Subsequent functionalization of hexagonal boron nitride after plasma proessing in solution for preparation of polymer composite materials

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Abstract: Plasma processing in solution is an effective surface modification method for hexagonal boron nitride (h-BN), because the excited species can form dangling bonds on the surface. In this study, the subsequent hydroxyl functionalization to the dangling bonds under an atmospheric environment was analyzed using electron spin resonance and Fourier transform infrared spectroscopy. When such functionalized h-BN was used for preparing a polyrotaxane composite material, the functionalization enhanced its flexible deformation.

Keywords: plasma in solution, hexagonal boron nitride. functionalization

1. Introduction

Hexagonal boron nitride (h-BN) is a superior thermally conductive and electrically insulating material, and h-BN/polymer composite materials have been developed for thermal management in electronic devices. However, the stable surfaces of h-BN limit surface functional groups and cause poor dispersibility of h-BN [1]. Plasma processing in solution is an effective method for surface modification of h-BN, because the excited species can break the B–N bonds and functionalized the surfaces with polar groups [2,3]. The functionalized groups are expected to increase zeta potential resulting higher dispersion of h-BN in polmer matrix, and achieve unform and flexible composite materials [3]. As for the mechanism of functionalization of h-BN via plasma processing in solution, it has been assumed that the dangling bonds on h-BN formed by the plasma could be functionalized with hydroxyl (OH) groups by subsequent oxidization [4]. The formation of dangling bonds via plasma processing was detected using electron spin resonance (ESR) measurements of plasma-treated h-BN, but the subsequent functionalization process has not been fully confirmed [4].

The purpose of this study is to reveal the subsequent functionalization to the dangling bonds formed by plasma processing in solution. Plasma processing in solution was performed on h-BN nanoparticles, and gradual functionalization to the formed dangling bonds under an atmospheric environment was analyzed using ESR measurements and Fourier transform infrared (FT-IR) spectroscopy. To confirm the effect of such functionalization in developing composite materials, the functionalized h-BN was applied for preparing flexible composite materials with polyrotaxane.

2. Experiments

Plasma processing in solution was performed on h-BN particles (Maruka, AP-170S) using devices demonstrated in our previous study [3]. The plasma was generated for 20 min in 1 L of distilled water containing 5 g of h-BN particles, using a stirring device (Nihon Spindle, Jetpaster) and a bipolar pulsed power supply (Kurita Seisakujo, MPP-HV-04-300 kHz). The applied pulsed voltage for plasma generation had a frequency of 300 kHz, a peak voltage of ±1 kV, and a pulse width of approximately 1 μs. The plasma-treated h-BN was captured using a membrane filter (Durapore) and dried under vacuum at temperature of 120 ℃ for 2 h. After these processing, the plasma-treated h-BN was exposure in an atmospheric environment at room temperature for up to 500 days.

The plasma-treated h-BN with different exposure days were analyzed using an ESR spectrometer (Bruker, EMX-plus) and a FT-IR spectrometer (PerkinElmer, Spectrum100). ESR measurements at room temperature using a microwave with frequency of 9.86 GHz was performed for the h-BN filled in a quartz glass tube to detect dangling bonds formed by plasma processing. FT-IR spectroscopy was conducted to detect the absorption caused by B–OH bonds.

Finally, the functionalized h-BN via plasma processing in solution and untreated h-BN were used for preparing composite materials with a polyrotaxane elastomer, which has a movable cross-linking structure achieving flexible deformation [2,3]. 0.2 g of the h-BN and 0.5 g of polycaploractone-grafted polyrotaxane (ASM, SeRM SH2400P) were compounded using 2.2 mL of dimethyl sulfoxide as solvent, 10 μL of hexamethylene diisocyanate as a cross-linker, and 30 μL of dibutyltin dilaurate as a catalyst. Further details of the preparation method were described in our previous paper [5]. After cross-linking reaction and removal of solvent, the tensile properties of obtained composite materials were measured using a uniaxial tensile tester (Shimadzu, EZ-S) for dumbbell-shaped specimens.

3. Results and discussion

Figure 1 shows ESR spectra of untreated h-BN and plasma-treated h-BN with 4, 112, and 495 days air exposure after the plasma processing. ESR spectra of plasma-treated h-BN exhibited a signal attributed to microwave absorption of dangling bonds, called three-boron centers. Three-boron centers are in-plane defects at the site of nitrogen, and their formation via plasma processing has also been confirmed in our previous study [4]. In this experiment, ESR measurements also showed

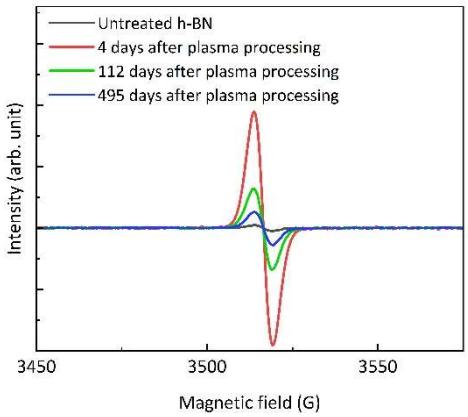

Fig. 1. ESR spectra of plasma-treated h-BN with different air exposure days and untreated h-BN.

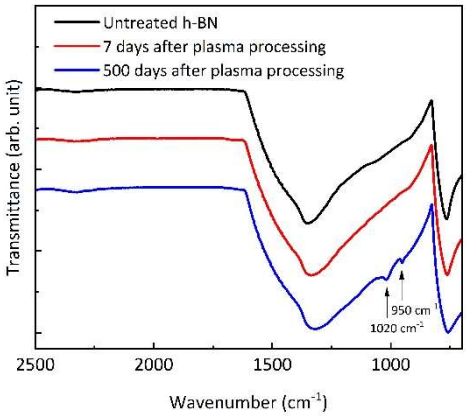

Fig. 2. FT-IR spectra of plasma-treated h-BN with different air exposure days and untreated h-BN.

that the signal from dangling bonds in plasma-treated h-BN was decreased during air exposure for up to 495 days. OH functionalization during the air exposure was confirmed by FT-IR spectra of the hBN, as shown in Fig. 2. The broad absorption bands around 760 and 1370 cm^{-1} are attributed to B–N stretching mode, and additionally, the spectrum of plasma-treated h-BN with 500 days air exposure have absorption peaks at 950 and 1020 cm^{-1}, which are attributed to B–OH stretching mode. Therefore, these results indicate that OH functionalization of the h-BN during air exposure was gradually progressed to dangling bonds formed by plasma processing in solution.

Such functionalized h-BN with 500 days air exposure after plasma processing was used for preparing a polyrotaxane composite. Figure 3 shows typical stress-extension ratio curves of polyrotaxane composites containing functionalized h-BN and untreated h-BN with 30 wt%. The functionalized h-BN composite tended to exhibit lower Young's modulus and longer extension until break than those of the untreated h-BN composite. It is suggested that the better dipersibility of functionalizated h-BN could suppress the stress concentration in composite materials and allow flexible deformation of polyrotaxane chains [3]. Therefore, the functionalization process observed in this experiment can be effective for developing flexible composite materials, and deserves further investigation e.g. for enhancing the functionalization rate.

4. Conclusion

In this study, gradual functionalization of plasma-treated h-BN under an atmospheric environment was analyzed using ESR measurements and FT-IR spectrometry. The changes in these spectra during air exposure for up to 500 days indicated OH functionalization to dangling bonds formed via plasma processing in solution. Such functionalized h-BN was used for preparing polyrotaxane composite materials, and this composite exhibited flexible deformation with lower Young's modulus and longer extension until break than those of a composite containing untreated h-BN. Because the air exposure of the plasma-treated h-BN nanoparticles in this study revealed slow subsequent functionalization which has not been observed with another plasma-treated h-BN in our previous study [4], this process might allow further detailed investigation to reveal the reaction mechanism for enhancing the functionalization of h-BN. Controlling subsequent functionalization could be an effective surface modification for developing flexible composite materials.

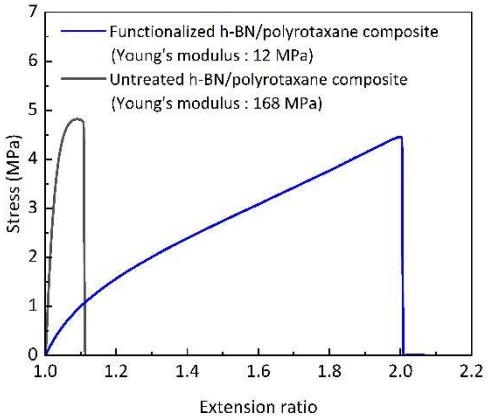

Fig. 3. Typical stress-extension ratio curves of polyrotaxane composites containing functionalized h-BN (air exposure for 509 days after plasma processing) and untreated h-BN.

5. References

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