Efficient mineralization of functional fluoropolymers by use of subcritical water with alkaline reagent

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Because of their unique properties such as heat-, chemical-, and weather resistances, fluoropolymers have been used in many cutting-edge applications such as optical fibers for 5G communications, binders for lithium-ion batteries and so forth. However, their recycling technologies have not yet been well established owing to their high stability; most of the wastes are disposed of in landfills. Furthermore, the mine production of high-purity fluorite (CaF_2 ore), the raw material for all fluoropolymers, is limited in a few countries. If fluoropolymer waste can be decomposed to F^- ions (i.e., mineralization) under mild conditions, F^- can be converted to CaF_2 by reaction with Ca^{2+} ion, which can contribute the recycling of fluorine element. Herein we report efficient mineralization of poly(vinylidene fluoride) (PVDF), poly (vinylidene fluoride-hexafluoropropylene) copolymer [poly(VDF-*co*-HFP)], and ethylene-tetrafluoroethylene copolymer (ETFE) by use of subcritical water in the presence of alkaline reagent.[1)]

Fig. 1 shows the reaction temperature dependence of the amounts of F^- and total organic carbon (TOC) formed in the reaction solution, where PVDF or poly(VDF-*co*-HFP) was reacted in 1.0 M of KOH for 6 h under argon. When the reactions were performed at 250 ºC, the F^- yields of PVDF and poly(VDF-*co*-HFP) reached 95±1 and 98%, respectively. The reactivity of poly(VDF-*co*-HFP) was higher than PVDF: even at 200 ºC, the F^- yield of poly(VDF-*co*-HFP) was 91%. Because the pH of the resulting reaction solution was high (13.3~13.8); most of CO_2 molecules formed were present in the reaction solution as CO_3^{2-}. Consistently, very little CO_2 amount was detected in the gas phase. Furthermore, black colored residue was present.

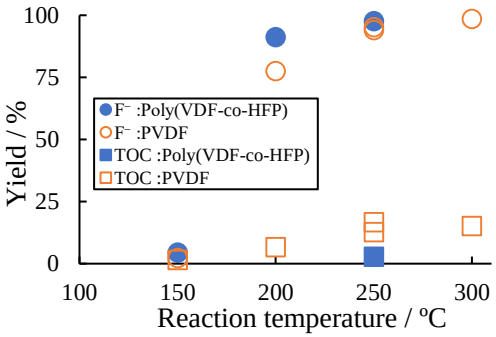

Fig. 1. Effect of temperature on the amounts of F^- and TOC. Each reaction was carried out for PVDF or poly(VDF-*co*-HFP) in 1.0 M of [KOH].

Formation of CaF_2 from these (co)polymers will be reported at the time of the presentation.

1) J. Hamaura, R.Honma, H. Hori, A. Manseri, B. Ameduri, *Eur. Poyml. J.*, **2023**, *182*, 111724.