

Properties and Applications of Thermoplastic Aromatic Polyimides Incorporated with Polysiloxane Segments

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ABSTRACT

In the recent years, several kinds of polysiloxane-*block*-polyimides (SPI) have been developed and used in advanced microelectronics, aerospace and printed circuit industries due to their distinguished properties as oxidative stability, low surface energy, high gas permeability, reasonably good thermal stability, good adhesion and excellent dielectric properties. Therefore, SPI is now commercialized as adhesive films and specialty coatings. Their adhesion properties have been known to depend strongly on the content and chain length of the PSX segments, probably because the structure and properties of the interface would be varied with them. In addition, the surface structure and properties of the coatings would affect their total performance and utility, although they have been little studied thus far. Particularly, it should have strong relationships with the surface and interface properties of SPI whether or how much these polymers have surface enrichment of the PSX segments as reported in the similar polysiloxane-*block*- copolyamide used as even a sort of biomedical materials. However, the chemical and solid state structures of the polysiloxane-*block*-polyimides have not been fully analyzed. In the present article, the viscoelastic, the morphological and the surface properties of several soluble SPI were analyzed by dynamic mechanical analysis (DMA), contact angle and X-ray photoelectron spectroscopy (XPS). It was revealed that the surface composition of the PSX segments is significantly different from the bulk composition in spite of its dependence on the polymer composition and that the surface enrichment of the PSX segments is induced in the process of microphase separation to form a low energy surface. The surface topography of the SPI films was also studied by atomic force microanalysis (AFM). These structural data would be essential for material design of the SPI-based adhesives and coatings.

Furthermore, a new class of vinyl-functionalized polysiloxane-*block*-polyimides were synthesized and characterized. The copolyimides were derived from 3,3',4,4'- benzophenonetetracarboxylic dianhydride (BTDA) / bis[4-(3-aminophenoxy)- phenyl]sulfone (BAPSM) combined with two kinds of vinyl containing diaminopolysiloxanes and imidized by solution method. They were highly soluble in various organic solvents. The vinyl groups of the copolyimides were reacted with various dihydrosilane compounds for crosslinking. The crosslinked products became insoluble in polar solvents and were analyzed and characterized. The tensile modulus of the copolyimides having a polysiloxane composition of 50wt% increased approximately twice after the crosslinking reaction,

while that of the copolyimides with compositions of 10 - 30 wt% was similar to that of the original copolyimides. Their thermal expansion coefficient below the glass transition temperature (T_g), α_1 , was nearly the same as that of the original copolyimides, while the coefficient above T_g , α_2 , decreased extremely compared with that of the original copolyimides. Subsequently, the vinyl groups in the polymer backbones were reacted with a little excess of diethoxymethylsilane in the presence of hydrogen hexachloroplatinate pentahydrate ($H_2PtCl_6 / 5H_2O$). Whereas the copolyimides thus functionalized with silicate were easily hydrolyzed and condensed, then the new class of crosslinked copolyimides were obtained in the usual preparation procedure of cast films. The resulting materials were insoluble even in polar solvents. The resultants are interested in study of the organic-inorganic hybrid materials.

INTRODUCTION

Polysiloxane *block* copolymers have been widely used as industrial and biomedical materials. Since the polysiloxane segment having hydrophobic and repellent properties shows high degree of incompatibility with most organic polymers, its introduction to organic polymers gives rise to formation of some very interesting morphological and rheological properties and characteristic surface chemistry in polysiloxane block copolymer. On the other hand, various wholly aromatic polymers have been developed in the past three decades and used as engineering plastics. Among them, aromatic polyimides have become an important class of high-temperature polymers, because of their thermal and oxidative stability, physical strength, high softening temperature, and solvent resistance. However, their processability has been somewhat problematic by conventional means. To improve this drawback, synthesis of polysiloxanes and aromatic polyimides has been examined over the last twenty years. The block copolymers can take advantage of taking the desirable properties of both materials. In general, aromatic polyimides and polysiloxanes are dissimilar in many physical and chemical properties whereas their thermal stability and chemical resistance are quite comparable. Polyimides are polar, rigid materials whereas polysiloxanes are non polar and flexible at room temperature. Since they are incompatible with each other, polymer blend is quite difficult. Accordingly, a large effort by both academic and industrial concerns has been directed toward preparing copolymers of the two materials which chemically linked together. However, their structure-property relationships, particularly, thermomechanical and morphological properties, have been little understood. One of the important aim of this work is to prepare a new class of polysiloxane-*block*-polyimides. Another aim of this work is to investigate the influence of the polysiloxane functionalities to surface, morphology and adhesive properties. Major new series of polysiloxane-*block*-polyimides were synthesized by the method of solution imidization of the polyamic acids prepared from aromatic dianhydrides with two phenylene rings, aromatic diamines with four phenylene rings and bis(3-aminopropyl)-polydimethylsiloxanes (PSX) with different number average molecular weight added as a part of diamine.

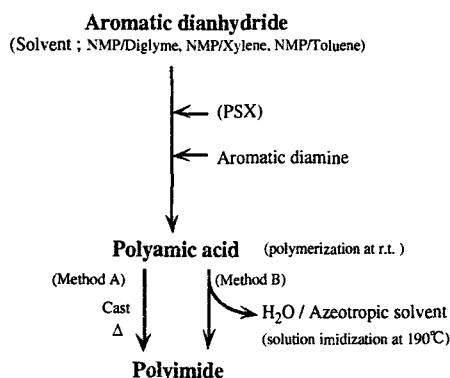
In addition, a new class of vinyl-functionalized polysiloxane-*block*-polyimides were synthesized and characterized. The copolyimides were derived from 3,3',4,4'- benzophenonetetracarboxylic dianhydride (BTDA) / bis[4-(3-aminophenoxy)- phenyl]sulfone (BAPSM) combined with two kinds

of vinyl containing diaminopolysiloxanes and imidized by solution method. They were highly soluble in various organic solvents. The vinyl groups of the copolyimides were reacted with various hydrosilane compounds.

EXPERIMENTAL

Preparation of PI and SPI Films

Aromatic polyimides have been prepared by the two-stage processes: the solution condensation of aromatic dianhydride and diamine to yield an intermediate polyamic acid and the subsequent imidization by either chemical or thermal dehydration of the polyamic acid. The previous studies illustrated that imidization of a cast film of polyamic acid involves complex physicochemical processes which should be interpreted by combining the fast and slow first-order kinetics. Recently, solution imidization with continuous water removal has been reported for the synthesis of soluble polyimides. The solution imidization with continuous water removal has been reported for the synthesis of soluble polyimides. In this case, the imidization is known to proceed by the second order kinetics. Some kinds of the polysiloxane-*block*-polyimides (SPI) developed thus far are soluble in aprotic polar solvents due to the decreased intermolecular interaction which should be given by the flexible polysiloxane segments. In these cases, both the polymerization reaction and the solution imidization are driven to a high level of conversion (see Scheme 1).



Scheme 1 Synthetic procedure of aromatic polyimides and copolyimides.

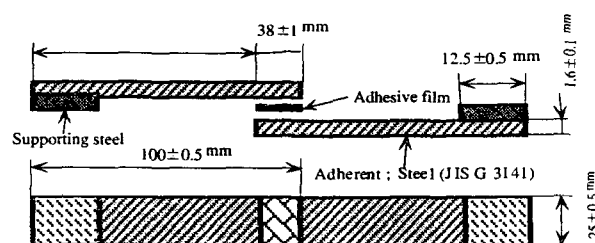
Instrumental Analyses

Dynamic mechanical analysis (DMA) was performed on a REOBIVRON DDV-II EP analyzer (Orientech Co., Ltd.). Static contact angles against water and ethylene glycol (EG) were measured using a Contact Angle Meter (Erma Co., Tokyo, Japan). XPS was conducted on an Electron Spectrometer ESCA 750 (Shimadzu Co., Kyoto, Japan). The relative content of silicon atom was estimated by calibrating the peak areas with the intensity factors of $C_{1s}=1.00$, $N_{1s}=1.77$, $Si_{2p}=0.86$, $O_{1s}=2.90$, and $S_{2p}=1.79$. EPMA was recorded on a spectrometer EMX-SM (Shimadzu Co., Kyoto, Japan). AFM was measured on a microscope (Digital-Instrument Co., Tokyo, Japan) with a contact mode. AFM was operated in contact and tapping mode, where typical forces were on the order of 10 nN and scanning rates were from 1 to 2 Hz with a 2 μ m scanner. Moisture permeation was measured

with a Water Vapor Permeation Tester (Lyssy Co., Ltd.) based on the JIS K 7129 method. Moisture sorption was determined by measurement of the weight increase of the polyimide films after the treatment at 23°C, 78 %RH, for 24 h.

Adhesion Test

Single lap shear strength was measured for steel joints adhered with the cast polyimide films. The steel plate used as a adherent was the one specified by JIS G 3141, and its surface was washed twice with acetone. The joints (see Scheme 2) were prepared by melt lamination of the polyimide film placed between the two steel plates. The lap shear strength of the steel joints was measured according to JIS K-6850 on an Autograph AG-500A (Shimadzu Co.).



Scheme 2 Preparation of steel joints for single lap shear bond strength measurement (SLSS) based on JIS K 6850.

RESULTS AND DISCUSSION

Viscoelastic Properties

Figures 1 and 2 show the results of dynamic mechanical analysis of the SPI. The storage modulus of the SPI with a PSX composition less than 30 wt% was in the order of 1GPa, while that of the SPI with a PSX composition of 50 wt% was significantly lower. SPI showed two drops of storage modulus corresponding with two peaks of loss modulus, while the PSX-free PI showed a very small drop at the lower temperature region of -100°C. These changes in thermomechanical properties are attributed to the a relaxations of the two segments; one appearing in the lower temperature range (T_{g1}) is due to the relaxation of the PSX segment, while the other in the higher temperature range (T_{g2}) is to that of the PI segment.

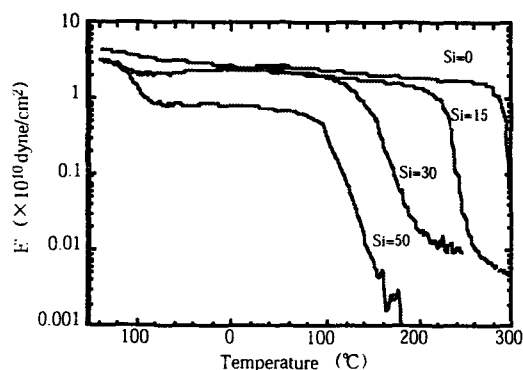


Figure 1. Temperature dependences of storage modulus (E') of PI and SPI of Series A with the PSX composition as indicated.

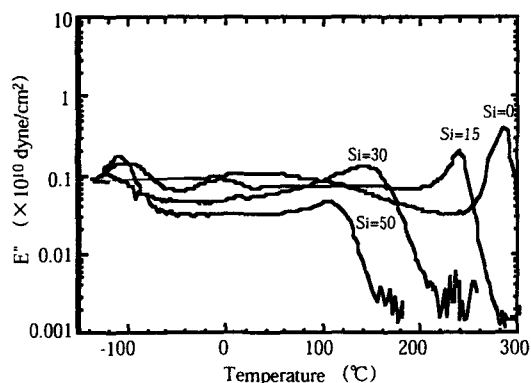


Figure 2. Temperature dependences of loss modulus (E'') of PI and SPI of Series A with the PSX composition as indicated.

Surface Topography

AFM is a very useful analytical tool to investigate the surface topography and nano-level-structure of insulating materials because of its high spatial resolution and capability of nondestructive observation. The image photographs of the surface topography obtained for the representative films are shown in Figure 3. It is noted that the surface of the PI film was flat and smooth, while that of SPI films was quite different from each other in terms of roughness

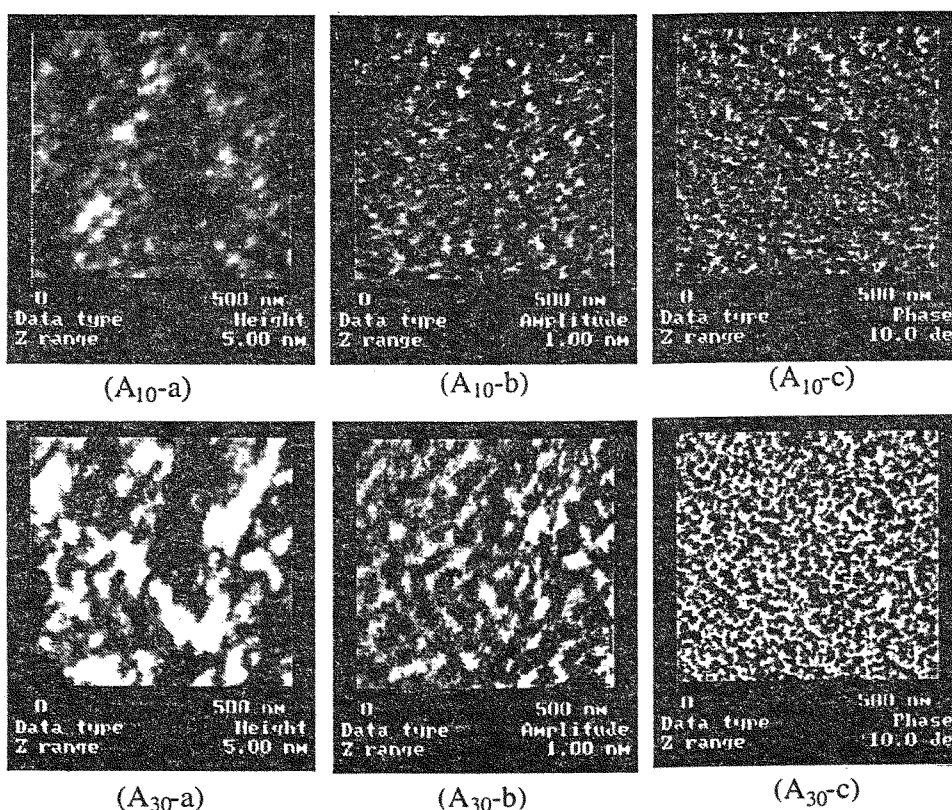


Figure 3. AFM topography, stiffness and phase images of the same area of A₁₀, A₁₅ and A₂₀ showing island-sea phase separated structures. Topography ((A₁₀-a), (A₃₀-a)): dark=low, bright=high. Stiffness ((A₁₀-b), (A₃₀-b)): dark=hard, bright=soft. Phase ((A₁₀-c), (A₃₀-c)): dark=high, bright=low.

Since the roughness of the SPI film containing 10 wt% of PSX 1,200 was much higher than that of the SPI film containing 10 wt% of PSX 750, the surface roughness should be related with the phase separation of the two segments. The long PSX segments, having higher cohesive energy than the short segments, should be more critically segregated from the PI phase to form larger domains called 'islands' in the 'sea-island' structure which is most likely formed during micro phase separation process. In the surface these domains are integrated to form large mounds of particle shape with increasing roughness. The small islands generated from the short segments, in return, are finely separated to stand up on the surface with a shape of steep valleys. Therefore, the surface roughness is considered to increase with increasing molecular weight of PSX. This type of morphological difference may also be influenced by the difference in miscibility or compatibility between the PSX and PI segments which is unknown in the present case.

Surface Tension

The surface tension and its polar and dispersion components of the SPI films were calculated putting. The results are plotted against the PSX composition in Figure 4. It is known that the polar component of the surface tension decreased with increasing PSX composition while the dispersion component showed an opposite tendency. Thus, the sum of both components, which is the surface tension, was the lowest at a PSX composition of 10 wt%. The lowest value of 22.5 mJ/m^2 is almost identical with the surface tension of poly(dimethylsiloxane) oil ($\gamma_s = 19.8 \text{ mJ/m}^2$, $\gamma_s^p = 19.0 \text{ mJ/m}^2$, $\gamma_s^d = 0.8 \text{ mJ/m}^2$). Therefore, the top surface of the SPI films is thought to be covered with PSX segments although its thickness should be in molecular order. We have reported that the peel strength of the joints adhered with SPI was lowered with increasing PSX composition. This fact can be reasonably explained by the increase of polar component, because the peel strength of the joints adhered with polymer film is known to have close relationship with its polar component.

The concentration of PSX segment in the surface of the SPI film was analyzed by XPS. Figure 5 shows a typical wide scan spectrum for each of the SPI films. In the latter spectrum the peaks due to C_{1s} , Si_{2p} , O_{1s} , N_{1s} and S_{2p} were detected at $295 \sim 280$, $110 \sim 95$, $540 \sim 525$, $410 \sim 395$ and $175 \sim 165$ eV, respectively, while in the former the peaks due to Si_{2p} were not observed. From these spectra the surface concentration of silicon atom was estimated and compared with the average bulk concentration of Si atom calculated from the polymer composition. Since the surface energy of poly(dimethylsiloxane) is very low, the PSX segments are expected to migrate in the more hydrophobic top surface to form a PSX-enriched surface. This type of surface enrichment of the polar component segment has been well known in other copolymer systems, but the effects of the PSX composition and molecular weight of the PSX segments have not yet been well understood particularly in the PI systems. Therefore, the depth profile of the PSX-enrichment was studied in detail. An SPI film (sample: A₂ - A₅) was subjected to the surface etching with the ordinary argon sputtering technique. The etching rate was estimated to be approximately $3.5 \sim 4.0 \text{ nm/min}$. The intensity of the Si_{2p} peak also decreased with increasing time of argon sputtering. The surface concentration of Si atom was estimated from these XPS spectra and plotted against time of argon sputtering for knowledge of the depth profile of PSX concentration.

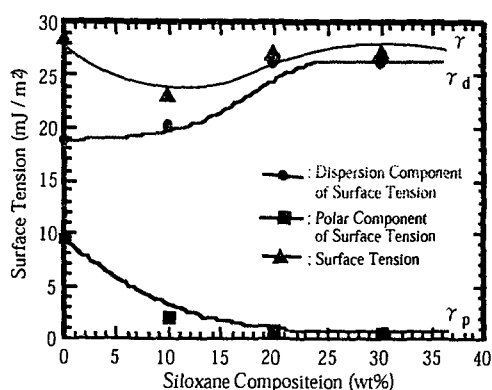


Figure 4. Surface tension of SPI of Series B as a function of the PSX composition at 25°C

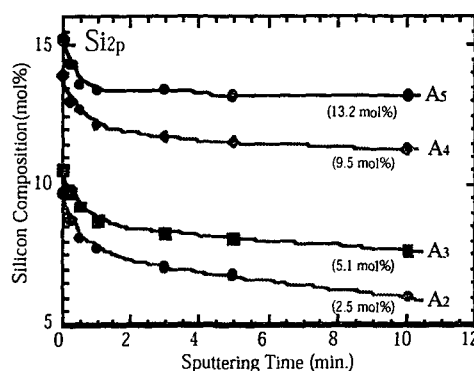


Figure 5. Surface concentration of Si atom as a function of sputtering time for various S-b-PI films with different PSX compositions. (The values in the parentheses indicate the average bulk concentrations of Si atom of the S-b-PI films.)

Residual Stress

The residual stress on silicon wafer can be controlled by incorporation amount of polysiloxane into polymer backbone, since residual stress is reduced due to the stress relaxation ability of polysiloxane segments. From the results, it was proved that the residual stress on silicon wafer is proportional to the tensile modulus of siloxane copolyimide, inspite of increasing the thermal expansion coefficient (see Figure 6, 7). This results provide additional knowledge which residual stress is affected by modulus of coatings. In addition, the property of low modulus could be also effective for the stress relaxation between IC chip and encapsulant. From these results, it is considered that the SPI are useful for specialty coating and adhesives in electronics industries such as a passivant, an specialty encapsulant and a die attach adhesives.

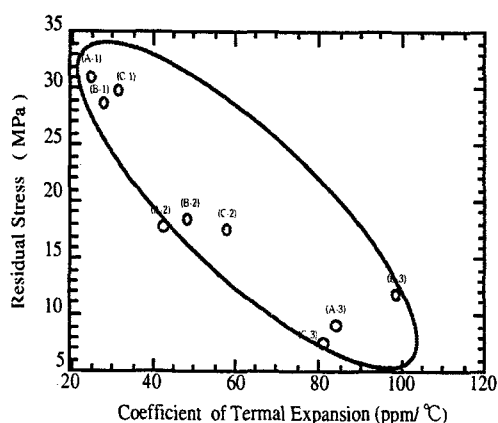


Figure 6. Relationship between thermal expansion coefficient and residual stress of polyimide coatings.

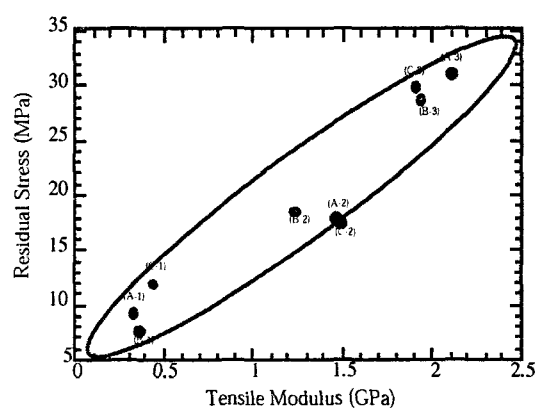


Figure 7. Relationship between tensile modulus and residual stress of polyimide coatings.

Adhesive Durability

A series of polyimides from BTDA/BAPSM were used for the study of adhesive durability under a highly humid condition (25 °C, 90%RH, 72hours). The polyimides with 10wt% of siloxane (PSX750, PSX1200) have excellent adhesive durability compared with the corresponding all-aromatic polyimides (see Figure 8). The introduction of polysiloxane into polyimide leads to lower moisture sorption (≤ 0.1 wt%) due to hydrophobicity of the polysiloxane. However, the 20wt% and 30wt% of polysiloxane incorporation lowered the adhesive durability of SPIs, in spite of their lower moisture sorption. On the other hand, moisture permeability was gradually increased with increase of the polysiloxane composition. The moisture permeabilities are decreased with increasing the density, since the density of SPI is decreased with increase of polysiloxane composition due to relatively large Van der Waals volume of polysiloxane segment. The polyimides with 10wt% of polysiloxane segments (PSX750, PSX1200) exhibit favorable properties such as low moisture sorption and low moisture permeability as shown in Table 1. These results show that polyimides with small amounts of polysiloxane component have specific interactions with water vapor. The interface between adhesive and adherend is probably stabilized by incorporation of a small amount of polysiloxane, since low moisture uptake and moisture permeability is achieved.

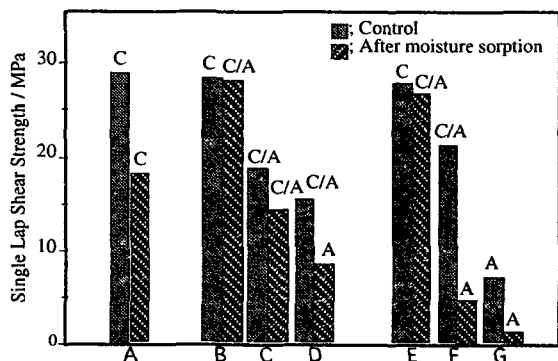


Figure 8. Single lap shear strength of SPI of BTDA-BAPSM-based polyimides after the treatment under the test conditions (25°C, 90 %RH, for 72 h (JIS K 6857)) (Failure mode; C: cohesive failure, A: adhesive failure, C/A: mixed mode failure).

Table 1. Relationship between retention of adhesive strength and moisture sorption and water vapor permeability.

Siloxane composition (wt%)	Moisture sorption 1) (wt%)	WVPC 2)	Strength retention 3)
A	0	0.6	66
B	PSX 750 10	<0.1	99
C	PSX 750 20	<0.1	74
D	PSX 750 30	<0.1	55
E	PSX 1200 10	<0.1	93
F	PSX 1200 20	<0.1	32
G	PSX 1200 30	<0.1	18

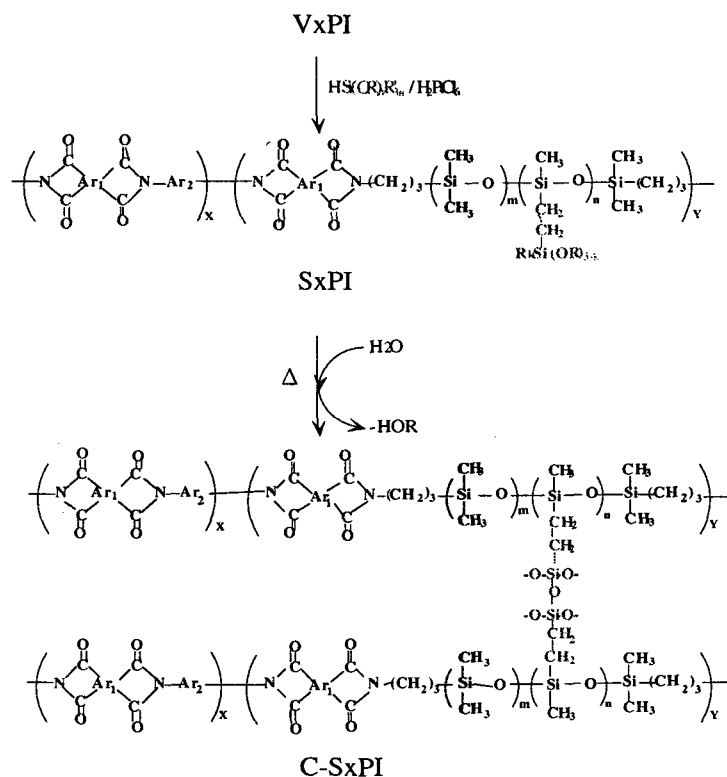
1) Under the test condition at 25°C, 90%RH for 72hrs.

2) Water vapor permeability coefficient (g/cm².sec.cmHg).

3) Strength retention(%)=100×(SLSS after the treatment)/(SLSS at control).

Properties of Polysiloxane-block-polyimides with vinyl functionality

A new class of vinyl-functionalized polysiloxane-*block*-polyimides were synthesized and characterized. The copolyimides were derived from 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) / bis[4-(3-aminophenoxy)- phenyl]sulfone (BAPSM) combined with two kinds of vinyl containing diaminopolysiloxanes and imidized by solution method. They were highly soluble in various organic solvents. The vinyl groups of the copolyimides were reacted with various dihydrosilane compounds for crosslinking. The crosslinked products became insoluble in polar solvents and were analyzed and characterized. The tensile modulus of the copolyimides having a polysiloxane composition of 50wt% increased approximately twice after the crosslinking reaction, while that of the copolyimides with compositions of 10 - 30 wt% was similar to that of the original copolyimides. Their thermal expansion coefficient below the glass transition temperature (T_g), α_1 , was nearly the same as that of the original copolyimides, while the coefficient above T_g , α_2 , decreased extremely compared with that of the original copolyimides. Subsequently, the vinyl groups in the polymer backbones were reacted with a little excess of diethoxymethylsilane in the presence of hydrogen hexachloroplatinate pentahydrate ($H_2PtCl_6 / 5H_2O$) as an acceleration catalyst of hydrosilylation reaction. The resulting products were also soluble in various organic solvents. Whereas the copolyimides thus functionalized with silicate were easily hydrolyzed and condensed, then the new class of crosslinked copolyimides were obtained in the usual preparation procedure of cast films. The resulting materials were insoluble even in polar solvents. Furthermore the resultants are interested in study of the organic-inorganic hybrid materials.



Scheme 3 Synthetic route and possible crosslinking reaction of the copolyimide functionalized with silicate (SxPI, C-SxPI)

List of Publications

1. N. Furukawa, M. Yuasa and Y. Kimura, *J. Polym. Sci., Part A*, **36**, 2237-2245 (1998)
2. N. Furukawa, Y. Yamada, M. Furukawa, M. Yuasa and Y. Kimura, *J. Polym. Sci., Part A*, **35**, 2239-2251 (1997)
3. N. Furukawa, Y. Yamada and Y. Kimura, *High Perform. Polym.*, **8**, 617-630 (1996).
4. N. Furukawa, Y. Yamada and Y. Kimura, *High Perform. Polym.*, **9**, 17-31 (1997).
5. N. Furukawa, F. Omori, M. Yuasa, Y. Yamada and Y. Kimura, *Nippon Kagaku Kaishi*, (5), 310-319 (1998)
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8. N. Furukawa, M. Yuasa and Y. Kimura, *Polymer*, **40**, 1853-1862 (1999)
9. N. Furukawa and Y. Yamada, *J. Adhes. Soc. Jpn.*, **31**(10), 435-444 (1995).
10. N. Furukawa, M. Yuasa, F. Omori and Y. Yamada, *J. Adhesion*, **59**, 281-294 (1996).
11. M. Shinohara, K. Saito, M. Hatakeyama, M. Yuasa and N. Furukawa, *J. Mol. Structure*, **441**, 189 (1998)
12. N. Furukawa, H. Katayama and Kenich Kitamura, *High Perform. Polym.*, **10**, 363-371 (1998)
13. N. Furukawa, M. Furukawa, Y. Yuasa, T. Fujiyama, F. Omori and Y. Yamada, *J. Adhes. Soc. Jpn.*, **33**, 2, 63-73 (1997)
14. N. Furukawa and Y. Kimura, *Recent Research Developments in Polymer Science*, in print.
15. N. Furukawa, T. Itahara, M. Yuasa, Y. Wada and H. Kato, *J. Adhes. Soc. Jpn.*, in print.