Solid State High-Resolution ^{15}N and ^{11}B MAS-NMR Study of Ammonia Borane-Polyethylene Oxide Composites

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Introduction

Ammonia Borane (NH_3BH_3) is a potential hydrogen storage material due to its high hydrogen content (19.6%) and it displays a solid-solid structural phase transition at 223 K. It has some drawbacks for practical application because of its slow hydrogen release along with the formation of unwanted byproducts and gases. Various studies have showed that adding polymers improve the hydrogen release properties including kinetics [1, 2]. In this study, bulk composites of AB/polyethylene oxide (PEO) were prepared and dehydrogenation properties were investigated via thermal methods, FT-IR and NMR. ^{15}N MAS-NMR was utilized to evaluate if there is any interaction between NH_3BH_3 and the polymer at room temperature. ^{11}B MAS-NMR studies were also conducted at room temperature as well as at 85° C to investigate the isothermal decomposition during several hours.

Experimental

A powder sample of NH_3BH_3 (97%) and polyethylene oxide (M_w = 400,000) were purchased from Sigma-Aldrich. The composites were prepared via sol-gel method and dried under vacuum with different ratios (ABPEO11 represents 1:1 mass ratio) [1]. Then it was packed in a 4.0 mm MAS rotor and used for ^{15}N and ^{11}B NMR chemical shift measurements on a wide bore 600 MHz magnet equipped with a Bruker Avance III NMR console using a spinning speed of 10 kHz. Experiments were performed at room temperature and at 85° C.

Results and Discussion

Figure 1 shows the ^{15}N NMR spectrum of NH_3BH_3 and its polymer composites at room temperature. At 600 MHz pristine NH_3BH_3 displays a single peak at 16.4 ppm shown in figure 1. Polymer composites with 1:1 ratio showed additional peaks due to the interaction of NH_3BH_3 and PEO, a possible formation of a H-bond between O atom of PEO and H atom of NH_3BH_3. Upon increasing the polymer content, the peak of NH_3BH_3 disappears supporting the interaction. Figure 2 displays the ^{11}B MAS-NMR spectra at 85° C every half hour for 6 hours. At 85° C the composites start to show additional peaks indicating the decomposition starting promptly. The main focus in the future will be to evaluate the interaction and investigate the dihydrogen bonding network of AB. The experiments on phase transition properties of the polymer composites of AB are planned.

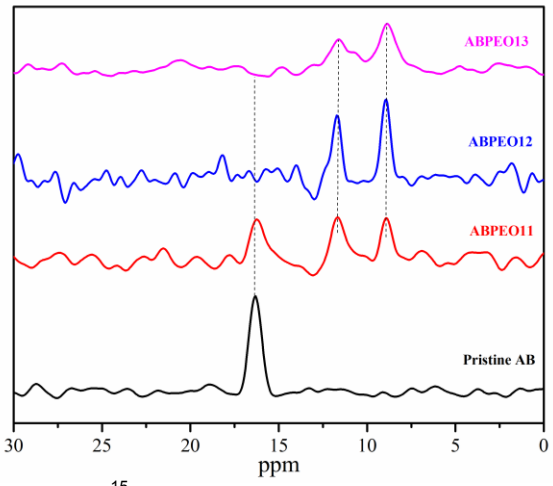

Fig. 1. ^{15}N NMR spectrum of NH_3BH_3 and its polymer composites.

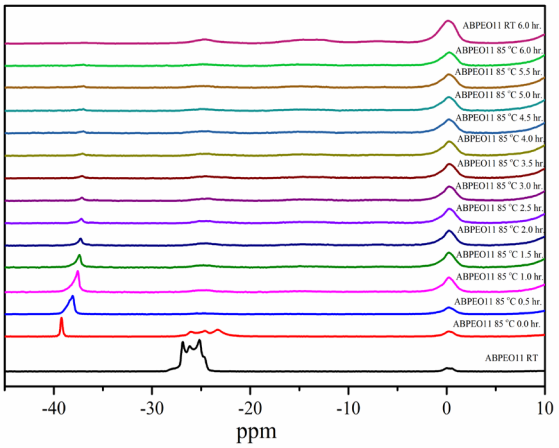

Fig. 2. ^{11}B MAS-NMR spectra at 600 MHz for ABPEO11 at room temperature and 85°C every half hour for 6 hours.

Conclusions

The 600 MHz ^{15}N and ^{11}B NMR measurements enable us to conclude that there is an interaction between NH_3BH_3 and polyethylene oxide. The isothermal study via ^{11}B also enabled us to find out polymeric composites readily decompose at 85° C which takes about 2 hours for NH_3BH_3. Adding the polymer matrix decreases the incubation time for H_2 release from NH_3BH_3. Future studies will investigate the phase transition behavior to understand the interaction between the polymer and NH_3BH_3.

Acknowledgements

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References

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