

D.m.a. and d.s.c, investigations of the β transition of poly(vinylidene fluoride)

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Abstract

The origin of the β transition in poly(vinylidene fluoride) (PVDF) is still a pending question. This transition has been studied by dynamic mechanical analysis (d.m.a.) and differential scanning calorimetry (d.s.c.) in dependence on sample annealing and dilution with ϵ -caprolactam (CPL). The β transition temperature is increased upon annealing and thus influenced by the polymer crystallization. Upon addition of CPL, there is no systematic shift in the β transition temperature, in contrast to the PVDF crystallinity that increases steadily. A shoulder on the low temperature side of the β transition peak is also observed as a result of annealing. It is shifted to lower temperatures when CPL is added, consistently with a glass transition. It thus appears that the so-called β -transition is sensitive to the amorphous material, but in a close relationship with the polymer crystallization. Comparison of the observations by d.s.c. and d.m.a. shows that the broad transition observed for the unannealed samples would result from the overlap of two transitions: the glass transition of the unconstrained amorphous phase and the glass transition of chains constrained by the crystalline phase. This situation can account for the complex dependence of the β transition on the polymer history.

Keywords: β transition; poly(vinylidene fluoride); poly(vinylidene fluoride)/ ϵ -caprolactam blends

INTRODUCTION

The transition behaviour of semicrystalline poly(vinylidene fluoride) (PVDF) has been extensively studied [1-10]. In addition to melting, PVDF usually exhibits at least two transitions that have been assigned to the α -transition and the β -transition, respectively, as the temperature is increased. It is accepted that the α -transition stems from molecular motions in the PVDF crystalline region [6-7]. However, two different mechanisms have been proposed for the β -transition.

Yano et al. [2-5] have concluded that the β -transition arises from the micro-Brownian motion of the main chain in the amorphous region, and thus is characteristic of the PVDF glass transition.

Paul et al [7] have reported that the β -transition temperature in miscible PVDF/poly(methyl methacrylate) (PMMA) blends only slightly changes when less than 40wt% PMMA is added. This observation disagrees with the expected decrease in the glass transition temperature upon addition of increasing amounts of miscible component. It is the reason why Hahn et al. [8-10] have proposed that the β -transition is more likely associated with a crystal—amorphous interphase. It is worth recalling that the PVDF/PMMA pair is completely miscible in the melt, at least below the lower critical solution temperature (LCST)¹¹. Expectedly, crystallization of PVDF from these monophasic blends depends on blend composition and cooling rate [5,7,12-15]. Two different models have been proposed to describe the phase morphology of the PVDF/miscible polymer blends. The first model is a three-phase model composed of crystalline lamellae, crystal—amorphous interphase, and mixed amorphous phase [10]. This model has emerged from analysis by small angle X-ray scattering. The β -transition is proposed to be characteristic of the crystal-amorphous interphase. The second model relies upon the coexistence of mixed amorphous phase, imperfect crystalline region, and nearly pure semicrystalline PVDF domains consisting of crystalline and amorphous phases [6]. This model rests on d.m.a. and d.s.c. The β -transition is then assigned to the PVDF amorphous region [6]. Recently, Martinez-Salazar et al. [13-14] have reported that the glass transition temperature-composition relationship for the completely amorphous PVDF/PMMA blends could be fitted by the Gordon-Taylor equation [16]. This result is in accord with previous observations by Hirata and Kotaka [6], at least until the PVDF content does not exceed 60wt%. Indeed, beyond this composition, PVDF starts to crystallize and discrepancy is reported to occur.

Flory was the first to propose that a crystal-amorphous phase had an important role in semicrystalline polymers [17]. Recent studies have suggested that the effect of crystallization on the transition of the amorphous phase was amplified by the chain stiffness. A fraction of rigid amorphous component as high as 70% has been accordingly calculated for stiff polymers, i.e. poly(oxy-2,6-dimethyl-1,4-phenylene) (PPO) [18], poly(thio-1,4-phenylene sulfide) (PPS) [19], poly(ether ether ketone) (PEEK) [20-21], and poly(ethylene terephthalate) (PET) [21]. The crystal-amorphous interfacial fraction in flexible polymers, e.g. polyethylene (PE) and PVDF, is comparatively small, e.g. less than 10% in linear PE [22-24]. However, according to Loufakis and Wunderlich [25] there would be

no detectable rigid amorphous component above the PVDF glass transition. In case of assignment of the β -transition to constrained chains in the amorphous region, this would mean that the whole amorphous phase (ca. 50%) would be constrained. So, the origin of the β -transition in PVDF remains an open question. In order to clear up that problem, the effect of annealing on the β -transition has been investigated for both neat PVDF and PVDF previously diluted with a soluble low molecular weight component, i.e. ϵ -caprolactam (CPL). These treatments are supposed to alter the chain mobility in the non-crystalline phase. A possible correlation between the imposed modifications and the β -transition has been searched for by d.m.a, and d.s.c.

EXPERIMENTAL

Poly(vinylidene fluoride) was Solef 1008 from Solvay Co., Brussels, and ϵ -caprolactam was purchased from Merck-Schuchardt (Darmstadt).

The PVDF/CPL mixtures were prepared in a Brabender internal mixer at 170°C for 30min, compression-moulded into 1 mm thick sheets at 200°C for 3 min, and finally quenched to room temperature. Although pure PVDF was annealed at 125°C for 2 days, the PVDF/CPL mixtures were annealed at 75°C for 1 day, in order to restrict the loss of CPL by vaporization.

Dynamic mechanical measurements were conducted with a Du Pont 983 Dynamic Mechanical Analyzer (DMA) at an oscillation amplitude of 0.2 mm (peak to peak), a heating rate of 5°C min⁻¹ and a 1 Hz frequency.

The melting behaviour of PVDF and PVDF/CPL mixtures was studied with a Du Pont 910 Differential Scanning Calorimeter (d.s.c.) under N₂ atmosphere, at a heating rate of 20°C min⁻¹.

The final composition of the PVDF/CPL mixtures was calculated from the original composition and the CPL weight loss determined for reference samples treated under the same moulding and annealing conditions as reported above.

RESULTS

Figure 1 shows the d.s.c. thermograms for unannealed CPL, PVDF and two PVDF/CPL mixtures. The melting temperature of pure PVDF at 177°C is shifted to a lower temperature upon the addition of increasing amounts of CPL. The melting point depression of PVDF is the signature of specific intermolecular interactions with CPL [26]. The melting temperature of pure CPL at 75°C goes unobserved in mixtures with PVDF (8 and 13 wt% CPL), which indicates that CPL is molecularly dissolved into PVDF, and has no opportunity to crystallize.

Furthermore, the addition of CPL is responsible for an increase in the heat of fusion of PVDF from 43 to 51 J g⁻¹. Thus, the PVDF crystallization is enhanced by dilution with small amounts of CPL. The crystallinity degree, χ , has been calculated as

$$\chi = \frac{\Delta H_m}{W\Delta H_m^0} \times 100(\%) \quad (1)$$

where ΔH_m is the experimental heat of fusion, and W is the PVDF content in the PVDF/CPL mixtures.

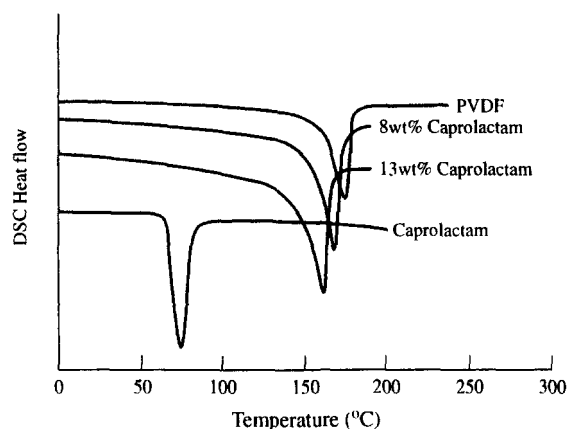


Figure 1 D.s.c. traces for PVDF, CPL and PVDF/CPL mixtures

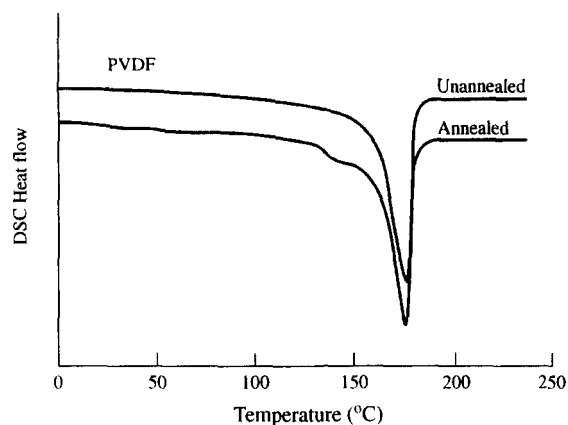


Figure 2 D.s.c. traces for neat PVDF, before and after annealing

A value of 90.4 Jg^{-1} has been used for ΔH_m^0 in agreement with a previous study [26], that has shown that PVDF crystallized under large supercooling conditions essentially form α -crystals of this ΔH_m^0 value [27]. According to equation (1), the crystallinity degree of PVDF is increased from 48 up to 53 and 56% upon the addition of 8 and 13 wt% CPL, respectively. Thus, CPL has a favourable effect on the extent of the PVDF crystallization, although at the expense of the crystal stability as shown by the significant decrease in the melting temperature.

Figures 2-4 illustrate the effect of annealing on the d.s.c. traces for PVDF (annealed at 125°C for 2 days) and PVDF/CPL mixtures (annealed at 75°C for 1 day). The loss of CPL during annealing is less than 0.2 wt%. Upon annealing of the PVDF samples, a shoulder appears on the low temperature side of the d.s.c. endotherms at ca. 130°C , whereas the main peak persists at 177°C (Figure 2) and the heat of fusion increases from 43 to 54 Jg^{-1} . The same general behaviour is observed for the CPL containing samples (Figures 3 and 4). Nevertheless, the additional shoulder is observed at decreasing temperatures, i.e. 125 and 90°C , when PVDF is added with 8 and 13 wt% CPL, respectively.

A shoulder on the low temperature side of the main melting peak has already been reported in the scientific literature [28-29] and explained by the melting of crystals formed during cooling of the melt and recrystallization upon heating.

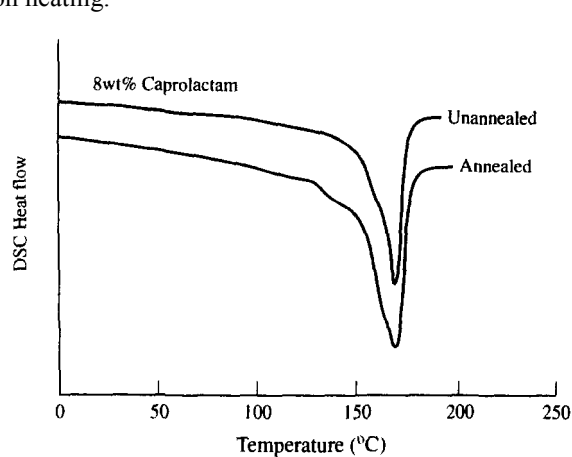


Figure 3 D.s.c. traces for PVDF diluted by 8 wt% CPL, before and after annealing

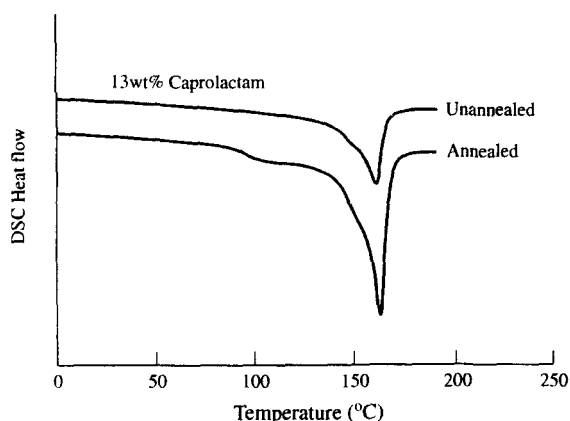


Figure 4 D.s.c. traces for PVDF diluted by 13 wt% CPL, before and after annealing

This explanation does not hold for the data in this work, since the shoulder is observed as a result of annealing. It has to be assigned to the melting of material that has crystallized during annealing. The independence of the main melting endotherm of PVDF upon annealing indicates that the crystal form is not changed into other known forms (e.g. γ and γ') of a different melting temperature [28]. Finally, there is no indication that CPL has crystallized during this thermal treatment.

Crystallinity of PVDF is increased upon annealing not only in the case of neat PVDF but also for mixtures with 8 and 13 wt% CPL, respectively (Table 1).

The thermal transitions that occur in PVDF have also been observed by d.m.a., as shown in Figure 5. Pure PVDF shows a broad β -transition from ca. -55°C up to 0°C with a maximum at ca. -27°C . This observation is in good agreement with data reported by Mijovic et al. [17] under similar testing conditions, i.e. maximum at -30°C and a transition temperature range extending from -55°C up to -15°C . Figure 5 also shows a broad α L-transition from 50 up to 150°C . The intensity of the β loss peak increases with the CPL concentration, whereas no systematic shift in the temperature at the peak maximum is observed. There is indeed an apparent increase in this temperature when 8 wt% CPL is added, compared to a decrease for 13 wt% CPL (Figure 5 and Table 1). Moreover, the β loss peak becomes broader as the CPL content is increased, as result of a concomitant increase of the upper limit and decrease of the lower limit.

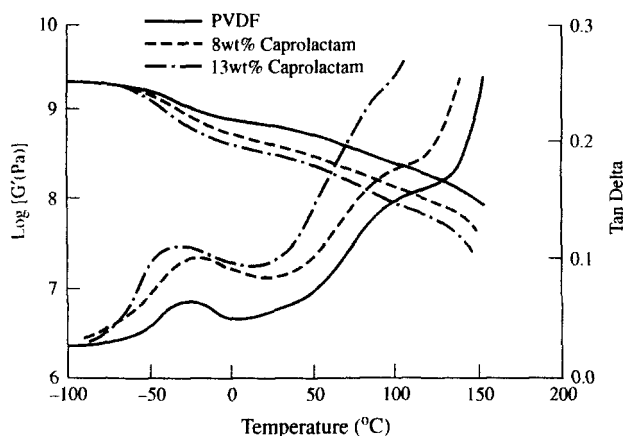


Figure 5 Storage modulus and $\tan \delta$ vs. temperature for PVDF and PVDF/CPL mixtures

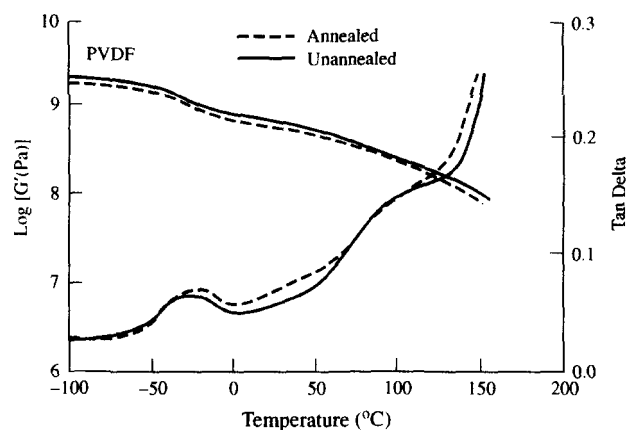


Figure 6 Storage modulus and $\tan \delta$ vs. temperature for neat PVDF, before and after annealing (125°C for 2 days)

Figures 6-8 illustrate the annealing dependence of the β -transition. This transition is increased by 8°C and it becomes asymmetric when PVDF is annealed for 2 days at 125°C (Figure 6). In contrast, Mijovic et al [30] have reported that annealing has no effect on the β -transition, but for a much shorter annealing time (i.e. 30 min) [17]. The increase in the β -transition temperature is 11°C (Figure 7) and 16°C (Figure 8), when PVDF is added with 8 and 13 wt% CPL, respectively. The addition of CPL is also responsible for an additional although faint shoulder at -50°C (8wt% CPL) and -75°C (13wt% CPL).

DISCUSSION

Effect of CPL on the so-called β -transition of PVDF is quite different from the effect reported in the scientific literature for the addition of poly(methyl methacrylate) (PMMA) to PVDF [7,8]. Although only the intensity of the β peak is increased with the PMMA content, addition of CPL to PVDF deeply changes both the intensity and the peak position.

If the β -transition is a glass transition, then the transition temperature should be systematically shifted toward lower temperatures as CPL is added, which is not observed (Table 1). The effect of annealing is a systematic shift of the β -transition toward higher temperatures, which is quite inconsistent with a glass transition (Table 1).

Table 1 Crystallization and relaxation in PVDF and PVDF/CPL mixtures

Composition	Melting point, $^{\circ}\text{C}$		β transition temperature, $^{\circ}\text{C}$		Heat of fusion ^a , Jg^{-1}		Crystallinity, %	
	Unannealed	Annealed ^b	Unannealed	Annealed ^b	Unannealed	Annealed ^b	Unannealed	Annealed ^b
Pure PVDF	177	177	-27	-19	43	54	48	60
8wt% CPL	170	169	-21	-10	48	54	53	60
13wt% CPL	164	163	-35	-19	51	70	56	77

^a Calculated by $\Delta H_m/W$, where ΔH_m is the experimental value, W the PVDF content in the PVDF/CPL mixtures ^b PVDF was annealed for 2 days at 125°C , whereas PVDF/CPL blends were annealed for 1 day at 75°C

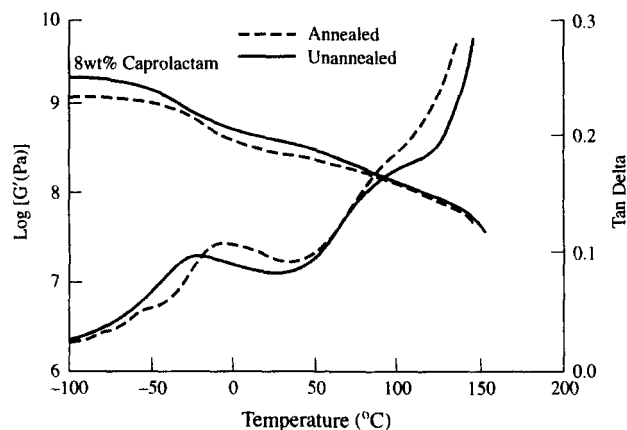


Figure 7 Storage modulus and $\tan \delta$ vs. temperature for PVDF diluted by 8 wt% CPL, before and after annealing (75°C for 1 day)

The invariance of the β -transition temperature over a large composition range from pure PVDF to blends containing 60wt% PMMA and the disappearance of this transition in completely amorphous blends led Hahn et al.[8-10] to assign the β -transition to a crystal-amorphous interphase. If it is so, the independence of the transition characteristic of the interphase means that the miscible PMMA is excluded from that particular phase. The experimental data reported in this work do not support the β -transition assignment proposed by these authors. Indeed, CPL appears to have two antagonistic effects on the chain mobility. As a diluent, CPL must increase the free volume of the amorphous PVDF and thus the segmental mobility. This effect would dominate in the PVDF/CPL blends containing 13 wt% CPL, that shows a clear shift of the β -transition toward lower temperatures compared to neat PVDF. As a second effect, CPL enhances the PVDF crystallinity (Table 1), which is expected to increase the relative volume of the PVDF chain segments constrained in the crystal-amorphous interphase, and possibly to strengthen these constraints. This effect would prevail when PVDF is diluted by only 8 wt% CPL, since the temperature at the peak maximum is then shifted toward higher temperatures. Nevertheless, the lower limit of this transition is simultaneously shifted toward lower temperatures which is consistent with dilution of the amorphous phase.

The effect of annealing on the β -transition temperature may not be dissociated from the effect on the PVDF crystallization. As proposed above, an increase in crystallinity creates additional constraints on the molecular mobility in the amorphous region, which may account for a shift of the β -transition toward higher temperatures. The magnitude of this effect must therefore depend on the intrinsic chain mobility and the annealing conditions, which are different for neat PVDF and PVDF/CPL blends.

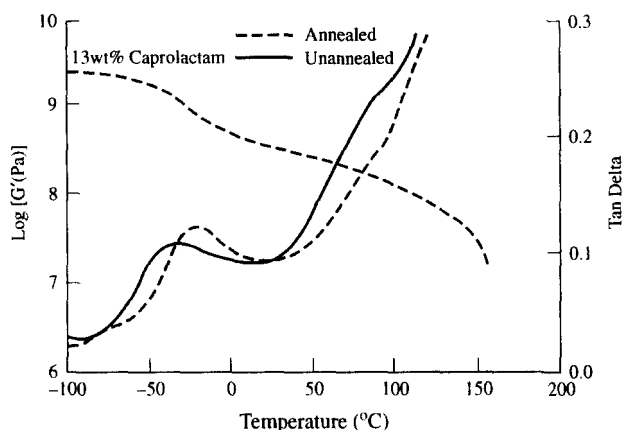


Figure 8 Storage modulus and $\tan \delta$ vs. temperature for PVDF diluted by 13 wt% CPL, before and after annealing (75°C for 1 day)

It is the reason why, shift in the β -relaxation for PVDF (Figure 6) may not be directly compared to the observations for the PVDF/CPL blends (Figures 7 and 8). Broadness of the β -transition of the unannealed PVDF has been proposed to reflect a large spectrum of constraints on the molecular mobility in the amorphous phase[31-32]. Figure 6 shows that annealing increases the asymmetry of the β -transition peak, to the point where it appears now to result from the overlap of two contributions tentatively assigned to the constrained chain segments (at ca. -20°C)

and to the unperturbed amorphous phase (at ca. -35°C). This lower transition should be the glass transition in agreement with T_g reported for the completely amorphous PVDF [13-14]. This observation would actually reconcile the two standpoints usually proposed for the origin of the β -transition. The main effect of annealing on the β -transition of PVDF seems to be a change in the relative importance of the two underlying phenomena, which seem to occur at an unchanged temperature. The annealing would favour the development of the interphase at the expense of the amorphous phase.

When the CPL is added, the β -transition becomes much broader as result of an extension toward both lower and higher temperatures (Figure 5). This observation is consistent with the explanation proposed above for the β -relaxation. Indeed, if the lower temperature contribution is actually a glass transition, it must be shifted toward lower temperatures upon dilution by CPL, as it is observed. Since the addition of CPL increases the crystallinity degree of PVDF (Table 1), it is not surprising that constraints on chain segments at the interphase are increased in volume and magnitude as well, so that partial shift toward higher temperatures for the interphase transition may be accounted for. The main effect of the annealing of the PVDF/CPL blends is to separate completely the two transitions (Figures 7 and 8). The glass transition is observed as a faint shoulder at decreasing temperatures when the amount of CPL is increased (-50°C for 8 wt% CPL and -75°C for 13 wt% CPL). In parallel, the interphase transition is shifted toward higher temperatures in a qualitative agreement with the increased crystallinity upon annealing (Table 1). Thus, this study leads to the conclusion that the phase morphology of pure PVDF basically consists of a crystalline phase, an amorphous phase, and crystal-amorphous interphase. The relative importance of these phases strongly depends on annealing and addition of a diluent.

CONCLUSION

The β -transition of PVDF strongly depends on the addition of a low molecular weight diluent (CPL) and on annealing, in such a way that this relaxation appears to be complex and result from at least two contributions: transition of a crystal—amorphous interphase observed as a relatively intense peak and a transition assigned to the non-constrained segments in the amorphous phase and visible as a weakly intense shoulder. These two transitions are very broad, which reveals a large spectrum of conformation and constraints for the chain segments that have not crystallized. This is clear in case of Figure 7 for the annealed PVDF previously diluted by 8wt% CPL. The temperature of -10°C reported in Table 1 for the higher temperature (and major) contribution is accordingly quite uncertain.

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