講演番号　　(未記入)

アラミドの錯体化による高誘電率・高耐熱性フィルムの創製

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Introduction

Polymers such as PVDF, BOPP, PET, and polyimide (PI) are commonly used as dielectric films in capacitors, sensors, and flexible substrates. PI exhibits high heat resistance and mechanical properties, but it has low thermal conductivity and high cost. Conversely, PVDF, BOPP, and PET are low cost and good processibility, but have relatively low heat resistance. All of these share the common disadvantage of needing significant addition of expensive fillers like titanium oxides to achieve sufficiently high dielectric constant and energy density. In addition, the recyclability of these materials is relatively limited when considering energy and time efficiency. Aramid, an organic fiber, possesses excellent toughness and heat resistance due to highly oriented polymer chains forming strong hydrogen bonds, and is used in protective clothing, paper, insulators, and composite materials. Because these are inexpensive mass-produced products, they are discarded in large quantities, and unlike glass and carbon fibers, there is relatively little activity in developing their recycling technology. Recently, it has been discovered that deprotonated aramid microfibers can be disassembled, and a technology for producing nanofiber membranes by reprotonation has been established. While the morphology and orientation of these aramid nanofibers (ANFs) can be controlled by the reprotonation conditions, high-performance applications are limited to mixing with fillers such as graphene, h-BN, TiO_2, and chitosan. However, there are no reports on methods for achieving structural control and functional expression in ANFs without relying on conventional fillers. In this study, we aim to create high-dielectric constant and high-heat resistant films by coordinating metal ions instead of protons under mild conditions in aramid nanofibers produced by the deprotonation method (Fig. 1).

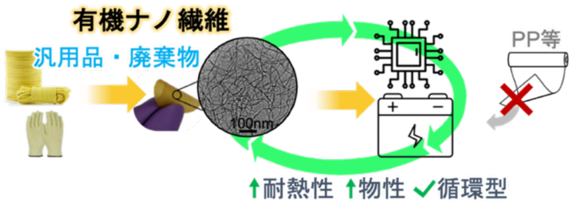

Fig. 1 Creation of heat-resistant dielectric films from recycled aramid nanofibers

Methods

Para-aramid (p-polyphenylene terephthalamide, Kevlar 29, Dupont) was dissolved by a deprotonation in a DMSO/KOH solution that was stirred for 24 hr at room temperature to create 2 wt% ANF solution. The solution was then transferred to smaller vials and diluted to 1 wt% with DMSO, followed by the addition of metal salt (Ag, Ca, Mg, Zn, Fe, Cu, Al) and vigorously mixed for 30 min followed by continuous stirring for 4 hr. ANF/ion films were then prepared by vacuum filtration after addition of acetone as a precipitating phase, followed by repeated washing in acetone and drying. The films were then evaluated for their dielectric properties using an impedance analyzer operating between 10 Hz – 5 MHz @ 1 V.

Results

The colors of the films vary depending on the ion, with Cu, Fe, and Ag showing the most Due to the random distribution of nanofibrils in the films, neat ANF does not exhibit strong diffraction peaks in the 18-23° region that represents the spacing between aromatic amide molecules. Metal ions tend to disrupt the ordered structure of nanofibrils and appear to slightly increase the spacing between molecules. XPS analysis revealed that both N and O coordinate with metal ions, although the precise coordination number is not yet clear. XRD and XPS data suggest that carbonate (Ca) and oxides (Cu, Fe, Ag) may have formed due to moisture and air exposure, which is further supported by color changes in the films.

Dielectric permittivity of the neat ANF is relatively low (2.6 @ 1 kHz), but a 50% increase was observed by coordination with Ag, Al, or Zn, and 100% increase by coordination with Ca or Mg. The oxides Cu and Fe showed an 8x higher dielectric permittivity (~15 @ 1 kHz), which is significantly higher than other polymer films without the use of conventional fillers.

Conclusions

This study reports preliminary findings on how coordination of conventional aromatic amide (aramid) fibers with metal ions can produce films with high dielectric properties, heat resistance, and recyclability for application in electronics and other devices.