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Thermal stability of poly(vinylidene fluoride) films pre-annealed at various temperatures

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Abstract

This paper investigates the relationship between the pre-annealing conditions and the thermal stability of uniaxially-drawn poly(vinylidene fluoride) (PVDF) films in order to clarify their technical limits in terms of temperatures that can be used for assembly processes and for practical applications. Specimens that are pre-annealed below their melting temperature apparently shrink in the stretch-direction when they are exposed to elevated temperatures above the pre-annealing temperature. Since the content of β-PVDF in the films decreases simultaneously with the shrinkage, their piezoelectric properties also deteriorate. In addition, there is a suggestion that the level of polarization in the remaining β-phase decreases significantly during annealing above 90–100 °C. However, the dimensions and the piezoelectric coefficients of the films remain stable during annealing below the pre-annealing temperature. Therefore, the thermal stability of PVDF films can be controlled practically by using the appropriate pre-annealing temperature. By contrast, the films were softened at 90–100 °C when the pre-annealing treatment was conducted above the melting temperature. The softening of films that are pre-annealed above the melting temperature is a different phenomenon from that observed in specimens that are pre-annealed below the melting temperature.

Keywords: Poly(vinylidene fluoride); Semicrystalline polymers; Piezoelectricity; Annealing; Shrinkage

1. Introduction

Poly(vinylidene fluoride) (PVDF) and its copolymers with trifluoroethylene (TrFE) or tertrafluoroethylene (TFE) are well known as typical ferroelectric polymers [1–3]. Two different crystalline phases that can exist in PVDF-based polymers (the β- and α-phases) are the most relevant for practical piezoelectric applications. The β-phase is especially important for realizing piezoelectricity, since it has the all-trans conformation structure [4–6], resulting in a net dipole moment. However, PVDF films often form the α-phase (non-polar phase) when they are fabricated using the melt-crystallization or solution-casting techniques. Mechanical stretching [2] and solid-state coextrusion [7] are generally utilized in order to obtain highly orientated β-phase. Although PVDF-based polymers can be obtained in a single crystal form [8], in most cases they are provided in a semicrystalline form in which the ferroelectric crystal regions are embedded in an amorphous matrix.

PVDF-based polymers have been utilized in several applications, such as switches, various sensors, accelerometers, audio (speakers and microphones) and ultrasound applications. Recently, ferroelectric PVDF films have started to be employed as tactile sensors in robotic applications [9–11]. In our research group, a super-flexible tactile sensor system that makes use of PVDF films has been successfully developed in order to realize artificial skin for humanoid robots and related applications [9,10]. With the advance of polymer electronics, the application of PVDF-based polymers is expected to be expanded in the near future.

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From the viewpoint of users of PVDF films, improving the thermal stability of these films is an important issue, as well as drastic improvements in their piezoelectric properties. For example, in order to improve productivity, the films are exposed to high temperatures during the assembly process when we fabricate tactile sensor systems. In addition, the limited temperature range for applications of the films has become a serious problem from the viewpoint of the reliability of the sensor systems.

Several projects were undertaken during the 1970–1980's to study the thermal degradation behavior of PVDF films [12–15]. When the films are annealed at elevated temperatures, they are found to shrink significantly in the stretch-direction. Johnson et al. [12,13] estimated an apparent activation energy for the thermal degradation process between 60 and 88 °C. They also suggested that some additional relaxation mechanisms exist above 100 °C. In addition, Kolbeck [14,15] pointed out that the shrinkage and the piezoelectric aging (decrease in piezoelectricity) phenomena both result from similar mechanisms associated with microstructural annealing effects. As a result of his work, it was found that decay of the piezoelectric properties occurs at temperatures above 60 °C. However, the issues that were clarified by these studies are only applied on a limited basis when examining the thermal stability of PVDF films, because the physical states of the films that were used in these studies are unclear. Because the thermal stability of PVDF-based films has also been reported to depend on the preparation conditions [1], the assessment of film stability using specimens with stipulated qualities needs to be conducted in order to obtain information that is widely applicable for various applications. The present work focuses on variations in the thermal stability of PVDF films depending on the pre-annealing conditions. The objective of this work is to discuss the dependence of the thermal stability and the piezoelectric degradation mechanism of PVDF films on the pre-annealing temperature.

2. Experimental procedure

Uniaxially-drawn PVDF films (Measurement Specialties Inc., Piezo Film: 52 μm thickness) which included Ni/Cu electrodes that were prepared by a sputtering process were used as the specimens in the present work. The manufacturer had already annealed the films at 60 °C during the fabrication process. Several specimens of the PVDF films were additionally annealed at 100, 120 and 130 °C for 3.6 ks (pre-annealing process). During the pre-annealing process, the films were placed between metal blocks in order to maintain their planarity.

The thermal analyses of the specimens were performed using a differential scanning calorimeter (DSC, dynamic scan under 8.33×10^{-2} °C s^{-1}) and a thermo-mechanical analyser (TMA, dynamic scan using a cylindrical probe (ϕ500 μm) under 8.33×10^{-2} °C s^{-1} with an applied load of 7×10^{-3} kg). Subsequently, the specimens that were pre-annealed at these temperatures were exposed to an isothermal chamber at 60–160 °C. The shrinkage of the specimens was measured after the exposure. The constituent phases of the specimens were identified by X-ray diffraction (XRD, Cu Kα radiation) analysis. When the identification of the constituent phases was conducted, we referred to existing diffraction data for α- and β-PVDF which takes the orientation of the crystallites into account, as reported by Davis et al. [16]. Furthermore, the piezoelectric coefficients ($|d_{33}|$) of the specimens were evaluated using a piezometer system (PIEZO TEST Inc., test frequency: 110 Hz, test force: 0.25 N) at ambient temperatures.

3. Experimental results

3.1. Thermal degradation behavior of the films pre-annealed at 60 °C

Fig. 1 shows an XRD pattern (reflection scan to the film surface) of a PVDF film pre-annealed at 60 °C. The XRD pattern indicates that the film is in a semicrystalline form containing both the α- and β-phases of PVDF. However, the main constituent phase of the film is found to be the ferroelectric β-phase.

In order to investigate the relaxation behavior of films pre-annealed at 60 °C during heating, dynamic DSC measurements were conducted in the temperature range between 30 and 250 °C. Fig. 2 shows the DSC profile of films that were pre-annealed at 60 °C. In the DSC profile, two different endothermic processes (60–80 °C and 150–160 °C) are detectable. The endothermic process at 150–160 °C corresponds to the melting of PVDF crystallites [17]. The endothermic process that is induced in the low temperature region can also be confirmed from the TMA measurement. Fig. 3 shows the variation in thickness of the films during the TMA measurement. The thickness of the specimen tends to increase with increasing temperature due to thermal expansion. However, the thickness increment becomes drastically larger above 60–80 °C. This drastic increase in thickness is caused by shrinkage in stretch-direction of the specimen. The volume flow in the

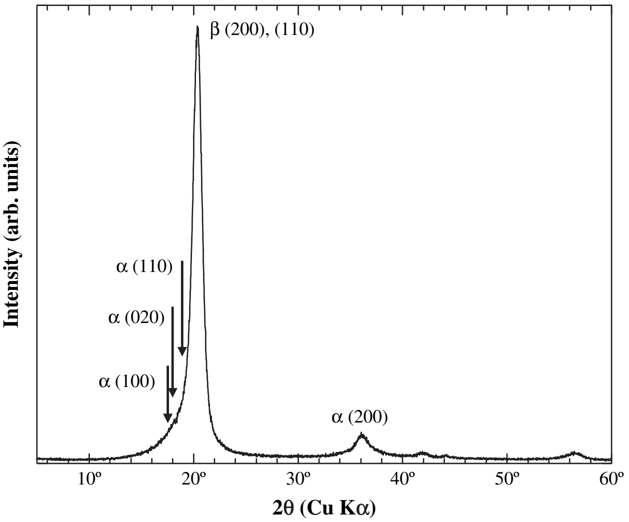

Fig. 1. XRD pattern of the PVDF film pre-annealed at 60 °C.