

# Polyimides Derived from Mellophanic Dianhydride (5) Applications to High-temperature Adhesives for CCL

Ryo Nomura and Masatoshi Hasegawa

*Department of Chemistry, Faculty of Science, Toho University, 2-2-1 Miyama, Funabashi, Chiba  
274-8510*

*TEL&FAX:+81-47-472-4960, E-mail: mhasegaw@chem.sci.toho-u.ac.jp*

We have so far studied an isomer effect on the film properties of polyimides (PIs) derived from three isomeric biphenyltetracarboxylic dianhydrides (BPDA), i.e., 3,3',4,4'-BPDA (s-BPDA), 2,2',3,4'-BPDA (a-BPDA), and 2,2',3,3'-BPDA (i-BPDA) [1–7]. The results revealed that PIs from a-BPDA and i-BPDA always possessed higher glass transition temperatures ( $T_g$ ), in spite of their highly distorted chain structures, in addition to higher thermo- and solution-processability than the stiffer structures of s-BPDA counterparts when common diamine components were used for a comparison. The higher  $T_g$  character can be explained in terms of steric hindrance-based restricted internal rotation around the biphenyl linkages of these isomeric BPDAs. The unique combined properties were also applied as excellent matrix resins for carbon fiber-reinforced composite materials.

The studies of such isomer effect were extended to isomeric PI systems based on two benzenetetracarboxylic dianhydrides, i.e., pyromellitic dianhydride (PMDA) and mellophanic dianhydride (MPDA). Ding et al. [8] first reported that MPDA has a trend to form some cyclic oligomers when a flexible diamine monomer such as 4,4'-methylenedianiline was used in the PI precursor polymerization. The present work proposes how MPDA-based PIs are suitable as novel high temperature-adhesives for copper clad laminates (CCL).

The molecular structures of MPDA-based PIs examined in this work are depicted in **Figure 1**. In order to avoid the formation of cyclic oligomers and to obtain higher molecular weights of PIs, we polymerized poly(amic acid)s (PAA) at a considerably high monomer content (30–40 wt %). After MPDA powder was all added into the diamine solution at one portion, the solution viscosities increased abruptly within 30 min, showing excellent reactivity of MPDA. After that, the solution viscosity, however, decreased very rapidly, probably owing to an equilibrium shift from high molecular weight PAA toward some cyclic oligomers. Then, at the timing where the solution viscosity reached a maximum value, we added an acetic anhydride / pyridine mixture into the PAA solution to carry out chemical imidization. In some flexible diamine systems, the chemical imidization proceeded in homogeneous solutions. In these cases, complete imidization was confirmed in the subsequently isolated powder samples. On the other hand, the use of 4,4'-ODA caused precipitation during the chemical imidization process owing to its poor solubility, consequently, led to a partially imidized sample.

MPDA /BAPP system ( $[\eta] = 1.57$  dL/g) showed good solubility in various common organic solvents at room temperature (for example, > 12 wt% in NMP). This enabled us to form high quality of PI film by the simple solution-casting process and drying at much lower temperatures than in thermal imidization process. In addition, the PI film possessed a relatively high  $T_g$  at 280°C, considerably high toughness (elongation at break,  $\epsilon_b = 161$  %), and good adhesion strength with an

electro-deposited copper foil (180° peel strength > 1.0 kgf/cm) as well as in three-layered CCL specimens composed of Cu foil / MPDA-PI adhesive / non-thermoplastic PI film (APICAL-NPI).

Our approach to further increase the  $T_g$  is to copolymerize 4,4'-oxydianiline (4,4'-ODA) with a minor fraction. Copolymerization of MPDA with BAPP (80 mol%) and 4,4'-ODA (20 mol%) allowed homogeneous chemical imidization in solution. The copolyimide film achieved a high  $T_g$  at 294°C without sacrificing other target properties. It should be noted that PI adhesives currently used in CCL possess much lower  $T_g$ 's (< 240–250°C). On the other hand, comparative systems, i.e., PMDA/BAPP and PMDA/BAPP80:4,4'-ODA20 systems showed insolubility in any aprotic organic solvents and poorer thermoplasticity above the  $T_g$ 's. The excellent solution processability of the MPDA systems means that their PI varnishes can be easily coated on a copper foil and/or a non-thermoplastic PI film (called “base film”) in the CCL fabrication processes. The excellent thermoplasticity and solution-processability intrinsic to the present MPDA systems are attributed to their bent chain structures at the MPDA moiety which probably acts effectively to weaken intermolecular interactions and to disturb local ordering. The results suggest that the MPDA systems are promising candidates as a new type of PI adhesives in CCL. We also prepared crosslinker-terminated MPDA systems with controlled molecular weights. This approach caused further increased adhesion strength. The detailed results will be also presented in this report.

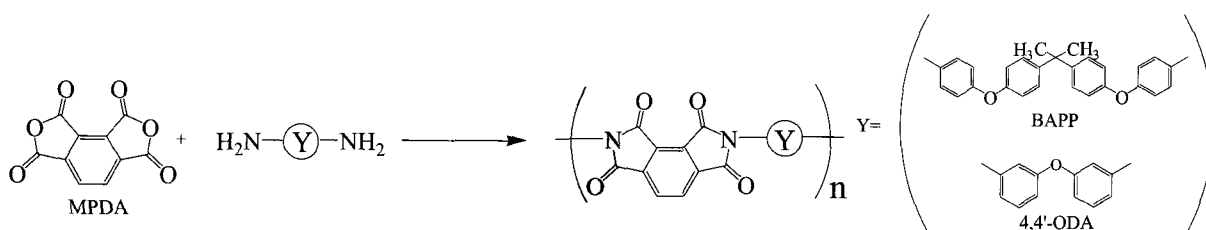


Figure 1 Structures of polyimides

## References

- [1] M.Hasegawa, N.Sensui, Y.Shindo, R.Yokota, *Macromolecules*, **32**, 387 (1999). “Structure and Properties of Novel Asymmetric Biphenyl Type Polyimides. Homo- and Copolymers and Blends”
  - [2] M.Hasegawa, N.Sensui, Y.Shindo, R.Yokota, *J. Polym. Sci.: Part B*, **37**, 2499 (1999). “Improvement of Thermoplasticity for s-BPDA/PDA by Copolymerization and Blend with Novel Asymmetric BPDA-based Polyimides”
  - [3] R.Yokota, S.Yamamoto, S.Yano, T.Sawaguchi, M.Hasegawa, H.Yamaguchi, H.Ozawa, R.Sato, *High Perform. Polym.*, **13**, 61 (2001). “Molecular Design of Heat Resistant Polyimides Having Excellent Processability and High Transition Temperature”
  - [4] M.Hasegawa, Z.Shi, R.Yokota, F.He, H.Ozawa, *High Perform. Polym.*, **13**, 355 (2001). “Thermo-processable polyimides with high  $T_g$  and high thermo-oxidative stability as derived from 2,3,3',4'-biphenyltetracarboxylic dianhydride”
  - [5] C.Chen, R.Yokota, M.Hasegawa, M.Kochi, K.Horie, P.M.Hergenrother, *High Perform. Polym.*, **17**, 317 (2005). “Isomeric Biphenyl Polyimides ( I ). Chemical Structure-Property Relationships”
  - [6] M.Kochi, C.Chen, R.Yokota, M.Hasegawa, P.M.Hergenrother, *High Perform. Polym.*, **17**, 335 (2005). “Isomeric Biphenyl Polyimides (II). Glass transitions and secondary relaxation processes”
- (more references →p112)