

Suppression of Void Formation in Particulate-Filled Polyimide Composites: Effects of Thermoplastic Matrices and Residual Solvent

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Composite films of polyimides (PIs) and inorganic particles are often fabricated by thermal imidization of a slurry mixture of the particles and a solution of PI precursor, poly(amic acid). A shortcoming of such a process is that water generated as a by-product may lead to formation of voids.^[1] We have recently investigated the relationship between structures and thermal conductivity (λ) of PI composites containing various grades of hexagonal boron nitride (hBN) and reported that voids were most frequently found when large, high aspect-ratio flakes are embedded because stacked layers of in-plane oriented particles function as obstructive barriers.^[2] For fabricating dense and void-free hBN/PI composite films, we investigated the effects of (1) thermoplasticization of the matrix and (2) curing conditions such as the solvent volatility and the amount of residual solvents on void fractions (ϕ_v). By using a thermoplastic asymmetric biphenyl type PI, *a*BPDA-ODA (*a*BPDI, Fig.1b) instead of its thermosetting symmetric counterpart, a complete suppression of voids and ca. 2.2% reduction in ϕ_v were observed at 40 and 50 vol% hBN contents, respectively (Figs.2,3). A clear correlation was found between the out-of-plane λ and the structures of the composites, quantified by ϕ_v and the orientation function f of hBN particles. Furthermore, as shown in Fig.3, a significant reduction in ϕ_v was achieved at high hBN contents (>40 vol%) in both thermosetting sBPDI and thermoplastic *a*BPDI composites by using less-volatile *N*-methylpyrrolidone (NMP, b.p.=202°C) instead of *N,N*-dimethylacetamide (DMAc, b.p.=165°C) as the solvent. Since reducing the drying time of the solvent further improved the composite density at high hBN contents (i.e. ϕ_v = 5.6 % at 60 vol% hBN), it is assumed that the amount of residual solvent and its plasticization of the matrix play key roles in suppression of void formation.

References

[1] Miyauchi, M.; Ishida, Y.; Ogasawara T.; Yokota, R. *Polym. J.*, **2013**, 45, 594. [2] Tanimoto, M.; Yamagata, T.; Miyata, K.; Ando, S. *ACS Appl. Mater. Interfaces*, **2013**, 5, 4374.

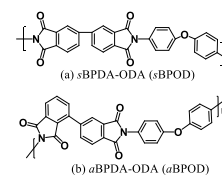


Fig.1 Chemical structures PI matrices

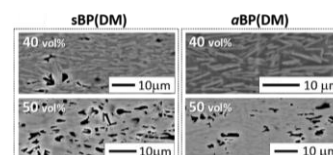


Fig.2 Cross sectional SEM images of hBN/sBP- and aBP-OD (DMAc) films

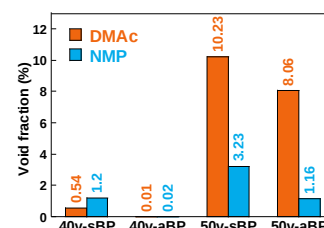


Fig.3 Void fractions ϕ_v of hBN/PI films