In situ Formed Three Layer Film by Isomerization of Fluorinated Polyisoimide in Polyethersulfone as a Matrix Polymer

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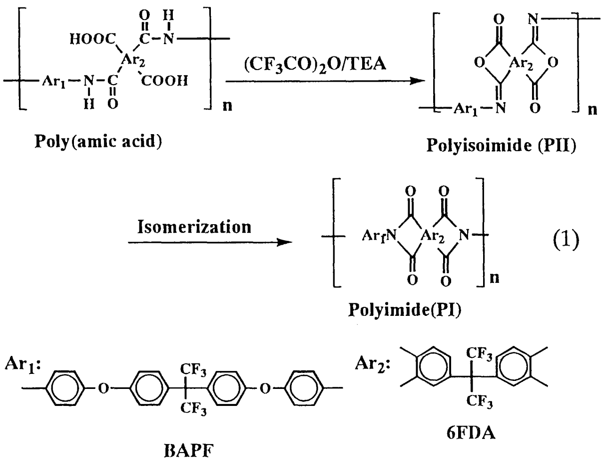
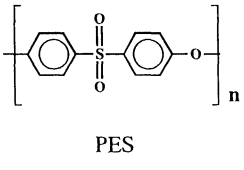
The novel three layer film comprised of a polyimide (PI)-polyether sulfone (PES)-PI structure has been developed. The film was cast from the homogeneous blend solution of polyisoimide (PII) and poly(oxy-1,4-phenylenesulfonyl-1,4-phenylene) (PES) in N,N-dimethylacetamide (DMAc) on to a glass plate. PII was prepared by the ring-opening polyaddition of 4,4'-hexafluoroisopropylidenebis(phthalic anhydride) (6FDA) and 4,4'-hexafluoroisopropylidenebis(p-phenyleneoxy)dianiline (BAPF) followed by treatment with trifluoroacetic anhydride (TEAA)-triethylamine (TEA) in N-methyl-2-pyrrolidone (NMP). The morphology of blend film was investigated by transmission electron microscopy (TEM). The formation of three layer film having a PI-PES-PI structure was confirmed by energy-dispersive X-ray analyzer (EDX).

Aromatic PIs possess an unusual combination of outstanding mechanical, electrical, thermal, and chemical properties. One of the important approaches is the incorporation of fluorine groups in the PIs back bone, most notably investigated and considerably extended the useful range of PI properties, which particularly respect to dielectric, moisture absorption or optical behavior. [1-3]

On the other hand, polyisoimide (PII) as a polyimide-precursor is a valuable intermediate to improve the processability [4, 5] of aromatic polyimide because PII has a higher solubility and lower Tg than those of corresponding PI and is easily converted to PI without elimination of volatile compounds.[6] In a preceding paper,[7] we reported the compatibility of PII having a rigid-rod structure and PES, and found that a transparent flexible film was obtained from the solution of PES and PII.




PES

In the course of studies on the compatibility of PIs and amorphous polymer matrix, we noticed the novel three layer film was formed by thermal treatment of a blend film of fluorinated PII and PES.

PII was prepared by the ring-opening polyaddition of 6FDA and BAPF, followed by treatment with TFAA-TEA in NMP (eq.1).

The polymer was confirmed to be the corresponding PII by infrared spectroscopy (FT-IR) and elemental analysis. The IR spectra exhibited a characteristic absorptions at 1800 cm^{-1} due to the isoimide carbonyl. Elemental analysis also supported the formation of expected polymer. Anal. Calcd for $(C_{46}H_{22}N_2O_6F_{12})_n$: C, 59.62% ; H, 2.39% ; N, 3.02%. Found : C, 59.44% ; 2.70% ; N, 3.03%. The inherent viscosity of the polymer in DMAc was 0.42 dL/g at a concentration of 0.5 g/dL at 30°C.

PES was chosen as a matrix resin. The compatibility between PII and PES (Victrex 4100p, Sumitomo chemical Co.Ltd.) was first studied for the solution blend in DMAc with the composition from 10/90 to 30/70 for PII/PES and 20/80 for polymer/solvent on a weight basis. All composition gave homogeneous solution even in the 30 wt% of PII. Subsequently, the composite films were prepared by casting onto glass plates and drying at 80 °C for 10 min, then residual solvent was removed by heating at 200 °C for 3 h *in vacuo*. During this heating process, the isomerization reaction of PII to PI was confirmed by FT-IR. Opaque and translucent films were obtained.

The morphology of these blend films was investigated using transmission electron microscopy (TEM). All the films were heterogeneous and had two phase structures with the

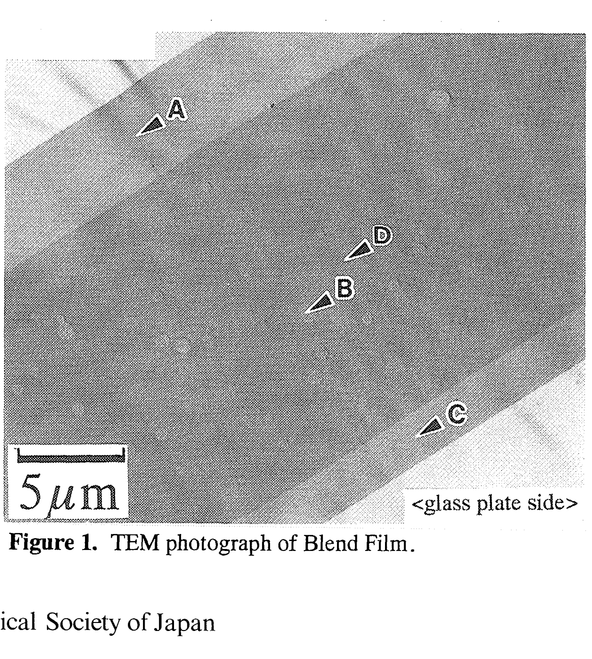


Figure 1. TEM photograph of Blend Film.

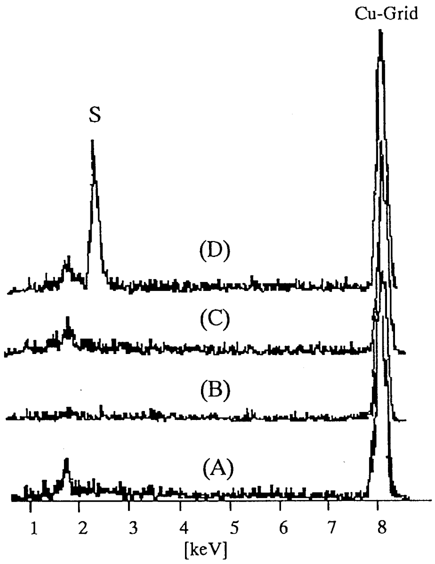


Figure 2. EDX anaysis of blend film;
(A): part A, (B): part B, (C): part C, (D): part D in Figure 1.

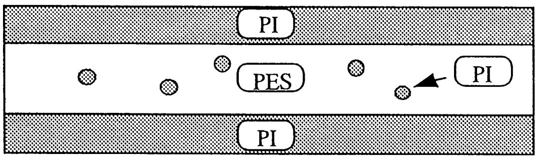


Figure 3. Cross-sectional view of blend film.

domain dispersed in the matrix. However, blend film containing 30 wt% PI has peculiar morphology. Figure 1 shows the ultramicrotomed cross-section of blend film (PII/PES=30/70) embedded in epoxy resin. The film was heterogeneous and has three layers having micro domains (ca.0.5 μm of diameter) dispersed in the middle layer. Although thickness of each layer is not uniform, these three layers were observed in whole area of the blend film. To clarify the component of each phase, domain and matrix in the TEM photograph was analyzed by energy-dispersive X-ray analyzer (EDX). The results were shown in Figure 2. In part D, the existence of sulfur atom based on PES was confirmed and no sulfur atom was detected in part A, B and C. These results indicate that the novel three layer-composite film having a PI-PES-PI structure as illustrated in Figure 3, is formed during thermal isomerization of PII in the PES matrix.

In the immiscible blend system which is based on the mixing of a rigid-rod polymer and random coil polymer, phase separation is easily induced and usually one component forms spherical particles in the other matrix component. However, in this case, PI forms exceptional two layers in addition to domains in the PES matrix. These kinds of three layer materials are applicable to adhesive, optoelectric device, insulation materials for microelectronic devices. The mechanism of this phase separation behavior is now under investigation.

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References and Notes

1 E. L. Yuan, "Polymer for microelectronics, PME '89, " ed by Y. Tabata, I. Mita, S. Nonogaki, K. Horie, S. Tagawa, VCH Publisher, NY and Kodansha Scientific Ltd., Tokyo, (1989), p.677.
2 T. Matsuura, Y. Hasuda, S. Nishi, and N. Yamada, *Macromolecules*, **24**, 5001 (1991).
3 G. Hougham, G. Tesoro, and J. Shaw, " Polyimides: Materials, Chemistry and Characterization" ed. by C. Feager, M. M. Khojasteh, and J. E. McGrath, Elsevier Science Publishers B. V., Amsterdam, (1989), p.465.
4 A. W. Chow, R. D. Hamlin, A. L. Landis, and K. S. Y. Lau, *J. Rheol*, **36**, 1651 (1992).
5 A. Mochizuki, T. Teranishi, and M. Ueda, *Polymer*, **35**, 4022 (1994).
6 A. Mochizuki, T. Teranishi, and M. Ueda, *Polym.J.*, **26**, 315 (1994).
7 A. Mochizuki, K. Yamada, M. Ueda, and R. Yokota, *Polym.J.*, *in press.*