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Thermal analysis of poly(vinylidene fluoride) film

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Abstract

When stretched, the crystal phase of poly(vinylidene fluoride), PVDF, exhibits a crystal to crystal α to ß phase transition [A. Lovinger, Poly(vinylidene fluoride), D.C. Basset (Ed.), Developments in Crystalline Polymers, vol. 1, 1982, p. 195]. Typical DSC analysis of this film results in analyzing the relaxed film, which would not be representative of the starting material. This paper will focus on the just mentioned relaxation effect.

Keywords: Poly(vinylidene fluoride) (PVDF); DSC; Film

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1. Introduction

Use of variable heating rates has long been a tool used by thermal analysts to study glass transition relaxation effects as well as reorganization of the crystallites that can occur during melting. Reorganization is a process when improvements or perfections of the initial metastable crystallites occur [1]. Reorganization is usually observed on heating as a double melting peak where the lower temperature peak represents the melting of the original metastable crystallites while the upper temperature peak corresponds to the melting of the crystallites perfected during the heating process. The faster the heating rate the more pronounced the lower temperature peak becomes since less time is available for the metastable crystal to perfect itself. Conversely, the slower the ramp the more pronounced the upper temperature peak, since more time has been allowed for the annealing process to proceed. Although reorganization was previously noted in poly(vinylidene fluoride), PVDF, by Nakagawa and Ishida [2], the effect of molecular weight on the reorganization process of PVDF was first presented at the 1997 NATAS conference [3]. In that paper it was found that reorganization was less profound as the molecular weight increased. The addition of a noncrystallizable unit into the PVDF crystal structure also has an affect on reorganization. As noted in the 1998 NATAS conference, the incorporation of noncrystallizable monomeric units into PVDF was found to retard the reorganizational response [4]. In this paper, variable heating rates were employed to study the response of crystal melting in PVDF films.

2. Experimental

Three different films of PVDF were selected for this study. They were fabricated by first extruding a 130 μm film, then uniaxially stretching to approximately either 100 or 28 μm. Retains for analysis were then taken upon extrusion and stretching. DSC was performed on a TA Instruments Q1000 system in the T4 mode with a refrigerated cooling accessory. A nitrogen purge was used for all analyses. Heating rates of 5, 10, or 20 °C/min were employed. The *Y*-axis for all overlays comparing heating rate effects was normalized. Although the current Q1000 software does allow comparisons in heat capacity as an axis option, we found that this option seemed to use the measured instead of the programmed heating rate to convert to heat capacity. All controlled cooling rates were performed at 10 °C/min and sample masses of 5–6 mg were typically used. Constrained film measurements were made using a hermetic pan with an inverted lid with the film ends held taut by the pan's crimped rim. Standard crimped aluminum pans were used for all other analyses.

3. Results and discussion

The 28 μm film showed a slightly higher degree of crystallinity, which is likely due to strain induced crystallization. However, all three films showed similar melting transitions after cooling from the melt at 10 °C/min provided that the heating rates were identical (see Fig. 1). This would indicate that the

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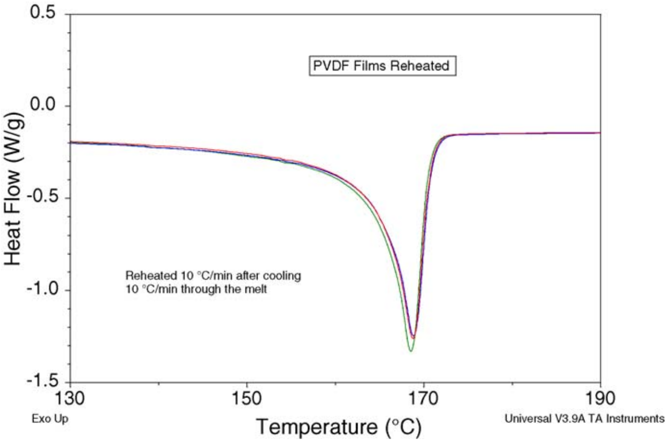

Fig. 1. Film reheats with the same thermal history.

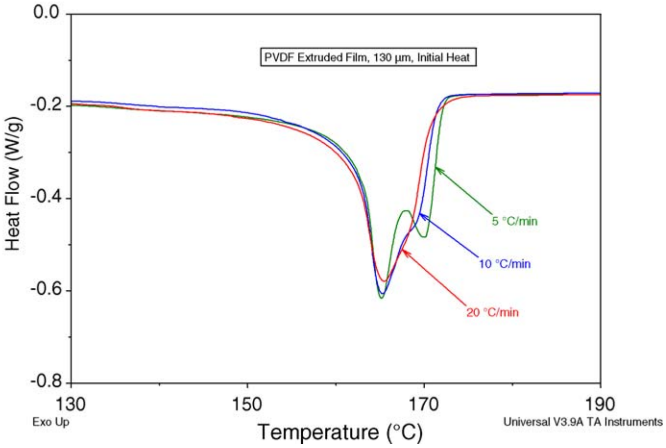

Fig. 3. Initial heats of extruded PVDF film.

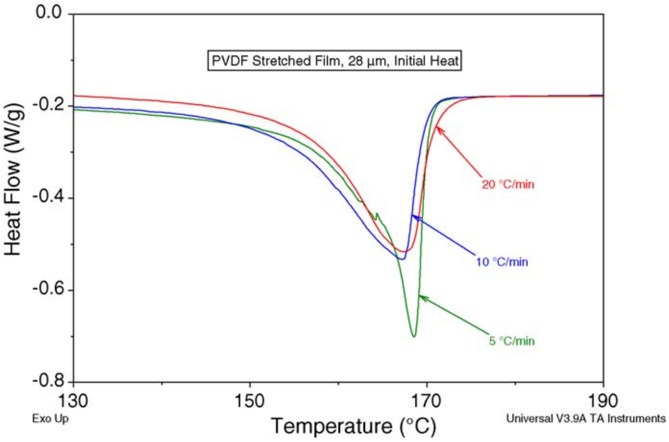

Fig. 4. Initial heats of stretched PVDF film.

starting material has not been altered. The initial heats of the films resulted in very distinctive profiles but all showing close melting point temperatures. That is, the 130 μm film showed an endothermic peak at 165 °C with a ill-defined high temperature shoulder while the 100 μm film showed a double endothermic peak at 165 and 169 °C. Finally, the 28 μm film showed a single peak at 167 °C (see Fig. 2). No apparent pattern could thus be discerned since one would assume an increased peak temperature for the highly stretched film. Looking at rate effects, one can now see that slower heating rates results in a more perfected melting peak for both the stretched and extruded film (see Figs. 3 and 4). Neither rate experiment showed a reorganizational effect. However, the stretched film showed a profound mass effect. Using a higher sample mass the melting peak was elevated as well as by constraining the film (see Fig. 5). As pointed out by Menczel et al. [5], oriented constrained films usually show a higher melting point than that of unconstrained films. Therefore restraining the film results in obtaining a better representation of the melting of the original strained crystals (see Fig. 6). It is likely that by compacting a higher sample mass in the same pan volume resulted in an increased melting point for the unconstrained films probably due to additional contact points between the film folds retarding the relaxation. However, for the most part analysis of the unconstrained film leads to the melting properties of a relaxed material. The relaxation that takes place upon heating seems to mask any reorganizational response.

Weinhold et al. [6], found that one needed to heat beyond the equilibrium melt temperature of 210 °C [7] of PVDF to destroy all the nuclei in an oriented film. They theorized that

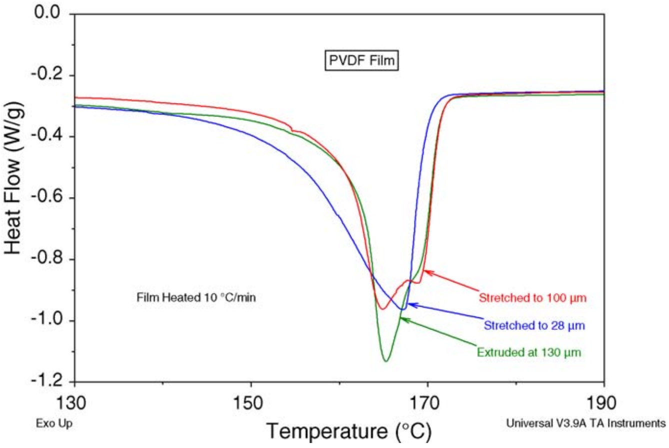

Fig. 2. Initial heats of PVDF films.

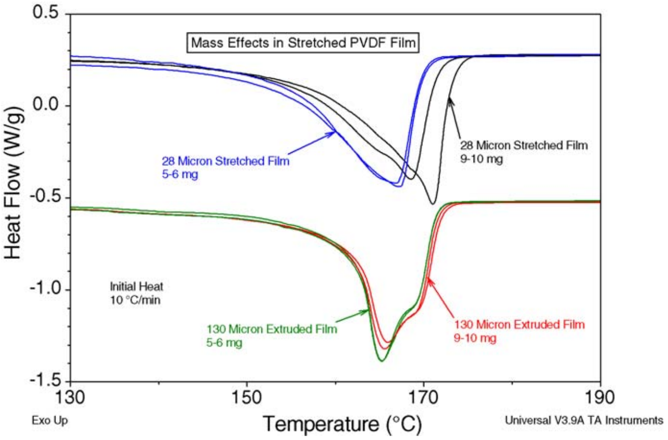

Fig. 5. Higher sample mass resulted in an increased melting temperature for the oriented film. Runs performed in duplicate.

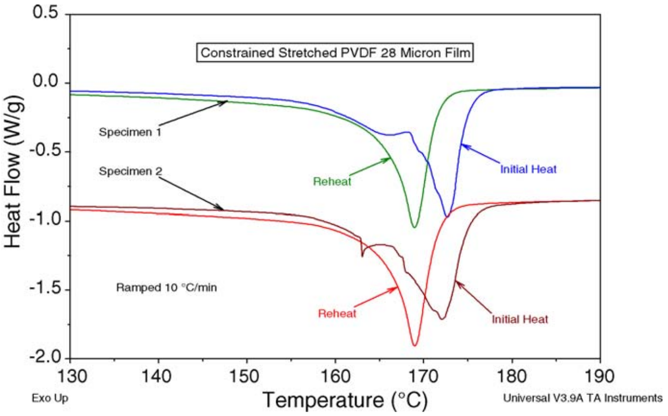

Fig. 6. Constraining the oriented film resulted in a higher melting peak.

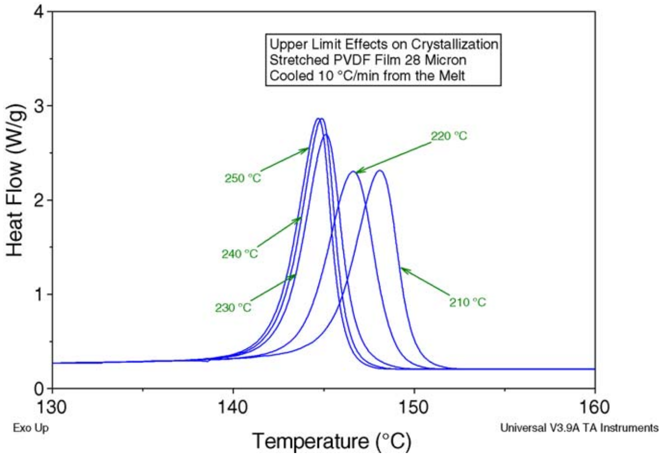

Fig. 7. PVDF 28 μm film cycled to increasing higher upper limits using 10 min holds. Hold temperatures are noted.

residual extended chain crystal nuclei remained even possibly above the equilibrium melting point. Repeating a similar experiment using hold times of 10 min, we found this to be the case for all three films. A peak temperature difference of 2–3.5 °C was recorded between the crystallization peak noted on cooling after a 210 °C hold (using 10 min hold times) to that of the 250 °C hold. The extruded film showed the smallest difference while the highly stretched film showed the greatest temperature difference between the cooling peaks for the two-hold treatments indicating that this is clearly a nucleating effect. Cycling to different hold limits found that this effect abated after heating to 230 °C (see Fig. 7). No such upper limit effect was noted for starting PVDF powder from which the films were fabricated. The powder showed a crystallization peak temperature over 10 °C lower than the films.

4. Conclusions

Oriented PVDF film was found to relax upon heating so that DSC analysis of an unrestrained film resulted in analyzing a relaxed material. Cycling to different upper limits resulted in a temperature difference between the cooling peaks noted. Although not as pronounced for the extruded film as compared to the stretched film, this effect was still present. This would indicate that only a small deformation is necessary to form these additional, probably raw nuclei.

References

[1] B. Wunderlich, E.A. Turi (Ed.), Thermal Characterization of Polymeric Materials, second ed., 1997, p. 205 (Chapter 2).
[2] K. Nakagawa, Y. Ishida, J. Polym. Sci.:Polym. Phys. Ed. 11 (1973) 2153.
[3] A.-G. Leray, L. Judovits, in: Proceedings of the 25th NATAS Conference, 1997, p. 72.
[4] L. Judovits, S.M. Dounce, in: Proceedings of the 26th NATAS Conference, 1998, p. 578.
[5] J.D. Menczel, M. Jaffe, W.E. Bessey, Films, E.A. Turi (Ed.), Thermal Characterization of Polymeric Materials, second ed., 1997, p. 1956.
[6] S. Weinhold, M.H. Litt, J.B. Lando, J. Appl. Phys. 51 (10) (1980) 5145.
[7] B. Wunderlich, Macromolecular Physics, vol. 3, Academic Press, New York, 1980.