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Polymer 42 (2001) 8799–8806

polymer

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Impact of nucleating agents of PVDF on the crystallization of PVDF/PMMA blends

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Received 20 December 2000; received in revised form 9 May 2001; accepted 11 May 2001

Abstract

The enhanced nucleation of poly(vinylidene fluoride) in its blends with PMMA, and its impact on the crystallization kinetics and overall crystallinity of the PVDF/PMMA blends are investigated. Since in the blends the growth rates are significantly slowed down and spread over a wider crystallization range, nucleation has a significant impact on the crystallization process. In particular, crystallization peaks are shifted upwards by up to 30°C for nucleated samples. These higher crystallization temperatures make it possible to reach, upon cooling, high degrees of crystallinity for PVDF/PMMA compositions down to 50/50, i.e. for blends which remain amorphous when not nucleated. © 2001 Published by Elsevier Science Ltd.

Keywords: Poly(vinylidene fluoride); Enhanced nucleation; PVDF/PMMA blends

1. Introduction

PVDF is widely used for its mechanical properties, chemical and weathering resistance and processing properties [1]. The major application of PVDF is in external architectural coatings (paints) [2]. In order to improve performance and reduce costs, PVDF is often blended with miscible acrylic polymers, which act as binders and help in the dispersion of pigments [3]. For PVDF/PMMA blends, DSC curves show a single glass transition and a depression of the melting point for PVDF compositions above 50% [4–10]. However, the thermal history of the sample has important bearings on the compatibility characteristics of the PVDF/PMMA system: for example, a single glass transition is observed only for completely amorphous blends.

For coatings formulations, earlier investigations have shown that a PVDF crystalline phase must be present, which implies that PVDF contents must be higher than 50%. A composition containing 70% of PVDF and 30% of PMMA (70/30) was found to have optimal physical and optical properties: gloss, hardness and solvent resistance. For PVDF contents higher than 80%, the hardness and flexural modulus decrease. Hence, the properties of PVDF/PMMA blends are optimal only in a quite narrow window of PVDF contents and are, in ultimate analysis, *highly dependent on the PVDF crystallinity*.

Design of optimal crystalline-amorphous blend compositions is therefore a major challenge, especially when considering that amorphous polymers may have a major *detrimental* impact on the crystallization rates of their crystalline partners. As an illustration, addition of only a small amount (0.5–5%, i.e. one to two orders of magnitude less than in the present PVDF-based systems) of poly(vinylbutyral) to linear polyesters (e.g. poly(ϵ-caprolactone)) reduces drastically the growth rates and reduces by several orders of magnitude the concentration of active, heterogeneous nuclei [12]. Similar observations have been reported for the PVDF–PMMA blends under investigation: sepiolite (a hydrated magnesium silicate) is a nucleating agent for PVDF, but this nucleating effect vanishes in PVDF/PMMA blends [13].

Building on the experience gained while investigating nucleating agents (NA) of PVDF reported in the companion paper [14], we present here the impact of NA (in particular PTFE) on the crystallization behavior of PVDF when blended with PMMA. We show that the kinetics of PVDF crystallization and the ultimate crystallinity of PVDF/PMMA samples are significantly enhanced by the use of NA. As a consequence, PVDF/PMMA blends with higher PMMA contents can be used as coatings without loss of physical and optical properties.

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PII: S0032-3861(01)00349-4

2. Materials and experimental techniques

2.1. Materials

The experiments are performed with the three different grades of commercial latexes of PVDF produced by ELF-Atochem and used in the companion paper: Kynar 500, 740 and 1000.

One PMMA homopolymer and two copolymers of methyl–methacrylate (MMA) and ethyl-acrylate (EA) (copolyMMA–EA) were produced by batch emulsion polymerization at the ELF-Atochem Research Center in Lacq (GRL). The two copolymers have identical compositions (90/10), slightly different molecular weights (5.65 and 10.7×10^5), and identical T_gs: 92°C. The T_g of PMMA (M_w 5.5×10^5) is higher: 115°C

The same commercially available PTFE latex and flavanthrone sample as used in the companion paper [14] were used as NA.

2.2. Sample preparation

PVDF/PMMA blends of various compositions which include PTFE as an additive are produced by slowly stirring the corresponding mixtures of latexes, which are then coagulated by freezing and dried, as described in the companion paper [14]. The PVDF/PMMA composition can be checked by thermogravimetry analysis of the dried powder, since PMMA decomposes at temperatures 100°C lower than for PVDF (350 versus 450°C).

A major difficulty encountered in the sample preparation deals with the removal of emulsifiers used in the polymerization process. As indicated in the companion paper, *three* washings are sufficient for pure PVDF coagulates: monitoring by conductimetry the emulsifier concentration in the water used for washing indicates that, as a result of a 10-fold decrease, the conductivity reaches that of pure water. Similar monitoring procedures for PVDF/PMMA blends indicate that the conductivity drops to reasonable values only after *nine* (!) washings. However, parallel thermogravimetry analyses show that these repeated washings have an undesired side effect, namely an excessive draining-off of PMMA. In view of these difficulties, the washing protocol used for pure PVDF was applied to the PVDF/PMMA blends as well, keeping in mind however that only three washings steps leave significant amounts of emulsifier in the samples. Also, due to the important draining-off of PMMA, blends with PMMA contents in excess of 60% could not be produced.

2.3. Experimental techniques

All crystallization experiments are performed in a Perkin–Elmer DSC4 instrument fitted with a Thermal Analysis Data Station (TADS), using as a rule heating and cooling rates of 10 K/min. Melting and crystallization temperatures are taken at the extremum of the peak. Glass transition temperatures (T_g) are determined in a Perkin–Elmer DSC7 equipped with a liquid nitrogen cooling tank. T_gs are measured during the second heating from −110 to +200°C at a 20 K/min rate.

3. Results

3.1. PVDF crystallized in the presence of PMMA and acrylic polymers

3.1.1. Glass transitions and melting temperature

Variation of glass transition temperatures and melting points with composition is a convenient indicator in the analysis of the blend compatibility of semi-crystalline and amorphous polymers — in the present case PVDF/PMMA. The resulting 'phase diagram' (Fig. 1) displays many features known from earlier studies [4–11], namely:

- for low PVDF concentrations ($< \approx 40$–50%), and even though only few data points are available (owing to the experimental difficulties described above) T_g decreases smoothly with PVDF concentration. This variation follows neither the standard Fox law (which rests on the addition of free volumes) nor that of blends (for

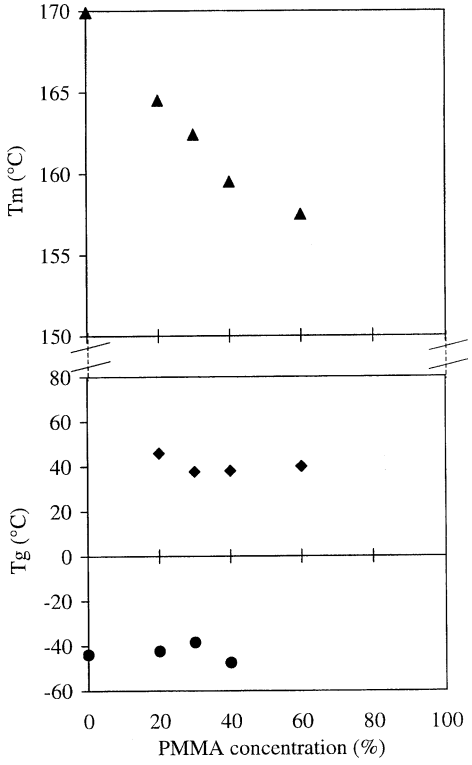

Fig. 1. Glass transition temperatures and melting temperatures (triangles) recorded for PVDF/PMMA blends as a function of PMMA content. Note that two glass transition temperatures are recorded for PMMA concentrations ranging from 20 to 40%. They correspond to amorphous PVDF (circles, near −40°C), and to the PVDF/PMMA blend, probably segregated in the fold surfaces of the lamellae (squares, near 40°C). PVDF sample: Kynar 740.

which T_g should be a weight average of the T_gs of the two components).

- above the 50/50 threshold composition, two features are noteworthy (i) the T_g of the blends level off at 40–50°C and (ii) at the same time, a low temperature T_g appears near −45 to −50°C which is the T_g of pure PVDF. This behavior indicates that for high PVDF concentrations, there are three different components: (a) a crystalline PVDF component which does not contribute to the overall T_g depression; (b) an amorphous phase of PVDF with a T_g characteristic of pure PVDF, suggesting that crystallization of PVDF generates also 'pure' amorphous PVDF domains (i.e. with no PMMA). This 'amorphous' PVDF phase has been associated with the fold surface of PVDF lamellae, which cannot include PMMA — if only for steric reasons (fold crowding at the lamellar surface), and which may be viewed as an interphase between PVDF crystallites and the amorphous PVDF/PMMA blend; (c) the latter PVDF/PMMA amorphous blend phase; its T_g remains constant (40°C), which in turn suggests a near constant phase composition, at a value close to 40% PVDF.

The variation of melting points with PMMA content displayed in Fig. 1 indicates that, in agreement with literature data, the melting point decreases by 12°C when the PMMA content increases from 0 to 60%. This behavior has been explained [10] in terms of the theory of melting point depression of a polymer-diluent system, as proposed by Flory and Huggins, and later elaborated on by Chow [9], who has included the effect of crystalline morphology in his analysis.

3.1.2. Overall crystallinities

The above variations of transition temperatures provide only a partial view of the processes which determine the crystallization and crystallization range of PVDF/PMMA blends. An analysis of the *crystallinities* reached after different thermal histories turns out to be more telling. These effects are investigated by examining the behavior of:

- blends of the sole Kynar 740 with PMMA over a wide compositional range and
- blends of Kynar 740 and Kynar 500 with the three different acrylic polymers but only for a fixed 70/30 composition.

Kynar 740/PMMA blends at various compositions. The crystallization behavior of Kynar 740 in blends with various ratios of PMMA is displayed in Fig. 2. Analysis of these data indicates that:

- melting temperatures (T_m) (cf. Fig. 1) and crystallization temperatures (T_c) (Fig. 2) decrease steadily with increasing PMMA content, as already indicated.
- the overall crystallinity (measured by ΔH_c) decreases even more dramatically: the 40/60 blend does not crystallize, at least for the thermal history used (cooling at 10 K/min). Note that the crystallinities displayed in Fig. 2 have been scaled to the amount of PVDF present in the sample by proportioning the measured ΔH_c values to an assumed ΔH_m of 25 cal/g for 100% crystalline PVDF.

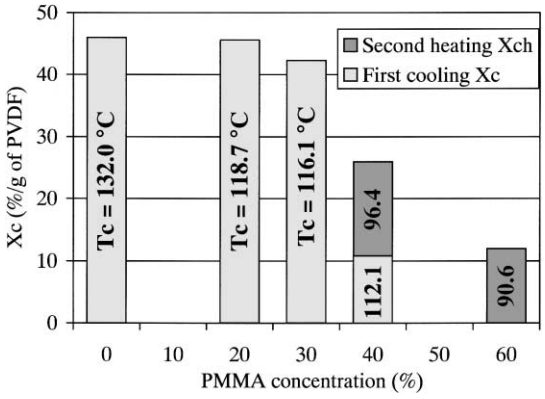

Fig. 2. Crystallinities of Kynar 740/PMMA blends reached after cooling from T_m and additional crystallinities generated upon heating. The crystallinities are represented by the boxes, with the crystallization peaks indicated (in DSC, with heating and cooling rates of 10 K/min). Initial crystallinities reached on cooling from the melt are shown in light grey. For PMMA compositions up to 30%, no additional crystallinity is induced on reheating the sample. To the contrary, for blends with 40–60% PMMA, additional crystallization takes place in the 90–97°C range upon reheating the sample. The extra crystallinity (shown in dark gray) *adds up* to that produced on cooling for the 40% PMMA blend, or even transforms an amorphous blend with 60% PMMA into a semi-crystalline material (with 12% crystallinity). In this critical composition range, the total crystallinities, and (for the 60% composition) even the physical state of the blend are therefore highly dependent on thermal history.

- Three domains can be recognized in Fig. 2:
  - for *high PMMA contents* (or PVDF concentrations ≤40%), no crystallization takes place,
  - for *low PMMA contents* (blends including at most 30% of PMMA), the crystallinity of PVDF remains constant at about 45%. This 'ultimate' crystallinity is reached during the first cooling, which displays a single, conventional crystallization peak (Fig. 3 (1) for a 70/30 composition. The corresponding melting curve is shown in Fig. 3 (2)).
  - an interesting *transition composition range* exists in the middle of the phase diagram, from 60 to 40% PVDF. In this composition range indeed, *the final crystallinity can be monitored to a significant extent by appropriate thermal histories*. On cooling, the crystallinity is very low: about 10% for 60% PVDF, and zero% for 40% PVDF (Fig. 2). However, these crystallinities *are not the ultimate achievable ones*. The PVDF component in the blend can indeed *reach higher crystallinities*, as illustrated by the impact of *reheating* the samples: additional crystallization takes place in the 60 and 40% PVDF samples, for which crystallinities *increase* by 16 and 12%, respectively. This additional crystallization makes it possible to

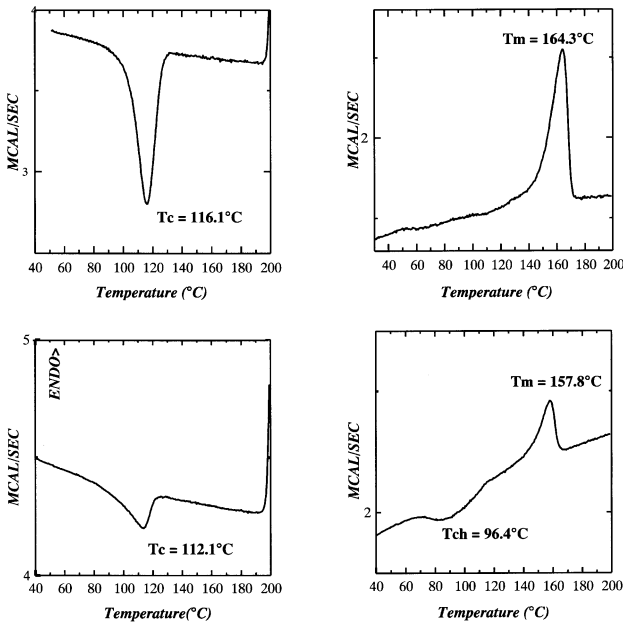

Fig. 3. Crystallization and melting curves for PVDF/PMMA blends with 70/30 (parts 1 and 2, top) and 60/40 (parts 3 and 4, bottom) compositions illustrating the crystallization processes of Fig. 2. Parts 1 and 3: crystallization peak on cooling from the melt; parts 2 and 4: DSC traces on reheating, with evidence for an additional crystallization peak (T_{ch}) for the 60/40 sample (part 4).

reach ultimate crystallinities of about 26 and 12%, respectively (for heating rates of 10 K/min). While these crystallinities remain low when compared to blends richer in PVDF, they are significantly higher than after the sole cooling process. This additional crystallization is manifested in the DSC thermogram by a very broad peak, the maximum of which is located $\approx$ 15°C below that observed on cooling (96 versus 112°C, for the 60/40 blend displaying the two crystallization processes most prominently). This original behavior is summarized and illustrated in the cooling and reheating DSC curves displayed in Fig. 3 (3) and (4).

The above behavior indicates that in the critical middle composition range, *the crystallinities reached on cooling are limited by the crystallization kinetics: nucleation and/or growth*. The observed behavior is indeed typical of polymers (iPS, PET, etc.) for which growth rates are so slow that they can be brought to a glassy state upon rapid quenching. These results also indicate (as also illustrated by the Wang–Nishi data [11]) that the $\approx$60/40 composition corresponds to a threshold in the crystallization behavior: on cooling, as a result of sparse nucleation and limited growth rates, the spherulites do not 'fill in' the sample. The crystallized blend is therefore made of spherulites dispersed in an amorphous matrix. Excursion to low temperatures (after crystallization has stopped) generates in the amorphous matrix additional nuclei, which in turn induce additional crystallization on heating, once 'sufficient' growth rates are reached in the low temperature part of the log $G = f(T)$ curve. As a consequence, the second T_c peak (T_{ch}, for T_C on heating) is always located at temperatures lower than T_c on cooling — a standard feature in the crystallization of iPS or PET.

Essentially the same reasoning applies for the 40/60 sample, with however the significant difference that crystallization upon cooling is altogether suppressed (Fig. 2).

Blends of different PVDF and acrylic polymers.

Data on transition temperatures as well as on crystallinities have been collected for various blend *components* and blend *compositions* using the procedures described above.

To evaluate the impact of *blend components*, a fixed 70/30 PVDF/acrylic polymer ratio has been used, while varying the Kynar samples and acrylic polymers. The corresponding results are listed in Table 1 and indicate that:

- the Kynar 740 crystallinities are not affected by the presence of the amorphous polymer: they are comparable to those of the homopolymer,
- the three 70/30 blends based on Kynar 500 exhibit the complicated behavior (with incomplete crystallization on cooling (T_{cc} peak) and additional crystallization on heating (T_{ch} peak)) analyzed in detail for the 60/40 Kynar 740/PMMA blend (cf. above and Fig. 3). This shift to higher PVDF composition is due to the slower growth rates (G) of Kynar 500, which themselves reflect the higher concentration of head to head defects [1].

Table 1
Crystallization temperatures, crystallinities and melting temperatures for 70/30 blends of PVDF (Kynar 740 and 500) and various acrylic polymers (indicated): crystallization peaks (T_c) and crystallinities on first cooling (T_c and X_c), on reheating (T_{ch}, X_{ch}), total crystallinities ($X_c + X_{ch}$) and melting temperatures (T_m)

Blend composition	T_c (°C)	X_c (%)	T_{ch} (°C)	X_{ch} (%)	$X_c + X_{ch}$ (%)	T_m (°C)
70% KYNAR 740						
+P(MMA/EA) 1	113.3	42.9	–	–	42.9	162.4
+P(MMA/EA) 2	109.2	40.0	–	–	40.0	162.0
+PMMA	116.1	42.3	–	–	42.3	164.3
70% KYNAR 500						
+P(MMA/EA) 1	87.0	21.1	47.9	3.4	24.5	154.9
+P(MMA/EA) 2	81.4	16.6	55.1	6.3	22.9	154.3
+PMMA	95.7	9.1	66.3	12.0	21.1	154.1

- Furthermore, it appears that, as a rule, the gap between T_{cc} and T_{ch} (crystallization peaks on cooling and on reheating, respectively) is more important for the low T_g or low molecular weight acrylic polymers, and that both T_{cc} and T_{ch} are shifted (by 12°C for the mid-range point) to higher values when the higher T_g PMMA is involved in the blend.

To summarize, the phase transitions determined for the PVDF/PMMA blends are in agreement with literature data [4–11]. Under the experimental conditions used, (i.e. for relatively slow cooling rates) PVDF crystallizes, at least partly, and displays a progressive decrease of its melting temperature with increasing PMMA concentration. The remaining PVDF/PMMA blend is amorphous, and has a near constant T_g, i.e. composition. Also, above the 50/50 threshold composition, an amorphous PVDF component (probably located at the lamellar surface) shows up through a T_g at −50°C. At lower concentrations of PVDF, no crystallization takes place, and only one T_g is measured. This behavior is found in all the blends considered in this study. Only small variations are observed, which can be linked with the molecular and physical characteristics of the blend components.

The above results indicate that the phase transitions of the PVDF/PMMA (or PVDF/P(MMA-EA)) blends are significantly affected by the crystallization of the PVDF component. This conclusion is best illustrated by the behavior of blends with 'intermediate' PVDF/PMMA compositions, for which crystallization taking place on cooling is *kinetically* limited. The mere observation of additional crystallization on heating indicates that, *on cooling, the 'spontaneous' nucleation and growth processes do not 'exhaust' the full crystallization potential of the blends*. As illustrated in the next section, *monitoring of the nucleation process* affects significantly the crystallization of PVDF in these blends.

3.2. Self-nucleation and heterogeneous nucleation of PVDF in PVDF/PMMA blends

As outlined in the companion paper [14], the procedure of self-nucleation can be used to 'calibrate' the efficiency of nucleating additives. It remains therefore an essential initial step in the investigation of nucleating additives for any crystallizable polymer system, including the present PVDF/PMMA blends. This 'calibration' was performed for the 70/30 composition only because the procedure is lengthy, and related samples display comparable trends. The impact of nucleation by addition of PTFE has been evaluated over a larger compositional range.

3.2.1. Self-nucleation and PTFE nucleation for 70/30 PVDF/PMMA blends

Self-nucleation experiments for the Kynar 740/PMMA 70/30 blend are performed using the methodology used for PVDF in the previous paper [14]. The limits of the efficiency scale are $T_{c1} = 116.1$°C and $T_{c2} = 138.7$°C. The lower T_{c1} corresponds to a non-nucleated sample (or more precisely, a sample nucleated only with residual heterogeneous nuclei). The higher T_{c2} corresponds to an ideally nucleated sample. Comparison with data for pure PVDF reveals two main features:

- The range of T_c of the blends is very broad: 22.6°C (13.8°C only for pure PVDF). This ΔT_c range almost compares with the largest one observed so far (≈ 25°C for isotactic polypropylene).
- The crystallization range is shifted to significantly lower temperatures than for pure PVDF: about 16°C. T_{c1} is 116.1°C versus 132°C for PVDF, indicating a significant slow-down of the overall crystallization rate, i.e. of the combination of growth rates and nucleation densities. As examined now, this shift of the crystallization range can be limited to a significant extent by incorporation of NA in the blends.

3.2.2. Addition of PTFE as a 'foreign' nucleation agent

The impact of PTFE as a nucleating agent has been considered for:

- blends with a *fixed composition* (70/30) but *different components*: various grades of PVDF and acrylic polymers have been tested.
- blends with *fixed components* (Kynar 740 and PMMA) but *different compositions* (ranging from 40 to 100% PVDF).

In both sets of experiments, the Kynar 740/PMMA 70/30 blend investigated in the self-seeding test provides a convenient calibration for the nucleating agent efficiency.

Blends with a fixed 70/30 composition

PTFE has been added in various concentrations to:

- Kynar 740 blended with PMMA and with a copolymer PMMA/EA (with c_{PTFE} ranging from 0.1 to 1.5% of the weight fraction of PVDF) and
- a Kynar 500/PMMA blend with a single 0.5% concentration of PTFE.

It was observed that the nucleating effect saturates very rapidly with PTFE concentration: a 10-fold increase (from 0.1 to 1% or 1.5%) has only a marginal effect. As a result, a constant PTFE concentration of 0.5% has been adopted in all subsequent experiments.[1]

The data for nucleated blends with PMMA (T_m, T_c and ΔH) are listed in Table 2 for Kynar 740 (using the PMMA/EA copolymer yields very similar results, not listed). The

[1] A note of caution is necessary. Since the draining-off washes away some PTFE, the concentrations of the nucleating agent are not known precisely; the figures given correspond to initial concentrations of the NA, whereas the actual ones may be lower.

Table 2
Comparison of crystallization and melting characteristics for 70/30 blends of PVDF/PMMA without and with NA. Note that for blends based on Kynar 500, the additional crystallization on heating (T_{ch}, X_{ch}) is suppressed with a nucleating agent

Kynar 740/PMMA (70/30)	T_c (°C)	ΔH_c (cal/g)	X_c (%)	T_m (°C)	ΔH_m (cal/g)		
Without NA	116.1	10.9	42.3	164.3	11.1		
+PTFE	132.3	10.4	41.7	166.1	11.4		
+Flavanthrone	129.7	11.1	44.4	166.2	12.0		
Kynar 500/PMMA (70/30)	T_c (°C)	X_c (%)	T_{ch} (°C)	X_{ch} (%)	$X_c + X_{ch}$ (%)	T_m (°C)	ΔH_m (cal/g)
Without NA	95.7	9.1	66.3	12.0	21.1	154.1	6.0
+PTFE	122.1	34.8	–	–	34.8	156.3	8.4

morphologies of non-nucleated and nucleated samples are compared in Fig. 4. Two main features emerge from these results:

1. As was the case for pure PVDF [14], PTFE, even at very low concentrations (0.1%), has a significant impact on the blends crystallization. The increase in T_c corresponds to nearly 80% of the crystallization range ΔT_{cmax} determined by self-nucleation.
2. The increase in T_c of the PVDF/PMMA blends is more important than for PVDF: 16.2°C for the Kynar 740 blends, ≈10°C for PVDF. However, one notes for future reference that the actual T_c of the nucleated blends remains significantly lower than for PVDF (e.g. 116.1 versus 132°C for Kynar 740).

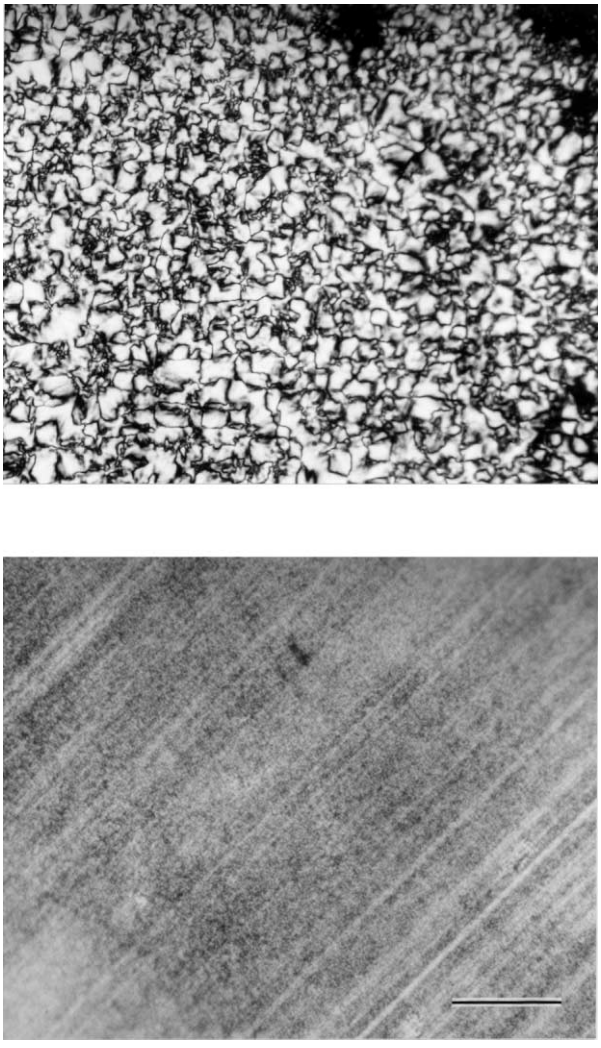

Fig. 4. Crystalline morphology of a PVDF/PMMA blend (Kynar 740) crystallized in the absence (part 1) and presence of PTFE nucleating agent. Optical micrographs, crossed polars; the oblique stripes in part 2 are caused by the microtome knife. Scale bar: 50 μm.

The crystallization kinetics of Kynar 500 nucleated by PTFE (Table 2) display essentially the same features, and notably a significant increase of T_c (≈26°C). Moreover, *the nucleated blend does no longer display a crystallization peak on heating* (whereas the non-nucleated blend *did*). In other words, the increased nuclei concentration makes it possible to reach complete crystallization *on cooling alone*: the added nuclei are sufficient to annihilate the 'kinetic' limitation of crystallization described earlier. The full impact of this increased overall crystallization rate can best be grasped when analyzing blends over a wider range of compositions, as detailed now.

3.2.3. Variable blend composition

The impact of PTFE nucleation on the *overall crystallinities* reached for blends with different *compositions* has been investigated for the sole Kynar 740/PMMA system, keeping the 'standard' 0.5% PTFE concentration (Fig. 5). Fig. 5 may be considered as a 'crystallinity phase diagram' of the blend and summarizes the major findings of the present study, which includes and expands the results displayed in Fig. 2. It indicates that '*maximum*' PVDF crystallinity can be attained on cooling over a much broader range of PMMA concentrations than for non-nucleated samples. Samples with 60% PVDF now crystallize 'fully' on cooling (no additional crystallization on reheating). The 40% blend which, when non-nucleated, does not crystallize on cooling (and reaches only 12% crystallinity on reheating) has, when nucleated, a crystallinity which is nearly 2/3 that of PVDF. Also, no additional crystallization takes place on reheating.

Similar results are obtained for blends based on other PVDFs. A 70/30 blend based on Kynar 500 (see Table 2) displays 'double' crystallization on cooling and heating when non-nucleated, reaching after the two processes at

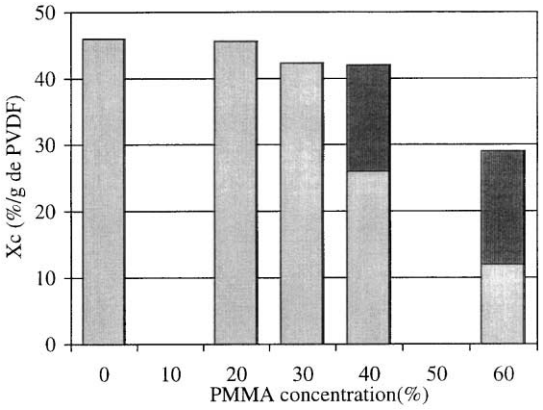

Fig. 5. Crystallinities reached for PVDF/PMMA samples (Kynar 740, 0.5% PTFE concentration) as a function of PMMA concentration. The crystallinities are scaled to the PVDF content of each blend. In light gray: total crystallinities that can be reached for non-nucleated samples, as illustrated in and reproduced from Fig. 2. Note that these crystallinities were reached either on cooling alone (for PMMA concentrations up to 30%) or by a combination of cooling and reheating for the 40 and 60% PMMa compositions. The crystallinities displayed in this figure for PTFE nucleated samples are reached after *a single cooling from the melt* at 10 K/min. Whereas PTFE nucleation does not influence the final crystallinities for PVDF and the two PVDF-rich blends, it has a dramatic effect on the 40 and 60% PMMA blends: on cooling *alone*, the 60% PMMA blend reaches nearly 30% PVDF crystallinity, whereas it would be amorphous in the absence of the PTFE nucleating agent.

most 50% of the PVDF crystallinity. Addition of PTFE induces 75% of PVDF crystallinity on cooling alone, and suppresses the additional crystallization on heating. The behavior of the Kynar 500 blends parallels that of Kynar 740 blends with a mere shift to lower PMMA concentrations for identical behaviors.

To summarize, addition of PTFE '*saturates*' the blend in nucleation centers: all the 'possible' crystallization takes place on cooling (at the 10 K/min cooling rates used). In other words also, the addition of PTFE changes both the *final crystallinity* reached in a critical composition range (depending on the system, for 50/50 ± 10/10) and the *way it is reached*, i.e. on cooling alone, which is of course an essential ingredient to consider in processing.

4. Discussion

The above results indicate that PTFE is a very potent nucleation additive for blends of PVDF and PMMA, or PMMA-co-EA polymers. If anything, PTFE would appear as more efficient for the blends than for pure PVDF, on account of the larger increase of T_c — which however translates in comparable efficiencies (i.e. taking into account the larger ΔT_c gap for the blends). Furthermore, the nucleating additive makes it possible to reach sizeable PVDF crystallinities for blends which would not 'normally' (i.e. on cooling) crystallize. It is of interest to analyze this behavior, and in particular to compare the very different responses of the PVDFs and of their blends with the acrylic polymers to the addition of PTFE NA. For this purpose, we follow closely the argument developed by Fillon et al. [15,16] when analyzing the crystallization behavior of self-seeded and nucleated isotactic polypropylene, for which comparable increases in T_c have been observed.

The peculiarities of the crystallization behavior of the blends may be rationalized on the basis of an intricate interplay of nuclei densities and variation of growth rates with temperature. In the present study, as in the investigation on PVDF [14], the crystallization temperature is determined as the maximum of the crystallization peak upon cooling at 10 K/min. As pointed out by Fillon et al. [15,16] the peak breadth is about 10°C, which translated in crystallization time, amounts to about one minute. The crystallization half time (corresponding to the position of the peak) is therefore 30 s: all our DSC scans produce peaks which are characterized by an *iso-crystallization half-time of 30 s*. If the anisothermal crystallization process in the DSC scan is approximated by an isothermal one (at the peak temperature) [15,16], it is possible to use the rate constant K of the Avrami equation, which is related to the crystallization half-time:

$$K = \ln 2/t_{1/2}n = (4\pi/3)NG^3$$

with N as the nuclei concentration, G the linear growth rate at T_c and $t_{1/2}$ the crystallization half-time.

In other words, the crystallization peaks in all our DSC runs, which are iso $t_{1/2}$ can equally well be defined as being iso NG^3: *the increase in N resulting from the addition of nucleating centers must be exactly compensated by a decrease in G*, i.e. by crystallization at higher temperatures. As a result, T_c depends critically on the *magnitude* of the growth rate: lowering the 'intrinsic' growth rates results in a lowering of the crystallization temperatures. The significant *shifts in* T_c noted in the present investigation are fully consistent with (and actually a different manifestation of) the known variation of G of PVDF/PMMA blends with temperature and PMMA content. Lovinger [16] observed almost a 10-fold decrease of the maximum growth rate of a PVDF/PMMA 67.5/32.5 blend relative to pure PVDF, as well as significant shifts (ranging from 15 to 40°C) to lower temperatures for equivalent growth rates.

The *width of the* ΔT_c range depends critically on the variation of G with temperature, and on the range of nuclei concentrations attainable by the nucleation process. As schematized in Fig. 6, a 10^3 fold increase in the concentration of nuclei must be compensated by a 10-fold decrease in G (in order to keep NG^3 constant). This 10-fold reduction in G may be achieved for significantly different ΔT_c, as illustrated by the two growth rates curves versus T_c which stand for pure PVDF and for a PVDF/PMMA blend, respectively. In other words, the increase of T_c with the addition of equally potent NA has highly different impacts on the T_c shift depending on the variation of *growth rates* with

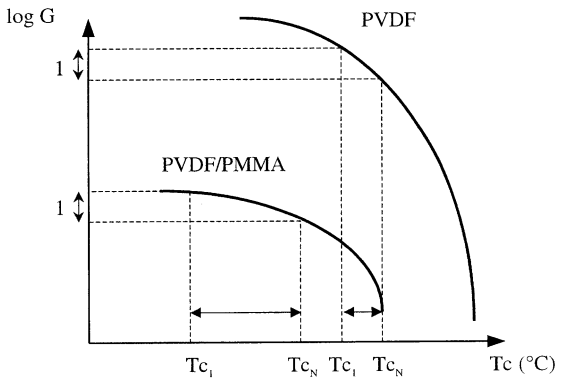

Fig. 6. Schematic illustration of the impact on T_c of a 10^3-fold increase of nuclei concentration N in two samples with widely different variations of growth rate with crystallization temperature. In both cases, a 10-fold decrease of G compensates for the increase in N, but is manifested but significantly different shifts in T_c.

temperature. The PVDF and PVDF/PMMA blends illustrate vividly this argument, since the same polymer is involved in the crystallization process, but in two different environments.

5. Conclusion

The nucleating impact of PTFE on PVDF, which has been shown to induce significant variations of the crystallization kinetics of the homopolymer, has an even more profound impact on the crystallization behavior of blends of PVDF and acrylic polymers. This impact is best attested by the unusually high overall efficiency, which amounts to 90% of the 'ideal' standard set by self-nucleated samples. It is also attested by the significant increase in T_c (over 25°C) achieved on simple cooling from the melt. The fact that PTFE *remains* a good nucleating agent in these blends also implies that the acrylic polymer does not interact with the surface of PTFE and does not 'poison' the nucleating ability of the PTFE. This straightforward transfer from the homopolymer to the blends does not hold true for every nucleating agent of PVDF: as indicated in the introduction, sepiolite, which is a nucleating agent for PVDF *looses* its efficiency in blends of PVDF with PMMA, presumably because its surface interacts preferentially with PMMA rather than with PVDF [13].

The profound modifications of the crystallization process of the blends as a result of enhanced nucleation are mainly linked with the rather slow variation of PVDF growth rates with temperature in these blends. They have however an interesting consequence: 'early' (i.e. at 25°C higher temperatures) crystallization on cooling induced by the nucleating agent makes it possible to crystallize blends with higher PMMA compositions, typically up to 50–60% as opposed to 30% for non-nucleated samples. This 30% composition limit was so far considered as the 'practical' limit (set actually by the *crystallization kinetics*) for industrially useful blend compositions. Since PTFE-nucleation of the blends enriched in PMMA induces a significant PVDF crystallinity, these blends with higher acrylic polymer contents should display properties comparable to those of their earlier, richer in PVDF counterparts.

Acknowledgements

The generous financial support of ELF Atochem to S.S. and the ICS is gratefully acknowledged.

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