

Thermal degradation of a poly (ethylene-co-methacrylic acid) ionomer investigated by solid-state ^{13}C NMR and ESR

(Department of Applied Chemistry, National Defense Academy of Japan) ○Shohei Mikage, Atsushi Asano

Keywords: poly (ethylene-co-methacrylic acid); thermal degradation; ESR; solid-state ^{13}C NMR

Poly (ethylene-co-methacrylic acid) (EMAA) ionomers, which carboxy groups are neutralized with Na^+ cations, are well known to show the excellent physical and chemical properties, such as strong toughness and good fabricability.¹ EMAA ionomers have been used as engineering and commercial materials for a long time and their structure and dynamics have been investigated by NMR and ESR measurements.^{2,3} It is also very important and interesting how the thermal degradation is affected by the existence of the ionic clusters. In this study, we examined EMAA and EMAA ionomers (EMAA-30Na and -54Na: the number represents the degree of neutralization) heat-treated at 200°C to reveal the structural change occurring during the thermal degradation using the solid-state ^{13}C NMR and ESR.

The radicals created after heat treatment were measured as a spin quantity with heating period by ESR (Fig. 1). It is obvious that the amount of radicals increases in two stages, and the quantity for EMAA-54Na became about twice and seven folds as compared to that for EMAA-30Na and for EMAA, respectively at 3000 min. However, the newly observed NMR peaks, which are attributed to the cross-linking structures produced with the radical residues, were much intense for EMAA rather than those for EMAA ionomers. The main product was a $\sim\text{CH}_2\text{-COO-CH}_2\sim$ bond created from -COOH and $\cdot\text{OCH}_2\text{-}$ functional groups which are resonated around 175 ppm (Fig. 2). The other reaction processes during thermal degradation will be discussed in detail.

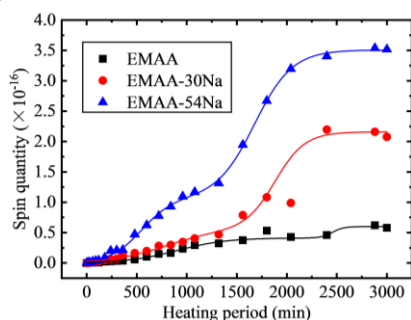


Fig. 1 Spin quantity vs. heating period.

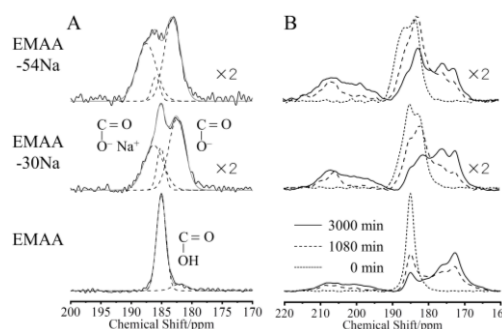


Fig. 2 Expanded ^{13}C CPMAS NMR spectra for C=O region; (A) before and (B) after heat treatment.

- 1) S. Yano, E. Hirasawa, Development of ionomer and ion containing polymer, CMC publishing, 2009.
- 2) H. Yoshimizu, Y. Tsujita, *Ann. Rep. NMR Spect.*, **2001**, 44, 1-22.
- 3) Y. Miwa, T. Kondo, S. Kutsumizu, *Macromolecules*, **2013**, 46, 5232-5237.