent of DMF and methanol. 3,4'-Oxydianiline(3,4'-ODA) and 4,4'-diaminodiphenyl sulfide(DDS) were synthesized by known methods.<sup>3,4</sup> Polymerization solvents like N,N'-Dimethyl acetamide(DMAc) and pyridine were dried by standard procedures prior to use.

### Preparation of Polyimide Powders.<sup>5-9</sup>

#### From polyamic acid:

**Method A:** Polyamic acid(PAA) obtained from PMDA and ODA was diluted to 5wt.% with DMAc and then refluxed with stirring. Continuous removal of water was carried out by the controlled distillation of solvent until imidization and particle formation were completed.

**Method B and C:** 50ml of 10wt.% PAA solution in DMAc was dropped into a 500ml of mixed solution of petroleum ether and acetic anhydride(4:1 by volume) at room temperature with vigorous mechanical stirring. The chemically imidized powder was kept at 220°C under

vacuum for further imidization. Method C used ethyl ether in place of petroleum ether.

#### *in situ* Polymerization and Imidization.

**Method D:** 0.02mole of PMDA solution in 70ml of pyridine was dropped into 0.02 mole of ODA solution in 200ml of pyridine with stirring at room temperature for 50min. The mixture solution was heated to maintain refluxing with the controlled distillation of solvent for 2hrs. During the reaction yellowish fine particles were precipitated. For the preparations of various copolyimide powders, 3 ~ 9mole % of comonomers were added in the polymerization reactions respectively. All the powder samples were washed with acetone, dried under vacuum, then treated at 300°C under N<sub>2</sub> for 3 hrs for further imidization.

**Molding and Sintering.** Polyimide powders were introduced into a dumbbell type mold, followed by compressing under 1000~3000kg/cm<sup>2</sup> pressure to give about 1mm thickness. Molded samples were allowed sintering in a furnace at 400°C for 6hrs under N<sub>2</sub> atmosphere.

## Results and Discussion

**Preparations of Polyimide Powders and Sintering.** In this study, in order to improve the processability for the bulk molding without the loss of heat resistance of polyimides, moldable powders of polyimides based on PMDA-ODA were prepared from the variations of reaction conditions and the incorporations of comonomers, such as m-PDA, 3,4'-ODA, DDS, and BTDA.

Polyimide powders were prepared through the different methods such as refluxing of polyamic acid and dropping dianhydride solution into diamine solution during reflux accompanied with controlled distillation of the medium solvent to complete the imidization reaction. The procedures are summarized in Table 1. Copolyimide powders were prepared via the lat-

**Table 1.** Representative Preparation Methods of Polyimide Powder Samples based on PMDA-ODA

Method	Sample	Powder Formation Form	Solvent Medium	Imidization Condition
A	Pa	Polyamic acid	DMAc	Reflux & distillation
B	Pb	Polyamic acid	DMAc	Ac <sub>2</sub> O/ethyl ether
C	Pc	Polyamic acid	DMAc	Ac <sub>2</sub> O/petroleum ether
D	Po	In-situ reaction of PMDA-ODA	Pyridine	Reflux & distillation

**Table 2.** Monomer Compositions for Copolyimide Powders

Sample	Dianhydride(mole %)		Diamine(mole %)			
	PMDA	BTDA	4,4'-ODA	m-PDA	3,4'-ODA	4,4'-DDS
P0	100		100	0		
P1	100		97	3		
P2	100		94	6		
P3	100		91	9		
A1	100		97		3	
A2	100		94		6	
A3	100		91		9	
S1	100		97			3
S2	100		94			6
S3	100		91			9
B1	97	3	100			
B2	94	6	100			
B3	91	9	100			

Samples were prepared via method D.

ter method which gives better results. Comonomers for copolyimide powders were chosen in the range of 3~9mole%. Monomer compositions are listed in Table 2. The obtained polyimide powders were compressed to form dumb-bell type specimens under the pressure of 1500~3000kg/cm<sup>2</sup>, and then heated for sintering at the temperature of 400~500°C, which were chosen over  $T_g$ , in the N<sub>2</sub> atmosphere.

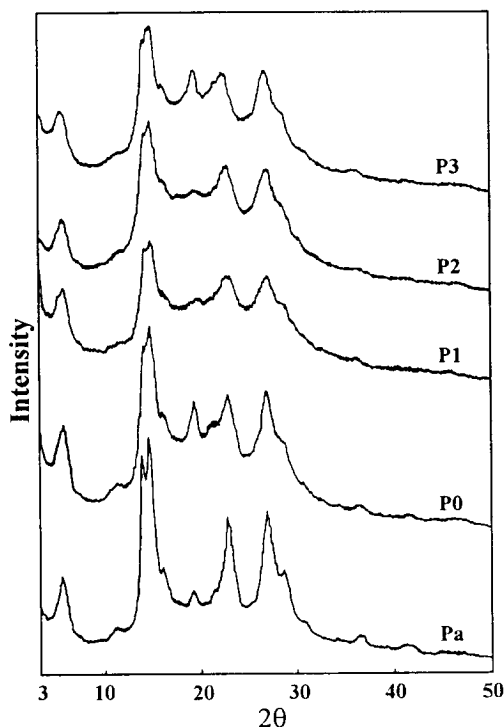
**Crystallinty.** PMDA based polyimide could be easily crystallized during polymerization when symmetric diamine like p-phenylenediamine is a counter part of diamine monomer. The less symmetric diamines such as ODA and m-PDA restrict crystallization but are known to

be crystallized according to the thermal treatment or annealing<sup>8</sup> to result in variations of crystallinity.<sup>11,12</sup>

In this work, The crystallinities of polyimide powders were found to be remarkably varied by the preparation method and the incorporation of comonomer type. The crystallinities were simply estimated from powder X-ray diffraction patterns as shown in Fig. 1 using the method of Matthews<sup>13</sup> expressed by

$$X = \frac{T_{cr}}{T_{cr} + T_{am}}$$

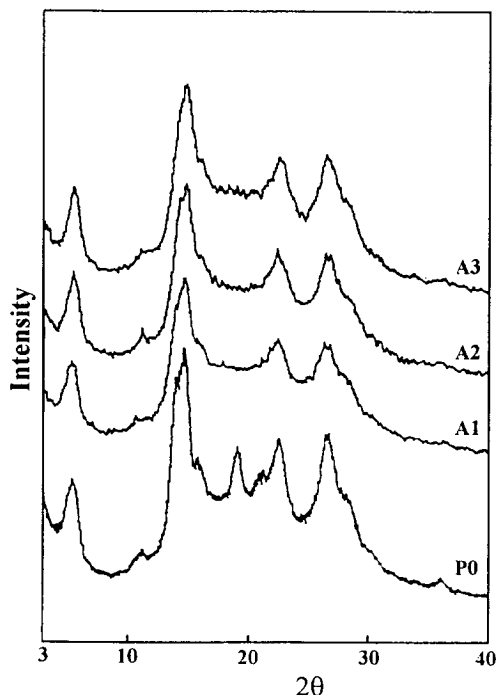
where  $T_{cr}$  is the total crystalline scattering



**Fig. 1.** X-ray diffraction patterns of powder samples based on PMDA-ODA polyimide and m-PDA modified copolyimides.

converted to the area between peak line and amorphous background line and  $T_{am}$  is the total amorphous scattering converted to the area under amorphous background line.

Pratt et al.<sup>14</sup> reported that initial crystallization occurred as the polyamic acid was converted thermally into the polyimide in the temperature range 150~200°C. On this point of view, we can understand that the rapid imidization under the lower temperature condition with unsymmetrical comonomers can lower the crystallinity during the imidization. As shown in Fig. 5, the crystallinities of powder samples were changed according to the preparation methods and the incorporation of comonomers. The difference of crystallinity between preparation



**Fig. 2.** X-ray diffraction patterns of powder samples based on 3,4'-ODA modified copolyimides.

method A and D is considered to be affected by the chain mobility during imidization. Since PAA refluxing is performed in solution environment at the initial condition, there are enough chance for chain rearrangement during imidization. While in-situ method does not offer sufficient time for chain rearrangement because precipitation occurs rather fast. These trends are also consistent with the results of particle size changes. The effect of comonomers on crystallinity is considered to depend on the symmetry of comonomer. The capability of comonomers for lowering crystallinity is found to be in the order of BTDA>m-PDA>3,4'-ODA>DDS as shown in Fig. 6. As increasing comonomer content in feed, the crystallinity reached minimum and then slightly increased. This phenomena may be due to the transition of physical property of copolyimide, which has a softer character accelerating chain rearrangement kinetically under the same imidization con-

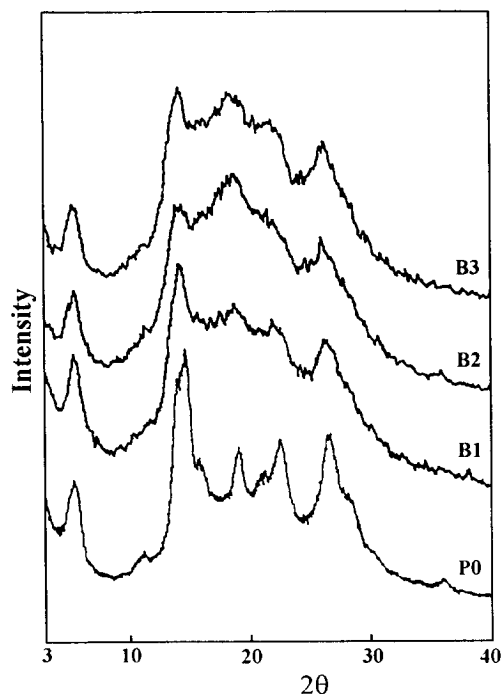


Fig. 3. X-ray diffraction patterns of powder samples based on BTDA modified copolyimides.

dition.

**Particle Size and Fractured Texture of Sintered Specimen.** As mentioned in crystallization behavior, the rate of precipitation mainly affected the particle size of resulting powders. The particle sizes estimated from the fracture images of sintered specimens by SEM are around  $5\mu\text{m}$  from method A and  $0.1\sim 0.2\mu\text{m}$  from method D as exhibited in Fig. 7. The chemical imidization methods(B and C) didn't give fine particle but bulky fibrous structures resulting in failure of molding. The evidence of binding between particles could be also verified by examining the textures of sintered specimens as shown in Fig. 7 and 8.

If the binding is effective, a sphere shape of particle is disappeared and then transformed to a fibrous wavy texture on fracturing. Consequently, it might be suggested that the lower crystallinity enhances the molecular diffusivity

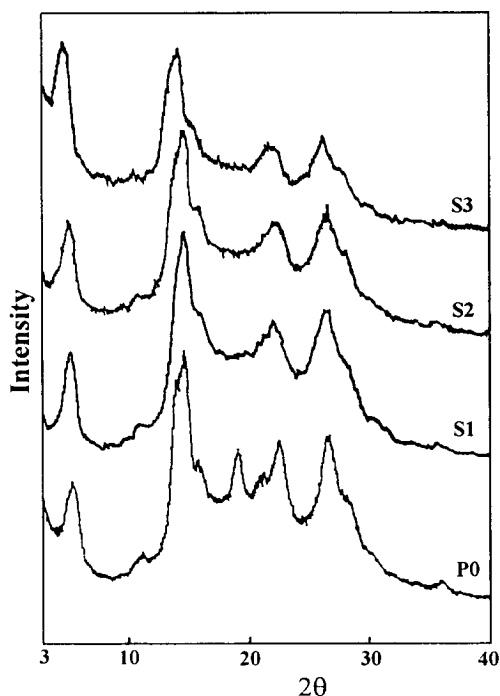


Fig. 4. X-ray diffraction patterns of powder samples based on DDS modified copolyimides.

between particles over the glass transition temperature and the higher fineness of particles offers larger contact area, resulting in a better moldability or a binding effect.

**Mechanical Strength of Sintered Specimen.** In order to compare the characteristics of various specimens, the samples prepared from compression molding to form the dumbbell shape with 2cm length under the pressure of  $1500\text{kg}/\text{cm}^2$  followed by sintering at  $400^\circ\text{C}$  for 6 hrs were chosen for analysis. Tensile strength was measured at  $25^\circ\text{C}$  and the comprehensive results are summarized in Table 3. These results depict that the moldability and the strength of sintered specimens are strongly related to the particle size and the crystallinity of powders.

The strength performance significantly depends on the particle size and the crystallinity as shown in the results of Pa and P0 which were prepared via different methods. Both the

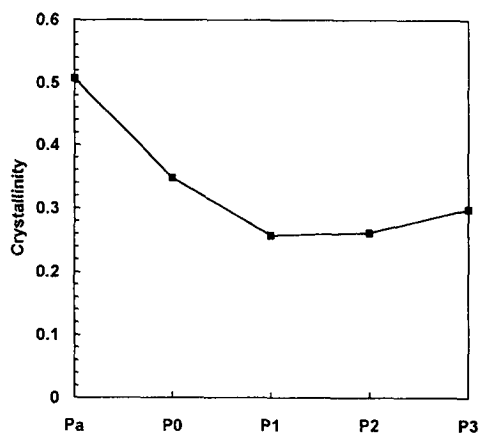


Fig. 5. Variations of crystallinity in PMDA-ODA based polyimide powders according to the preparation methods (Pa, P0) and incorporation of third monomer(m-PDA).

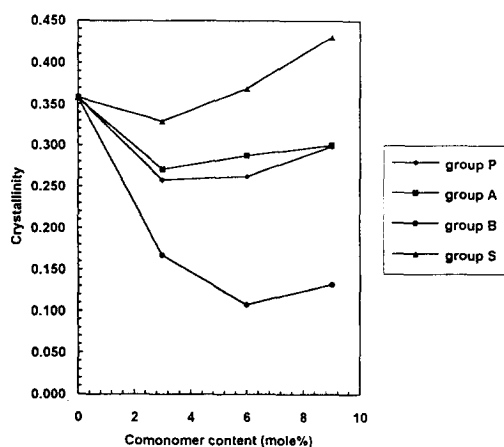


Fig. 6. Crystallinity changes with participated comonomer contents in various copolyimides powders.

finer particle size and the lower crystallinity contribute to the surface adhesion between polyimide particles and might perform a better mechanical strength.

Though the lower crystallinity exhibited more effective binding effect on particles, inconsistency between different comonomer systems was observed. This may be due to the different mechanical properties between amorphous and crystalline phase in each copolyimide. Mechani-

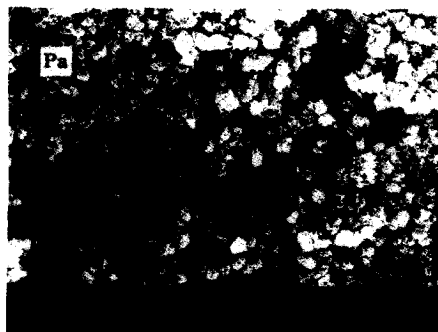


Fig. 7. SEM micrographs of fractured surfaces of sintered samples indicating particle size from preparation method A(sample Pa) and D(sample P3).

cal strength was increased with the applied pressure on compression molding and reached a maximum near  $3000\text{kg/cm}^2$  of pressure, resulting in about  $700\text{kg/cm}^2$  of tensile strength in the case of P0, implying that high pressure molding facilitated the compact packing of particles.

## Conclusion

Fine powders of polyimides were prepared via various methods in order to examine the sintering behaviors of infusible aromatic polyimides. Significant changes of crystallinity and particle structure were observed when comonomers and different preparation methods were applied on particle formation. The difference of crystallinity between preparation methods is considered to be affected by the chain mobility during



**Fig. 8.** SEM micrographs of fractured surfaces indicating transformation of particle morphology via inter-particle binding during sintering of P0 and B1.

imidization. Since the method of PAA refluxing is performed in solution environment at the initial condition, there are enough chance for chain rearrangement during imidization. In-situ method does not offer sufficient time for chain rearrangement because precipitation occurs rather fast. These trends are also consistent with the results of particle size changes. The effect of comonomers on crystallinity is considered to be related with the symmetry of comonomers. The capabilities of comonomers for lowering crystallinity were found to be in the order of BTDA > m-PDA > 3,4'-ODA > DDS.

As a result from the related characteristics and fracture textures of sintered samples, it may be concluded that mechanical strength performance and moldability of polyimide powder are closely related with the degree of fineness and the crystallinity of polyimide powders, which facilitate binding of particles. The evidence of binding between particles could be also verified by examining the textures of sintered specimens. Consequently, it might be suggested

**Table 3.** Characteristics of Sintered Polyimides and Powder Molding

Sample	Crystallinity	Observed Particle size( $\mu\text{m}$ )	Fractured Texture	Tensile Strength ( $\text{Kg/cm}^2$ )
Pa	0.507	$\sim 5$	S	150
P0	0.348	$\sim 0.1$	F	510
P1	0.257	$\sim 0.1$	F	520
P2	0.262	$\sim 0.1$	F	410
P3	0.299	$0.1 \sim 0.2$	FS	350
A1	0.271	$0.1 \sim 0.7$	FS	300
A2	0.288	$0.1 \sim 0.7$	FS	340
A3	0.300	$0.1 \sim 0.7$	FS	380
S1	0.329	$0.1 \sim 1$	SF	180
S2	0.369	$0.1 \sim 1$	SF	190
S3	0.431	$0.1 \sim 1$	SF	210
B1	0.167	$\sim 0.1$	F	560
B2	0.108	$\sim 0.1$	F	530
B3	0.132	$\sim 0.1$	F	510

F: Fibrous textures occurred in the fracture surface of sintered polyimide.

S: Sphere structures were still remained.

Crystallinity was estimated using the method of Matthews.<sup>11</sup>

that the lower crystallinity enhances the molecular diffusivity between particles over the glass transition temperature and the higher fineness of particles offers larger contact area, resulting in a better moldability or a better mechanical strength of a sintered specimen. In this work, some sintered bulk samples could reach the 60 ~ 70% of the tensile strength given by solvent-casted polyimide films.

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