

## Surface modification of hexagonal boron nitride using plasmas in solution for development of polymer composite materials

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The surface modification using plasmas in solution is able to improve dispersibility of materials in aqueous media and polymer matrix via functionalization of the surfaces with polar groups. Our group has developed flexible and thermally conductive composite materials with polymers and inorganic particles, such as hexagonal boron nitride (hBN) whose surfaces were modified via plasma processing in solution.<sup>[1-2]</sup> Because of their high thermal conductivity and electrical resistivity, hBN has been used as fillers in polymer composites to realize flexible thermal management materials in electronic devices. Especially, the plasma-modified hBN particles had better dispersibility than untreated hBN, and suppressed stress concentration around aggregates in composites resulting in improving their mechanical properties such as flexibility and stretchability.<sup>[1]</sup> However, these plasma-surface modification has unexplored aspects, such as evaluation methods of surfaces for exploring more effective modification. This presentation introduces our researches exploring the effective surface modification via plasmas in solution through evaluation, for developing advanced hBN/polymer composites.<sup>[2,3]</sup>

In these researches, plasma processing in hydroquinone aqueous solution was applied to hBN particles (255475, Sigma-Aldrich), via utilizing the zeta potentials of plasma-modified particles as the indicator of surface modification. Plasmas generated in hydroquinone aqueous solution by bi-polar pulsed voltage from a power-supply (MPP-HV04, Kurita Seisakujo) could form amorphous carbon layers on hBN particles, which were confirmed by Raman spectroscopy and scanning transmission electron microscopy (STEM) equipped with an energy-dispersive X-ray spectroscopy (EDS) as shown in Fig. 1. The hydroquinone-aided plasma-modified hBN (HQpBN) would have abundant polar groups on the carbon layers, and actually showed higher negative zeta potentials than those of untreated hBN as shown in Fig. 2 (a). The zeta potentials were measured by using particle

tracking analysis (ZetaView PMX 110, Particle-Metrix) for hBN particles dispersed in pH 3–9 solution. The zeta potential should cause electrostatic repulsion between hBN particles in solution as well as polymer mixtures. Then, HQpBN and untreated hBN were applied for fabrication of composites with polyrotaxane elastomers.

Polyrotaxane elastomers, called as slide-ring materials, have unique mechanical properties in flexibility and stretchability. To utilize these unique properties of polyrotaxane in composites, uniform dispersion of fillers is required to avoid interfering polymer behavior.<sup>[1]</sup> The hBN particles were combined with polycaprolactone-grafted polyrotaxane (SeRM SH2400P, ASM) to fabricate polyrotaxane composites with hBN concentration of 30 wt%. Observation of the composites using X-ray CT (SkyScan1278, Bruker Inc.) as shown in Fig. 2 (b) revealed uniform dispersion of HQpBN composites unlike untreated hBN composites, corresponding with the results of zeta potential measurements. This uniform dispersion also improved the mechanical properties of polyrotaxane composites, such as longer extension and lower Young's modulus. Moreover, the plasma-modified hBN in these studies sustained the hBN's properties in composites such as thermal conductivity and electrical resistivity. Therefore, such plasma-surface modification has realized the development of advanced composites with rubber-class flexibility and metal-class thermal conductivity, by facilitating flexible deformation of polyrotaxane and enabling orientations of dispersed fillers.<sup>[4]</sup>

### References

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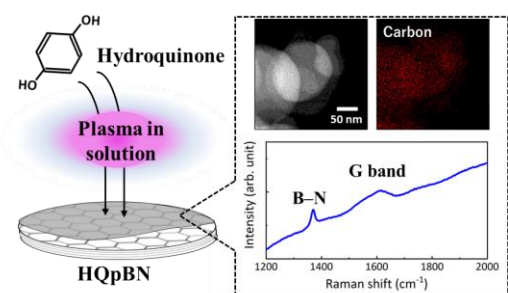


Fig. 1. Schematic of carbon layer formation on hBN with STEM/EDS images and Raman spectrum<sup>[3]</sup>

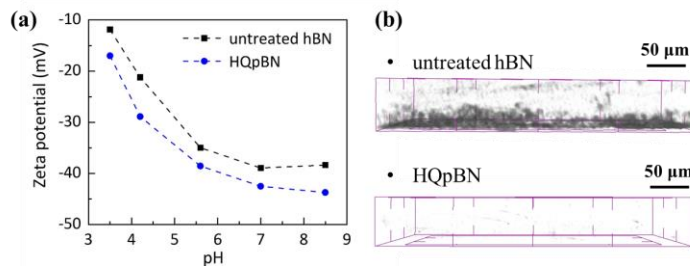


Fig. 2. (a) zeta potential of HQpBN and untreated hBN (b) X-ray CT images of polyrotaxane composites with untreated hBN and HQpBN<sup>[2]</sup>