

Chemical Structure and Properties of Polyimides Derived from Asymmetric Diamines (p-ODA and p-TPEQ)

Ayumi ANDOH (安藤あゆみ)¹, Masahiko MIYAUCHI (宮内雅彦)², Yuichi ISHIDA (石田雄一)³
Rikio YOKOTA (横田力男)²

¹Graduate School of Science and Technology, Nihon University, 1-8-14 Kanda surugadai Chiyoda-ku Tokyo 101-8308

²Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency (JAXA), 3-1-1 Yoshinodai Sagami-hara city Kanagawa 252-5210; Tel:+81-50-3362-5710. E-mail:yokota.rikio@jaxa.jp

³Advanced Materials Group, Aerospace Research and Development Directorate, JAXA, 6-13-1 Ohsawa, Mitaka city, Tokyo 181-0015

1. Introduction

Aromatic polyimides (PIs) are attractive for aerospace applications because of their excellent thermal and environmental stabilities, and high resistant properties. Previously, Yokota et al. reported that an asymmetric PI prepared from asymmetric and nonplanar biphenyl tetracarboxylic dianhydride with 4,4'-diaminodiphenyl ether (4,4'-ODA) have a higher glass transition temperature (T_g) and molecular mobility above T_g than those of symmetric PI (s-BPDA-PI). We also reported that a PI film derived from an asymmetric of oxydiphthalic dianhydride, namely a-ODPA with a flexible ether linkage exhibited higher T_g and high molecular mobility at temperature region above T_g than those of s-ODPA-PI. Moreover, PI(a-ODPA/4,4'-ODA) was found to have excellent heat-sealing properties, i.e. it could be found to be heat-sealed within a few minutes at 350 °C with maintaining the original strength. The increased T_g , high molecular mobility and thermal adhesiveness can be explained from the suppressed internal rotation of ether linkage between two phthalimide groups. However, the detailed thermal and mechanical properties of PI films derived from asymmetric diamines have not been studied enough.

In this study, we report the effects of chemical structure of PIs derived from novel asymmetric diamines: 2-phenyl-4,4'-diaminodiphenyl ether (p-ODA) and 2-phenyl-1,4-bis(4-aminophenoxy)benzene (p-TPEQ) which have a phenyl group as a side chain on the thermal and mechanical properties of their films

2. Experimental

After the preparation of the DMAc solution in which corresponding diamines were dissolved dianhydride was added at room temperature. The heterogeneous solution was stirred for 6 hours at room temperature to afford the polyamic acids (PAA). The molecular weight of PAA were adjacent to almost 0.5(dL/g) with an addition of phthalic anhydride (PA) at a 15 wt% solids concentration. PAAs were

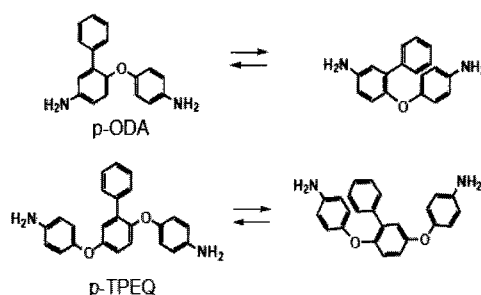


Fig.1. Chemical structures of asymmetric diamines

converted to the corresponding PIs by typical method of thermal imidization. PAA were cast onto glass plate, dried in oven at 60 °C for 2 hours, and then cured up to 250 °C by stepwise heating of 50 °C/0.5 h + 150 °C/0.5 h + 200 °C/0.5 h + 240 °C/0.5 h onto glass plate under vacuum. Then these PAA films were removed from the substrate. These PAA films were wrapped in aluminum and cured up to 350 °C by stepwise heating of 250 °C/0.5 h (+ 300 °C/0.5h + 350 °C/0.5h) under vacuum.

3. Results and discussion

Fig. 2 and Fig. 3 show the DMA data of various PI films to compare the effect of asymmetric structures of diamine on the molecular motilities of PI chains. PI(s-BPDA/4,4'-ODA) and PI(s-BPDA/1,4,4-APB) films show the small drops of E' above T_g , indicating that these PIs formed high

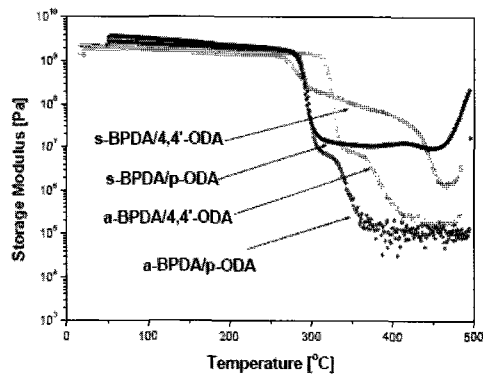


Fig.2. DMA curves of p-ODA-PIs

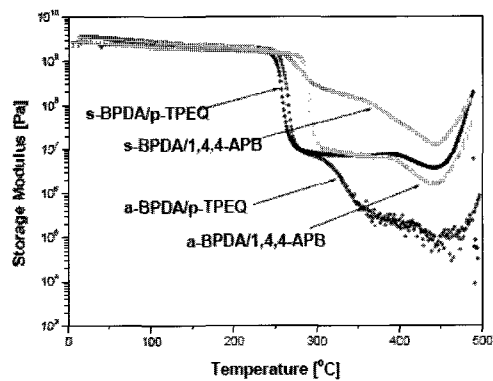


Fig.3. DMA curves of p-TPEQ-PIs

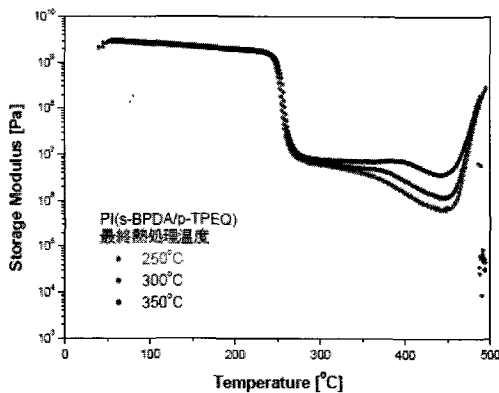


Fig.4. DMA curves of s-BPDA/p-TPEQ

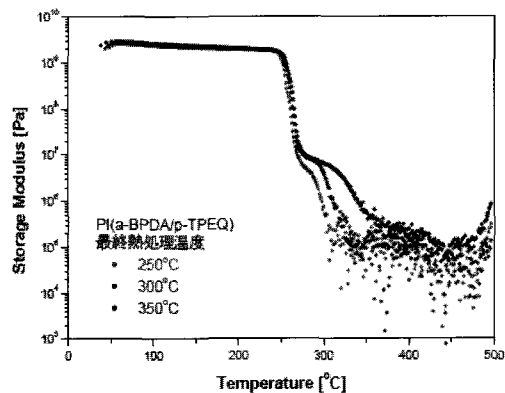


Fig.5. DMA curves of a-BPDA/p-TPEQ

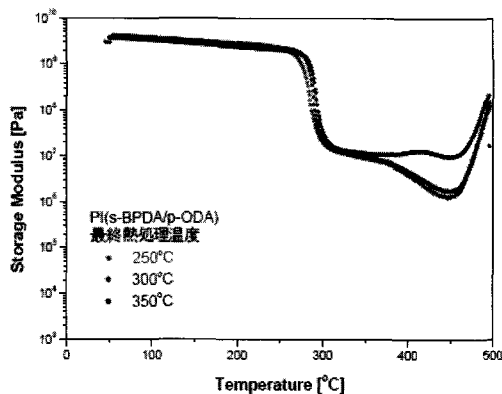


Fig.6. DMA curves of s-BPDA/p-ODA

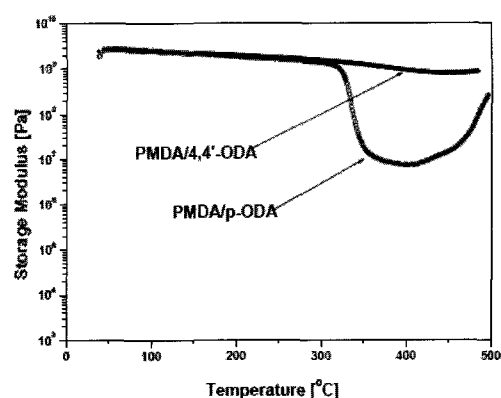


Fig.7. DMA curves of PMDA/p-ODA

ordered structures attributed to the symmetric and planar structures of s-BPDA. On the other hand, PIs derived from p-ODA or p-TPEQ showed the large drops of E' above T_g , indicating that these PIs form amorphous structures. On the basis of above results, the formation of amorphous PIs was found to be mainly depended on the asymmetry of dianhydride.

Fig. 4-6 show the DMA data of PI(s-BPDA/p-TPEQ), PI(a-BPDA/p-TPEQ) and PI(s-BPDA/p-ODA) cured at the different temperatures. In general, aromatic PIs with symmetric and planar structures were proceeded to the formation of ordered structure by curing at higher temperature. On the other hand, asymmetric PIs were not thought to be proceeded to form ordered structure by curing due to their amorphous structure. However, PIs derived from asymmetric diamine observed in Figure 4-6 seem to have a trend of extending the rubbery plateau region by curing at higher temperature. Similar phenomena were also observed in the case of PIs derived from a-BPDA with symmetric diamine (4,4'-ODA or 1,4,4-APB). These behaviors are thought to be depended on a tangle of polymer chains and polymer structure in the amorphous regions. These detail observations are now under considerations in terms of a difference in molecular weight and by using of wide-angle X-ray diffraction measurements.

In addition, Fig.7 shows the DMA data of PI(PMDA/p-ODA) . PI(PMDA/p-ODA) film also showed the large drop of E' to 10^7 Pa above T_g , indicating that asymmetric and nonplanar structure of p-ODA, and steric hindrance of phenyl group were found to cause PMDA-based PIs to give a high molecular mobility.

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polyimides had good solubility both in polar aprotic solvents and in some common organic solvents. All the polyimides were amorphous with high T_g and exhibited excellent thermal stability and mechanical properties.

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