Synthesis and Properties of Siloxane Containing Copolyimides

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실록산이 함유된 폴리이미드의 합성과 물성

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Abstract : Siloxane containing copolyimide(SPI) was synthesized from 3, 3', 4, 4'-benzophenonetetracarboxylic dianhydride(BTDA), 4, 4'-methylene dianiline(MDA), 4, 4'-oxydianiline(ODA) and amine-terminated polydimethylsiloxane(PDMS). Homopolyamic acid(HPAA) in tetrahydrofuran(THF) was reacted with PDMS to obtain siloxane containing polyamic acid(SPAA) followed by the thermal curing to manufacture SPI. SPAA and HPAA exhibited inherent viscosity value of 0.35~0.48dl/g. Glass transition temperature of SPI ranged in 258 °C~264 °C. SPI had a lower T_g than that of HPI. ODA based HPI and SPI showed slightly higher T_g values, thermal stability, and water content.

요 약

3, 3', 4, 4'-Benzophenontetracarboxylic dianhydride(BTDA)와 방향족 디아인민 4, 4'-oxydianiline(ODA) 및 amine terminated polydimethyl siloxane(PDMS)을 이용하여 homopolyimide(HPI)와 siloxane 함유 polyimide (SPI)를 합성하였다. 제 1 단계 반응-생성물인 homopolyamic acid(HPAA)는 극성용매인 N-methylpyrrolidone (NMP)을 이용하여 얻었다. 제 1 단계에서 얻은 HPAA 와 tetrahydrofuran(THF)에 녹인 세 종류의 PDMS(분자량 $M_n = 1700$ g/mol, 4000 g/mol, 7000 g/mol)를 30 wt % 로 반응시켜 siloxane-copolyamic acid(SPAA)를 얻은 후 이를 thermal curing 하여 SPI 를 얻었다. SPI 및 HPI 의 precursor 인 SPAA 와 HPAA 의 inherent viscosity 는 0.35~0.48 dl/g 이었다. 함수율은 SPI 는 최저 0.998 %, HPI 는 최저 1.88 % 정도였다. BTDA/MDA/siloxane 계의 유리전이온도는 258 °C-267 °C 이었다. 열중량 분석 결과 BTDA/ODA/siloxane 계의 경우가 BTDA/ MDA/siloxane 계보다 다소 높은 분해 온도를 갖는 것으로 나타났다.

1. INTRODUCTION

There has been continuing needs for high temperature and high functional polymeric materials in electronics and aerospace industry. Especially, heterocyclic or ladder-type polymer materials received much attention. Among these materials, homopolyimide (HPI) has been used for adhesives, coatings and composite materials due to its high thermal stability at elevated temperature[1]. Despite its excellent physicochemical properties and high temperature resistance, HPI received a limited application due to the difficulty in processability[2].

Therefore, the research has been focused on the incorporation of flexible functional groups in the main chain of polyimides[3,4,5]. Synthesis and properties of pyromellitic dianhydride (PMDA)/4, 4'-oxydianiline (ODA)[6], 3, 3', 4, 4'-benzophenone tetracarboxylic dianhydride (BTDA) / ODA[7], BTDA/4, 4'-methylene dianiline (MDA)[8], BTDA/p-phenylene dia-

mine (p-PDA)[9], and hexafluoroisopropylidene-2, 2-bis (phthalic acid anhydride) (6FDA)[10,11] system has been already reported. The siloxane containing polyimide from monomeric siloxane diamine and PDMS has been published too[12]. For siloxane incorporated block or copolyimides, synthesis of BTDA/4, 4'-diaminodiphenylsulfone (DDS)/siloxane[13], mechanical properties of BTDA/siloxane diamine/MDA [14] and photophysical properties of BTDA/ODA/siloxane diamine[15] have been already revealed. Gas separation membranes composed of aliphatic diamine/BTDA or biphenyltetracarboxylic dianhydride (BPDA)/PMDA have been studied by several authors [16].
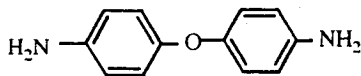
In this study, siloxane containing polyimide (SPI) were synthesized from BTDA/MDA (or ODA)/oligomeric siloxane diamine. The thermal stability, mechanical properties and water content of SPI were investigated for possible future application in gas and organic separations.
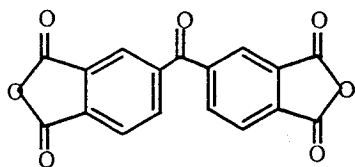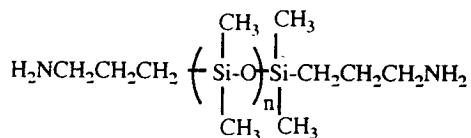

3,3'-4,4'-Benzophenonetetracarboxylic
dianhydride (BTDA)
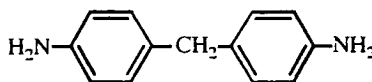
4,4'-Methylenedianiline (MDA)

4,4'-Oxydianiline (ODA)

Polydimethylsiloxane (PDMS)

n = 21, 52, 94

Fig. 1. Chemical structure of monomers.

2. EXPERIMENTAL

2. 1. Reagents

Chemical structures of tetracarboxylic dianhydride and diamines used in this study were illustrated in Figure 1. BTDA was obtained from Aldrich Chemical Co. and recrystallized from acetic anhydride followed by drying at 170 °C for 28 hours under vacuum prior to use. ODA and MDA were from Aldrich Chemical Co. and used after recrystallization in ethanol. Amine-terminated poly (dimethyl siloxanes) (PDMS, $M_n = 1700$, 4000, 7000 g/mol) were from Shinetsu Co. and coded as PDMS-1700, -4000, -7000 depending upon the molecular weight, respectively. Tetrahydrofuran (THF) and N-methylpyrrolidone (NMP) were dehydrated with calcium hydride and distilled at atmospheric pressure and under reduced pressure, respectively.

2. 2. Preparation of Poly (amic acid)

To prepare the siloxane containing polyamic acid (SPAA), 2.17 g (0.0118 mol) of MDA (or 2.363 g ODA) was dissloved in 200 ml of NMP at room temperature and added with 3.802 g (0.012 mol) of BTDA and 141.5 ml of NMP to remove any BTDA slurry remaining in a flask. Polymerization reaction was carried out at 0 °C for 20 minutes and continued at room temperature for 80 minutes to obtain homopolyamic acid (HPAA). To obtain SPAA, 27.4 ml of PDMS in 168.2 ml THF was reacted with HPAA for 30 hours at room temperature. Resulting solutions of HPAA and SPAA were precipitated three times in acetone and methanol, respectively, and filtered and dried at 80 °C under vacuum for a day. Samples are designated as BM, BMA, BMC, BME, BO, BOA, BOC and BOE, where B, M, and O represent BTDA, MDA and ODA, respectively, and A, C, and E mean PDMS-1700, -4000 and -7000, respectively.

2. 3. Preparation of Polyimides

Dried HPAA and SPAA powders were dissloved in NMP with the solid contents of 20 wt %. The solution was cast on a glass plate and preheated for 20 minutes at room temperature. It was thermally baked stepwisely according to the following conditions to obtain HPI and SPI : for HPI, 100 °C, 380 mmHg, 1 hr ; 200 °C, 1 mmHg, 1 hr ; 260 °C, 1 mmHg, 3 hr ; and 280 °C, 1 mmHg, 100 min.

2. 4. Characterization

Chemical structures of HPAA and SPAA were confirmed by using FT-IR (Nicolet, Model 5 DX). Inherent viscosity (η_{inh}, dl/g) was measured at 25 °C with NMP(0.5 wt %), using Ubbelodhe viscometer.

Thermal transition behaviors were studied using DSC (Du Pont, Model 910) attached to thermal analyzer 2100 computer system at a heating rate of 20 °C/min under a nitrogen (50 ml/min).

Thermogravimetric analysis (TGA, Du Pont, Model 951) was conducted from 40 °C to 1000 °C at a programmed heating rate of 20 °C/min under nitrogen inlet. A black residue obtained at 1000 °C after TGA runs was analysed by FT-IR.

Wide-angle X-ray scattering (WAXS, Rigaku Denki) was used to measure crystalline character of polymers. Instron (Toyo Baldwin, UTM-400) was utilized to measure mechanical properties. The cross-section of broken samples after tensile test was observed by scanning electron microscopy (SEM, Jeol, Model JSM-35 CF). Solubilities of samples in polar aprotic solvents were carried out.

3. RESULSTS AND DISCUSSION

3. 1. IR analysis

Fig. 2 illustrated FT-IR spectra for HPAA and HPI from BTDA/ODA. For HPAA, ν_{N-H} appears at 3500 cm^{-1} ; $\nu_{C=O}$ at 1720 cm^{-1} ; ν_{O-H} at 3300 cm^{-1} – 2300 cm^{-1} (broad) ; $\nu_{C=O}$ for amide I at 1660 cm^{-1} ; ν_{N-H} for amide II at 1545 cm^{-1}. For HPI, $\nu_{C=O}$ (sym) at 1778 cm^{-1} ; $\nu_{C=O}$ (asym) at 1720 cm^{-1}, other characteristic peak for HPI appears at 1378 cm^{-1} attributed to $\nu_{CN(CO)NC}$ and peak at 728 cm^{-1} is for imide IV band. These spectra for BTDA/ODA series are similar to what

Fig. 2. FT-IR spectra of (a) homopolyamic acid and (b) homopolyimide from BTDA/MDA.
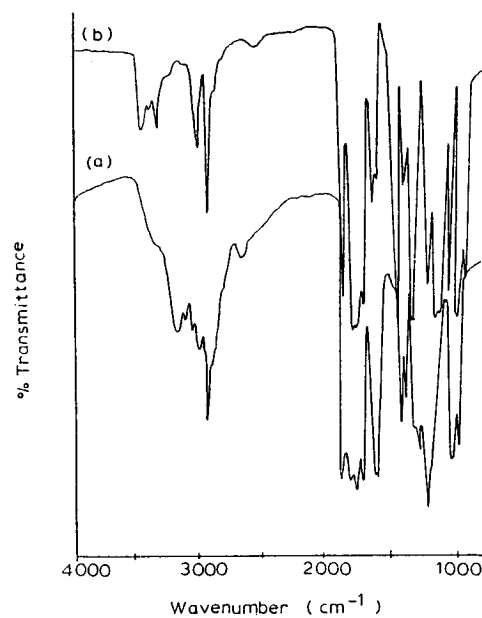

Fig. 3. FT-IR spectra of (a) siloxane-co-polyamic acid and (b) siloxane-copolyimide from BTDA/MDA/PDMS-7000.

Numata[19] reported for BTDA containing HPI. Disappearance of v_{N-H} at 1545 cm^{-1} indicated that HPAA changes into HPI due to the formation of imide ring after thermal curing of HPAA[20].

Fig. 3 exhibited FT-IR spectra for SPAA and SPI from BME and BOE. Characteristic peaks for SPAA appeared at 1260 cm^{-1} (v_{Si-CH3}) and 800 cm^{-1}, at 1090 cm^{-1} (v_{Si-O}) and strong peak at 2900 cm^{-1} (v_{C-H}) of methyl groups in PDMS.

3. 2. T_g, Inherent Viscosity and Water Contents

Table 1 summarized T_g of synthesized polymers. For BTDA/MDA and BTDA/ODA series, T_g of SPI is lower than that of HPI attributed to an incorporation of flexible siloxane in the main chain. PDMS has T_g of $-123\,°C$ and is a rubbery polymer while HPI is a glassy material. A copolymer of these two is believed to contain both rubbery and glassy blocks. A bond length of -Si-O- in flexible siloxane chain is 1.64 Å

Table 1. Measurement of Glass Transition Temperature, Inherent Viscosity, Water Uptake, Weight Loss, and Mechanical Properties

Sample	T_g ($°C$)	η_{inh}	Water Uptake(%)	T_{10}^{b} ($°C$)	R_{tar}^{c} (%)	TS^d (Kg/mm^2)	EL^e (%)
BM	280	0.35	2.230	562	40.31	9.26	—
BMA	258	0.35	0.83	507	33.33	6.34	—
BMC	261	0.34	0.87	528	39.66	5.35	1.44
BME	264	0.34	0.998	564	48.25	2.48	3.32
BO	295	0.34	3.6	576	58.55	12.55	1.41
BOA	248	0.48	0.96	557	55.68	7.64	2.58
BOC	267	0.37	1.4	548	50.44	6.77	13.3
BOE	275	0.44	1.88	562	46.02	4.17	24.9

a) See experimental section.
b) T_{10} is the temperature at 10 wt% loss.
c) R_{tar} means the weight residue at 1000 $°C$.
d) TS = tensile strength.
e) EL = elongation percent at break.

while that of -C-C is 1.54 Å. A bond angle of -Si-O-Si- is 1.43 ° and -O-Si-CH$_3$- is 110° while that of -C-C- is 109.5 °. Therefore, a siloxane containing polymer has more flexible structure and less steric hindrance resulting in a diminished molecular densification[18].

The chain length and contents of siloxane block greatly influenced the thermal and mechanical properties[13]. For SPI, T_g increased as the molecular weight of PDMS was raised from 1700, 4000 and 7000 g/mole. It is speculated that as the chain length in reacting PDMS became longer, their reactivity with BTDA in the polymer was lowered so that PDMS contents were reduced while imide content increased. The distribution and morphology of PDMS in the main chain may influence T_g, and this subject will be treated in a separate article. McGrath *et al.*[13] also reported a similar study using the BTDA/DDS /PDMS system in that the thermal transition temperature increased with the molecular weight of PDMS. We have used the MDA and ODA while McGrath *et al.* used DDS as aromatic diamines. Aromatic diamines affected T_g regardless of an introduction of siloxane following in the order ; ODA>MDA>DDS[13]. The inherent viscosities of the samples were in the range of 0.35~0.48 dl/g.

The water content of SPI was lower than that of HPI due to the presence of hydrophobic siloxane segments in the main backbone. The sample containing high molecular weight silicone block showed increasing water content. That is, the water content of BME was higher than BMA, that of BOE was higher than BOA.

3. 3. Thermogravimetric Analysis

Figs. 4 and 5 showed thermogravimetric analysis of homopolyimides and copolyimides. The temperatures of 10 % weight loss were determined to be 562 °C and 576 °C for HPI from BTDA/MDA and BTDA/ ODA, respectively. Polyimides from BTDA/ODA and BTDA/ODA/PDMS showed a higher decomposition temperature compared with HPI and SPI that contai-
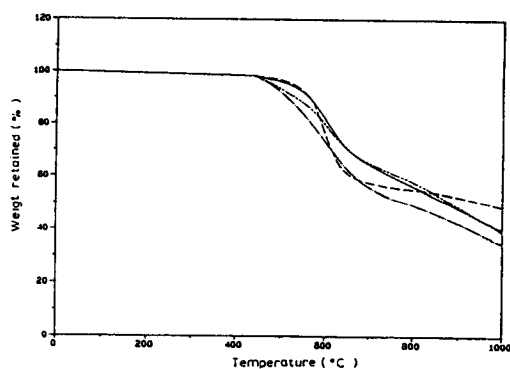

Fig. 4. Thermogravimetric analysis of homopolyimide (——) and siloxane copolyimides of BMA(— · —), BMC(— · · —) and BME(······) from BTDA/MDA.
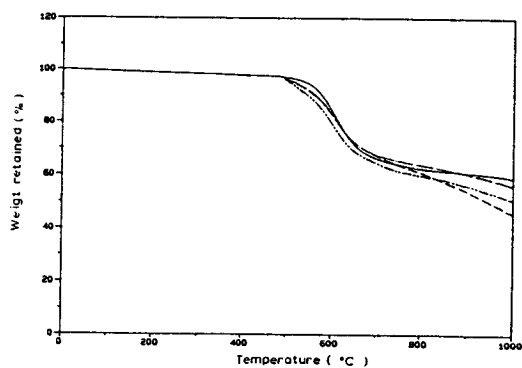

Fig. 5. Thermogravimetric analysis of homopolyimide (——) and siloxane copolyimides of BOA(— · —), BOC(— · · —) and BOE(······) from BTDA/ODA.

ned MDA. It was attributed to a greater thermostability of ODA than MDA in the main chain. The methylene (-CH$_2$-) groups in MDA were easier to degrade due to the active hydrogens attached to benzene ring. An incorporation of siloxane block in polyimides reduced a decomposition temperature compared with HPI, due to the lower bond energy of siloxane than that of imide linkage.

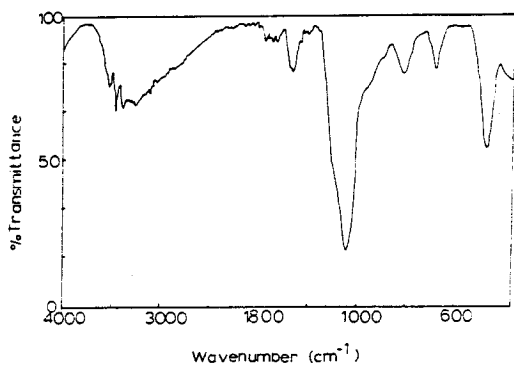The residual weight percent of HPI and SPI at 1000

Fig. 6. FT-IR analysis of residue obtained from sample BOE after thermogravimetric analysis heated to 1000 °C.

Fig. 7. X-ray diffraction patterns of (a) homopolyimide and siloxane copolyimides of (b) BMA, (c) BMC and (d) BME from BTDA/MDA.

°C was measured and listed in Table 1. Here again, BTDA/ODA system showed greater residual weights than for BTDA/MDA system.

Fig. 6 showed FT-IR spectra for black residue of SPI remaining after burning at 1000 °C. The main characteristic peaks appeared at 1088 cm^{-1}, 808 cm^{-1} and 671 cm^{-1}. It is believed that its sturcture is probably SiO$_2$ or, -quartz of SiO$_2$ or the silicate of both[13, 17].

3. 4. X-ray Analysis

Fig 7 and 8 showed X-ray scattering patterns of BTDA/MDA and BTDA/ODA systems. For SPIs there appeared two broad peaks at around 2 θ = 10° and 15° indicating that they were in an amorphous state. Naota et al. reported that the asymmetry of BTDA disturbed the crystallization in the polyimide[16].

3. 5. Mechanical Properties

The tensile strength and elongation at break (%) of samples were listed in Table 1. Tensile strength at break was 9.26 and 12.55 Kg/mm^2 for BTDA/MDA and BTDA/ODA, respectively. SPI generally showed a lower mechanical stength than HPI had. HPI and SPI containing ODA exhibited better mechanical properties than those having MDA. Mechanical strength
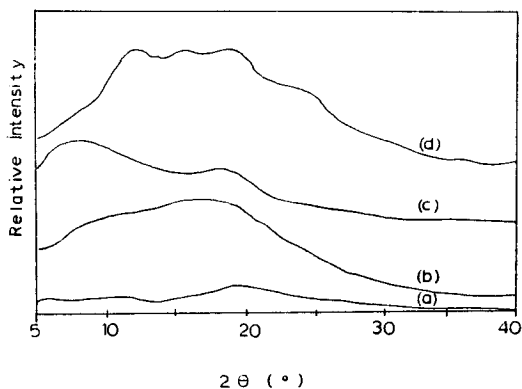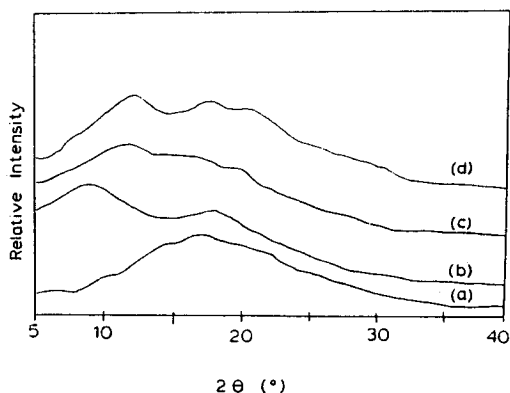

Fig. 8. X-ray diffraction patterns of (a) homopolyimide and siloxane copolyimides of (b) BOA, (c) BOC and (d) BOE from BTDA/ODA.

was lowered as the molecular weight of PDMS became larger. Elongation at break generally increased as the chain length of PDMS became longer.

Scanning electron microscopic pictures in Fig. 9 showed that the cross-section of HPIs broken after mechanical test had a dense surface and cross-section while surfaces of SPIs were dense but there existed pores present inside of the film. Pores may be formed due to the formation of water which caused a phase

(a)

(b)

Fig. 9. Scanning electron microscopic pictures from cross-section of (a) BM and (b) BME.

(a) (b)

separation of polymer chains containing siloxane segments during the film-forming process[13,14]. Therefore, although it was expected that mechanical properties increased with the molecular weight of PDMS, there appeared a reverse tendency due to the porous structure of SPI films.

3. 6. Solubility

Solubilities of SPAA and HPAA are listed in Table

Table 2. Solubility Test of SPAA and PAA

Solvent	Sample							
	BM	BMA	BMC	BME	BO	BOA	BOC	BOE
DMF	S	S	S	S	S	S	S	S
NMP	S	S	S	S	S	S	S	S
DMAC	S	S	S	S	S	S	S	S
DMSO	S	S	S	S	S	S	S	S
PYRIDINE	S	S	S	S	S	S	S	S
TOLUENE	I	I	I	I	I	I	I	I
CCl_4	I	I	I	I	I	I	I	I
HCOOH	PS	PS	PS	PS	I	I	I	I
THF	I	PS	PS	PS	I	PS	PS	PS

* S=soluble, I=insoluble, PS=partially soluble.

2. SPAA was dissolved in polar aprotic solvents such as NMP, THF, dimethyl acetamide (DMAC), and dimethyl sulfoxide(DMSO), while polyimides were not dissolved. We anticipate that, if the siloxane contents increase or, if random copolymerization methods are utilized, solubility of SPI will further be enhanced[2, 4].

4. CONCLUSION

In the present study, homopolyimides and siloxane containing copolyimides were prepared from BTDA /ODA or MDA without or with PDMS. T_g and thermal stability of siloxane containing copolyimides were lower than those of homopolyimides. SPI and HPI was an amorphous polymer. SPI had a lower value in water sorption than HPI because of hydrophobicity of siloxane block. Tensile strength of SPI was about 7. 5~2.5 Kg/mm² and a maximum percent of elongation at break was 25 %.

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