



High-temperature polymers overcoming the trade-off between excellent thermoplasticity and low thermal expansion properties



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ABSTRACT

An index describing the sharpness of glass transitions is proposed in this work. This index is closely connected to thermoplasticity, which was determined as the slope of logarithmic storage modulus ($\log E'$)–temperature curves, that is, $-d \log E'/dT$ at a point just above the T_g determined by dynamic mechanical analysis (DMA). The main purpose of this work was to obtain high-temperature polymeric materials while simultaneously achieving low coefficients of thermal expansion ($CTE < 20 \text{ ppm K}^{-1}$) and excellent thermoplasticity with higher indices ($-d \log E'/dT > 0.3$) as an empirical benchmark without rubbery plateau (RP) regions in the DMA curves. However, it was very difficult to accomplish this goal because of the presence of a clear trade-off between lower CTE and higher thermoplasticity as observed in common polymer systems. Therefore, we designed a series of diamines incorporating benzoxazole (BO) units to develop novel poly(benzoxazole imide)s (PBOIs) with the expectation of weakening the intermolecular forces present in the systems by decreasing the amount of imide C=O groups. The combination of an ether-linked BO-incorporating diamine and a rigid tetracarboxylic dianhydride led to a PBOI with somewhat improved thermoplasticity and a significantly decreased CTE, however, it was difficult to completely remove the RP regions. On the other hand, a *meta*-phenylene-linked BO-incorporating diamine was effective in erasing the RP regions with a considerably high index ($-d \log E'/dT = 0.60$) while keeping a relatively low CTE. This system was modified by copolymerization with a minor fraction of a *p*-linked BO-incorporating diamine. The resultant copolymer attained a low CTE (16.7 ppm K^{-1}) close to that of copper foils and a high index ($-d \log E'/dT = 0.37$) without RP regions. A reasonably high adhesion strength was also observed for the hot-compressed laminates between the copolymer film and copper foils. The copolymer prepared possessed a very high T_g of 362 °C, sufficient ductility, a relatively low water uptake of 1.57%, and the highest rank of non-flammability. Thus, the PBOIs developed in this work offer useful materials for potential applications as adhesive-free flexible printed circuits.

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1. Introduction

The importance of high-temperature functional polymers and their extensive applications have increased in recent years, because they contribute significantly to the enhanced performance/functionality, downsizing, and lightening of various electric/electronic devices. The most reliable high-temperature polymeric materials to date are aromatic polyimides (PI). PIs possess excellent combined properties, including considerably high glass transition temperatures (T_g) that overcome the solder-reflowing processes, high

resistance to chemicals, good dielectric and mechanical properties, and excellent electric insulation properties, based on their extra-high purities due to the absence of monomeric residues and metallic/ionic contaminations in the resins [1–6]. Recent researches in the field of PIs and their applications have addressed the dimensional stability of PI films against multiple heating–cooling cycles in the device fabrication process. When the thermal dimensional stability of PI layers is insufficient, they suffer significant expansion/contraction that is concomitant with the thermal cycles, which leads to serious problems, such as misalignment and adhesion failure of various microelectronic components, laminate warping, and electrode breakdown. The most direct strategy to overcome this instability involves reduction of the coefficients of thermal expansion (CTE) along the film plane

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(X–Y) direction in its glassy state. Low CTE characteristics ($<20 \text{ ppm K}^{-1}$ as a general target) are closely related to a very high level of PI main chain alignment along the X–Y direction (in-plane orientation) during thermal imidization [7,8], and this phenomenon is known to occur more notably in PI systems that possess more linear and rigid backbone structures [9–20] as shown in Fig. 1. However, the molecular design of PIs with low CTE results in their loss of thermoplasticity, which, in contrast, are hindered by these linear and rigid backbones. A range of monomers that are effective in increasing the thermoplasticity of PI films is shown in Fig. 2. These monomers typically involve long/flexible spacers, distorted and asymmetric structures with flexible connecting groups (e.g., ether linkages), and bulky side groups [21–33]. In particular, the incorporation of an all *meta*-linked 1,3-bis(3-phenoxy)benzene (1,3,3-PB) unit is the most effective method to improve the thermoplasticity of PI films, although it also typically results in a significant deterioration of the desired thermal properties (CTE and T_g). Thus, it is in principle difficult to overcome the trade-off between lower CTE and higher thermoplasticity. If this issue could be resolved, new potential applications for these PI films would be possible as shown in Supplementary data 1.

Current interlayer dielectrics composed of glass fiber cloth/epoxy resin composites in multi-layered circuit boards possess insufficient dimensional stability against thermal cycles because of their high CTE values originating from the epoxy matrix resins. If novel high-temperature polymeric materials possessing both low CTE and excellent thermoplasticity replaced these epoxy-based resins, however, multi-layered circuit boards with excellent dimensional stability could be obtained.

Epoxy-type adhesives with high CTE values are also currently used as laminates between low-CTE PI films (base films) and copper foils in double-sided flexible copper clad laminates (FCCL), which are employed as starting materials for flexible printed circuits (FPC). Low-CTE and thermoplastic heat-resistant polymers would enable us to produce adhesive-free FCCLs and thereby, the thermal dimensional stability of FPCs could be significantly improved. There are at present, however, no practical polymeric materials that simultaneously possess low CTE, excellent thermoplasticity, and very high T_g , because of the severe trade-off in properties mentioned above. In this work, we propose a series of novel low-CTE and highly thermoplastic high-temperature polymers, based on poly(benzoxazole imide)s (PBOI) [34–36].

2. Experimental

2.1. Materials

2.1.1. Monomer synthesis

A series of diamines incorporating benzoxazole (BO) units were synthesized according to the reaction scheme shown in Fig. 3.

GABO-OBA. 4,4'-Oxybis(benzoic acid) was refluxed in thionyl chloride at $80 \text{ }^\circ\text{C}$ for 3 h, and thionyl chloride was removed by azeotropic distillation with benzene to obtain 4,4'-oxybis(benzoic acid) dichloride (OBC, m.p. $91 \text{ }^\circ\text{C}$). 2-Amino-5-nitrophenol [2A5NP, 45 mmol] was dissolved in anhydrous γ -butyrolactone (GBL, 24.6 mL) in the presence of pyridine (45 mmol, 3.6 mL) as an HCl acceptor in a sealed flask. In a separate sealed flask, OBC (20 mmol) was dissolved in GBL (20.9 mL). The 2A5NP solution was cooled at $-20 \text{ }^\circ\text{C}$ and the OBC solution was slowly added using a syringe with continuous magnetic stirring, after which the reaction mixture was stirred at room temperature for 5 h. The reaction mixture was poured into a large quantity of water and the precipitate formed was collected by filtration, and dried at $100 \text{ }^\circ\text{C}$ in vacuum. The yellowish solid (10.5 g) was dissolved in GBL (37 mL) in the presence of *p*-toluenesulfonic acid (*p*-TSA, 0.951 g) and refluxed at $200 \text{ }^\circ\text{C}$ for 4 h. The precipitate formed was washed with GBL, ethanol, and water, collected by filtration, and recrystallized from dimethyl sulfoxide (DMSO), and vacuum-dried at $100 \text{ }^\circ\text{C}$ for 12 h. The nitro groups of the product (m.p. $263 \text{ }^\circ\text{C}$) were reduced as follows: the dinitro compound (4.70 g) was dissolved in *N,N*-dimethylformamide (DMF, 45 mL) and Pd/C (0.45 g) was added as a catalyst. The reaction mixture was refluxed at $100 \text{ }^\circ\text{C}$ for 5 h in a hydrogen atmosphere. After the catalyst was removed by hot filtration, the filtrate was slowly poured into a large quantity of water. The precipitate formed was recrystallized from a mixture of DMSO/toluene, collected by filtration, and dried under vacuum at $120 \text{ }^\circ\text{C}$ for 12 h. The molecular structure of the product was confirmed to be the desired diamine (6ABO-OBA) from the following data; FT-IR (KBr, cm^{-1}): 3355 (amine N–H), 1630 (NH_2 deformation + oxazole C=N stretching), 1493 (1,4-phenylene), 1248 (central diphenyl ether C–O–C); ^1H NMR (400 MHz, DMSO-*d*₆, δ , ppm): 8.13 (d, 4H, $J = 9.0 \text{ Hz}$, 3,3',5,5'-protons of the central diphenyl ether), 7.40 (2H, 4,4'-protons of the BO unit), 7.27 (d, 4H, $J = 8.8 \text{ Hz}$, 2,2',6,6'-protons of diphenyl ether), 6.82 (sd, 2H, $J = 1.9 \text{ Hz}$, 5,5'-protons of BO), 6.66 (s, 2H, 7,7'-protons of BO), 5.46 (s, 4H, amine); Anal. Calcd (%) for $\text{C}_{26}\text{H}_{18}\text{O}_3\text{N}_4$ (434.45):

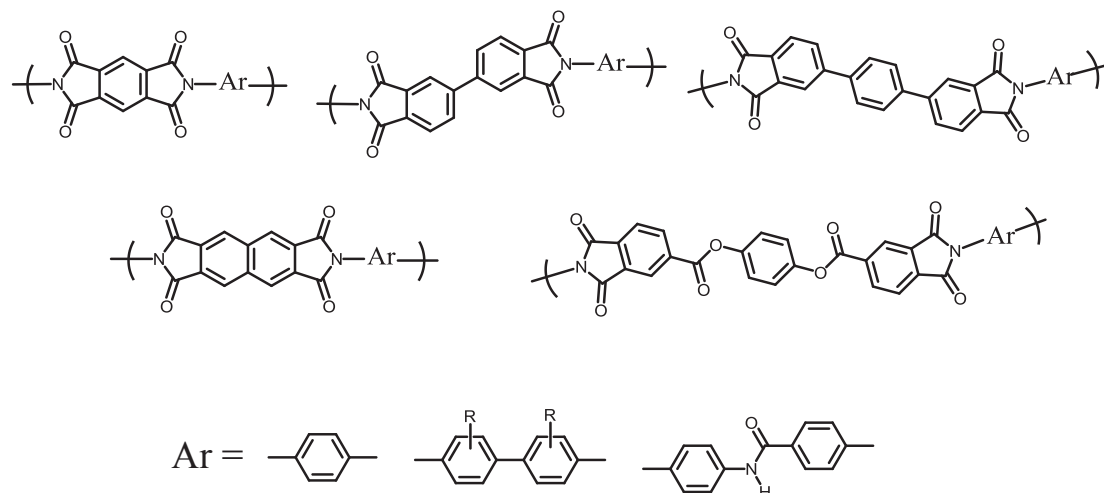


Fig. 1. Examples of chain structures of low-CTE polyimide systems.

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