

Nucleating Polymer Crystallization with Poly(tetrafluoroethylene) Nanofibrils

Karin Bernland, Paul Smith

Department of Materials, ETH Zurich, Zurich 8093, Switzerland

Received 26 January 2009; accepted 19 March 2009

DOI 10.1002/app.30425

Published online 2 June 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The ability of nanofibrils of poly(tetrafluoroethylene) (PTFE) – *in situ* generated during compounding – to efficiently nucleate crystal growth of the bulk polymers isotactic polypropylene (i-PP), high-density polyethylene (HDPE), polyoxymethylene (POM), polyamide 12 (PA12) and poly(ethylene terephthalate) (PET) is demonstrated. Enhanced nucleation is shown to occur already

at PTFE contents as low as 0.001% w/w in i-PP and HDPE. In addition it was found that compounding with PTFE lead to improved clarity of the latter polymers. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 281–287, 2009

Key words: polymer nucleation; poly(tetrafluoroethylene)

INTRODUCTION

The ability of solid poly(tetrafluoroethylene) (PTFE) to promote crystal growth of other species is well known, and was most conspicuously demonstrated in earlier work, in which friction-deposited, highly oriented layers of this polymer were shown to induce oriented crystallization of a most unusual, broad spectrum of materials, including biological species and inorganic and organic compounds, as well as a variety of polymers.^{1–6} Although this technique may be academically interesting and of potential relevance for creating oriented thin layers for use in, for instance, opto-electronic components,⁷ it evidently would not appear practical to employ this approach to enhance nucleation of semi-crystalline bulk polymers, commonly applied to reduce processing cycles, achieve better control of the nucleation density, or beneficially alter their solid-state structure to improve mechanical or optical properties (e.g.,^{8–12}).

In this study we explored the unique characteristic of virgin, i.e., as-polymerized PTFE to readily deform below its melting temperature, even under modest shear, to yield virtually endless fibrils of nanoscopic width—a well-known phenomenon¹³ that forms the basis for the production of porous, so-called expanded PTFE, better known as Goretex^{®14–16}—to *in situ* create an ultra-large, oriented surface that could provide the previously discussed beneficial nucleating substrate. Previous attempts by Van der Meer et al.¹⁷ already demonstrated the potential of this approach in their

study of compounding isotactic polypropylene (i-PP) with particles of PTFE of different sizes and molecular weights. These authors once more showed that PTFE of high molecular weight indeed can be deformed into fibrillar scaffolds, onto which i-PP was found to nucleate, leading to an improvement of selected mechanical properties. Here we report an expansion of the previous work,¹⁷ in which we employed suspensions of fine particles of virgin ultra-high molecular weight PTFE. The latter were blended and subjected to controlled shear during compounding below the melting temperature of PTFE, with five common thermoplastic bulk polymers, i.e., i-PP, high-density polyethylene (HDPE), polyoxymethylene (POM), polyamide 12 (PA12), and poly(ethylene terephthalate) (PET), for which efficient nucleation of some remains a challenge.^{18–22} More specifically, we directed our attention to thermal- and optical properties, as well as crystallization kinetics of the bulk polymers in the presence of PTFE, both in the previously described form of fibrillated particles and—for reference purposes—as friction-deposited orientation layers.

EXPERIMENTAL

Materials

The polymers used were i-PP (Moplen HF 500N, Basell, Rotterdam, The Netherlands); HDPE (HD 7048, DSM), $M_n = 21$ kg/mol and $M_w = 104$ kg/mol; POM, (Delrin 100, DuPont, Geneva, Switzerland); PA12 (UBESTA 3014U, UBE Engineering Plastics SA, Düsseldorf, Germany) $M_w = 14$ kg/mol, for layers grown from solution and UBESTA 3030XA, $M_w = 30$ kg/mol, for melt-compounding; and PET, 200255 (Aldrich, Basel, Switzerland), $M_v = 18$ kg/mol. All polymers

Correspondence to: P. Smith (paul.smith@mat.ethz.ch).

TABLE I
Peak Crystallization Temperatures, T_c (DSC) of Polymers Neat and Crystallized onto Friction-Deposited PTFE Layers

Polymer	Solvent	Polymer concentration (% w/w)	T_c (°C)	PTFE content (% w/w)	T_c neat (°C)	T_c on PTFE (°C)
i-PP	<i>p</i> -Xylene	0.5	80	0.3	112.1	125.7
HDPE	<i>p</i> -Xylene	0.5	78	0.3	115.8	116.9
POM	DMF	0.1	120	0.2	147.6	148.8
PA12	DMF	0.5	107	0.5	145.7	155.3
PET	DMSO	0.3	140	0.6	205.6	223.0

were freeze milled and dried before use. PTFE was received as an aqueous dispersion (Teflon® TE-3893 N) from DuPont.

Sample preparation

Oriented PTFE layers were prepared by friction deposition onto microscopy slides, as described elsewhere.¹ Films of i-PP, HDPE, POM, PA12, and PET were grown on these layers from dilute solutions. For details regarding solvents, concentrations, and crystallization temperatures, see Table I.

Bulk polymer/PTFE mixtures were prepared by adding selected amounts of the PTFE dispersion to the milled polymers, followed by mixing and drying in a vacuum oven at 70°C. The mixtures were subsequently compounded in a laboratory, corotating mini-twin-screw extruder (Technical University Eindhoven, Eindhoven, The Netherlands) for 10 min under a nitrogen blanket, at the manufacturer-recommended processing temperature for each bulk polymer—above their melting temperature but below that of PTFE. Reference samples of the neat polymers, i.e., without PTFE, were produced in the same manner.

Films for optical microscopy studies were prepared by melt-compression molding the compounded material—below the melting temperature of PTFE—between two glass slides, and quenching to room temperature. For scanning electron microscopy studies (SEM) and tensile testing, films with a thickness of 0.1–0.5 mm were prepared by melt-compressing the polymers, also at $T < T_{m, PTFE}$, for 5 min, followed by quenching in a cold press.

Circular samples (thickness 1.1 mm and diameter 25 mm) for optical characterization of i-PP and HDPE comprising fibrillated PTFE were prepared by injection molding the previously compounded material, using a laboratory, mini-injector (DACA Instruments, Santa Barbara CA). The material was melted and kept for 2 min at 240°C under a nitrogen blanket before being injected into the mold that was kept at room temperature.

Thermal analysis

Thermal analysis was conducted using a differential scanning calorimeter (DSC 822e, Mettler Toledo,

Switzerland) calibrated with Indium. DSC thermograms were recorded under nitrogen at standard heating and cooling rates of 10°C/min unless indicated otherwise; the sample weight was about 10 mg. In each run, the samples were kept for 5 min at the highest temperature ($T < T_{m, PTFE}$) prior to cooling in order to ensure complete melting of the bulk polymers, and to prevent self nucleation. The crystallization temperatures reported here correspond to the peak temperatures in the DSC thermograms.

Optical microscopy

Optical microscopy was carried out with a Leica DMRX microscope (Leica Microsystems, Germany) equipped with a hot stage (FP82TM, Mettler Toledo, Switzerland). For isothermal crystallization experiments samples were quenched to the selected crystallization temperature at the fastest rate possible ($\sim 40^\circ\text{C}/\text{min}$). Before each cooling experiment the i-PP, HDPE, and PET films were kept for 2 min at the highest temperature in order to ensure complete melting, while those comprising POM and PA12 were kept at the maximum temperature only for 1 min to minimize thermal degradation.

Scanning electron microscopy

Samples for SEM studies on i-PP/PTFE blends were cut from the compression-molded films, and etched for 1 h using the permanganic etchant described by Olley and Bassett,²³ comprising two parts of sulfuric acid per one part of orthophosphoric acid and 2% w/w of potassium permanganate. This etchant degraded both crystalline and amorphous polypropylene, but left the PTFE intact. The etched samples were coated with a thin layer of platinum, and imaged using a LEO 1530 Gemini (LEO Elektronenmikroskopie GmbH, Oberkochen, Germany).

Optical properties

The optical characteristics haze and clarity were determined for the injection molded samples according to ASTM standard D1003,²⁴ using a Haze-Gard Plus® apparatus (BYK Gardner GmbH, Germany).

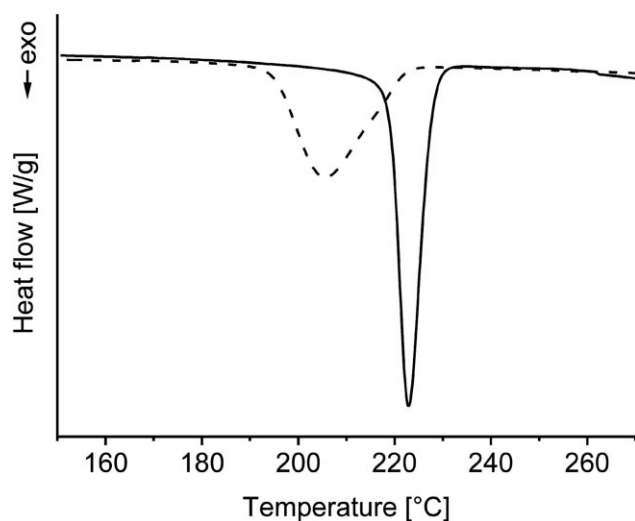


Figure 1 DSC cooling thermograms for neat PET (- - -) and PET crystallizing onto a friction-deposited PTFE layer (-).

All reported values are the average of the measured values for at least three samples.

RESULTS

Polymers onto oriented PTFE layers

In a first set of experiments, it was reestablished that the friction-deposited PTFE layers induced oriented growth of all polymers tested. Invariably, in the optical microscope, shish-kebab-like structures of the solution-crystallized bulk polymers were detected along the oriented strands of PTFE. After complete drying, the various PTFE/polymer layers were collected from the microscopy slides and inserted into DSC pans for thermal evaluation. The crystallization temperatures, T_c , recorded for the polymeric materials grown from the melt onto the PTFE layers are listed in Table I, together with the corresponding values of the neat bulk polymers. As can be seen, PTFE invariably increased the T_c of the polymers examined, and the thermograms featured sharper crystallization endotherms than those of the neat polymers, as illustrated for PET in Figure 1, indicative of efficient nucleation and crystallization of the materials when in contact with friction-deposited PTFE layers.

Compounded blends

Initial experiments were conducted to establish the influence of different compounding parameters, notably speed and time, on the fibrillation behavior of the solid PTFE particles in the molten bulk polymers. For this purpose i-PP comprising 1% w/w of PTFE particles were compounded at 230°C for peri-

ods ranging from 2–15 min and screw rotation speeds from 10 to 300 rpm. The mixed material was discharged and compression molded into films, also at 230°C, and etched as described in the Experimental section. Representative SEM images of samples compounded for 5 min at 20 rpm and 10 min at 200 rpm are shown in Figure 2. These photomicrographs reveal the well known, intriguing fibrillation of virgin PTFE particles in an intermediate state [Fig. 2(a)], where much undeformed material is still present, and an advanced phase [Fig. 2(b)] featuring numerous fine, virtually endless filaments of diameters well below 1 μm . The latter were deemed to be adequate for the purpose at hand, and, unless indicated otherwise, compounding for 10 min at 200 rpm was adopted.

Subsequently, the nucleating efficiency of the thus fibrillated PTFE was evaluated by optical microscopy and DSC. The optical micrographs in Figure 3 show the initial nucleation and crystal growth phase, as well as the final morphology, of isothermally crystallized samples of the melt-compounded neat bulk polymers and the mixtures containing 1% w/w

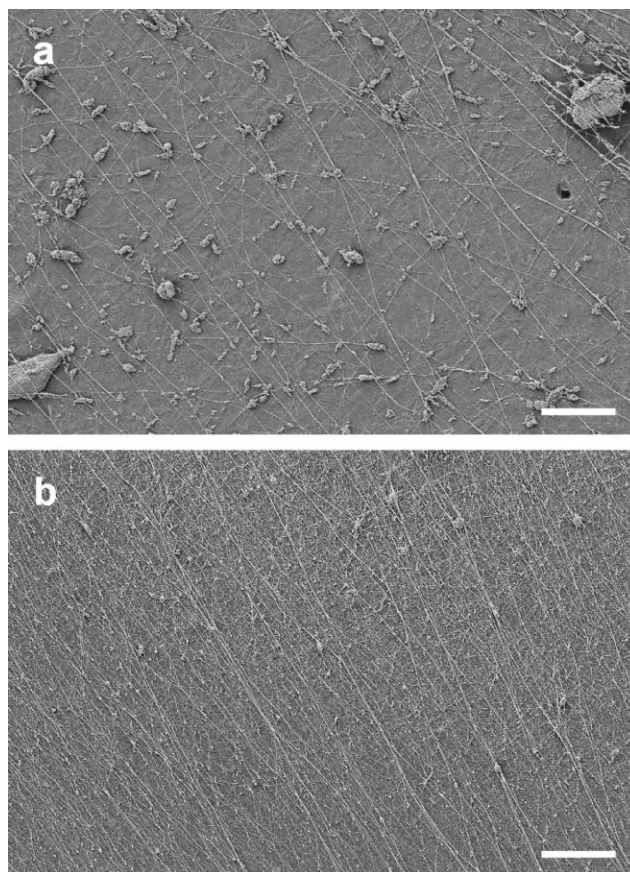


Figure 2 Scanning electron micrographs of etched, melt-compression molded films of i-PP comprising 1% w/w of PTFE particles fibrillated during compounding at 230°C for (a) 5 min at 20 rpm and (b) 10 min at 200 rpm. Scale bars 20 μm .

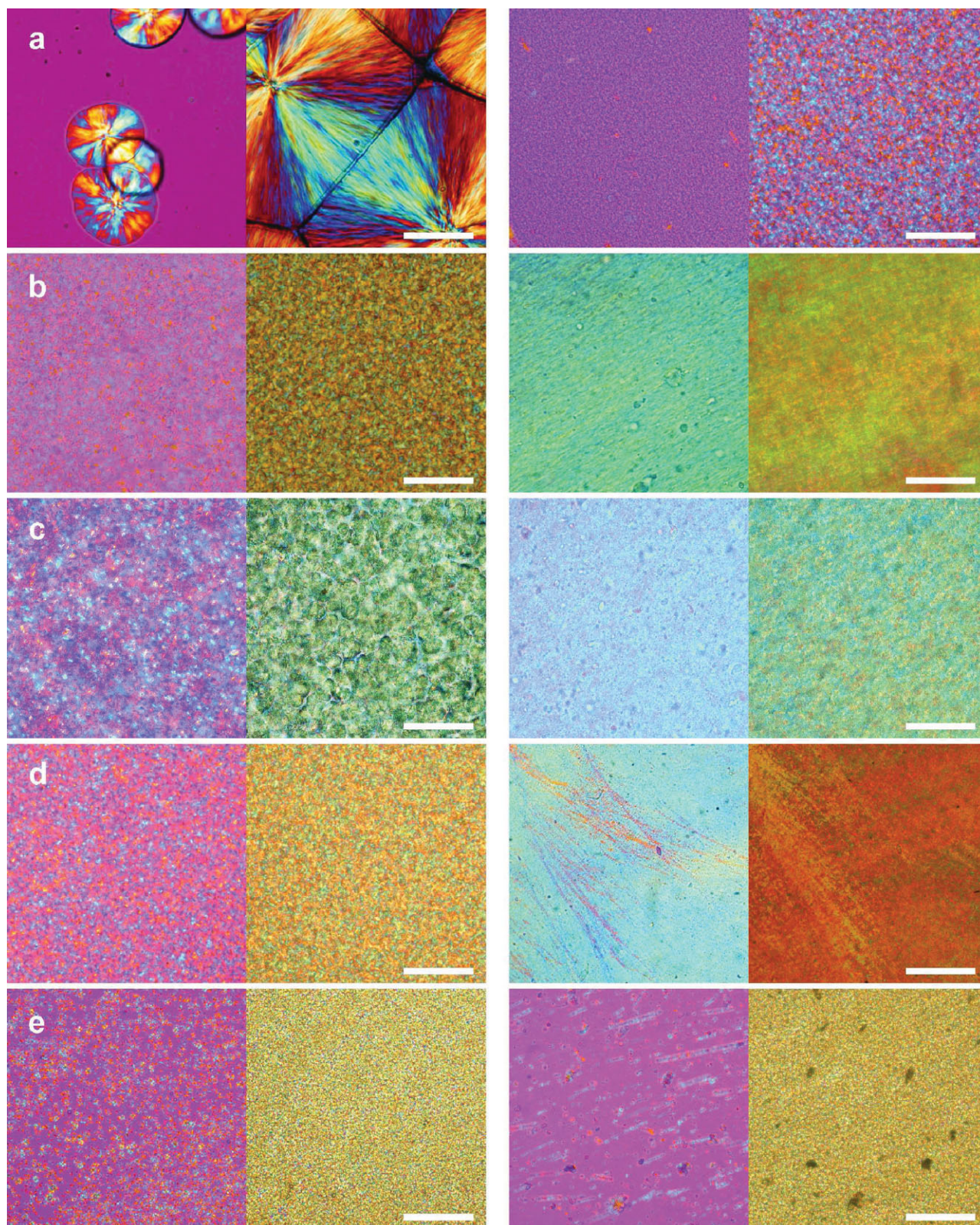


Figure 3 Optical microscopy images (crossed polarizers, $\frac{1}{4} \lambda$ plate) of melt-compounded neat i-PP, HDPE, POM, PA12, and PET (a–e: left column) and the same polymers containing 1% w/w of fibrillated PTFE (right column). The samples were isothermally crystallized from the melt at 138, 125, 160, 165, and 235°C, respectively. Each set of images show the initial (left) and the final (right) stage of crystallization. Scale bars 100 μm . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

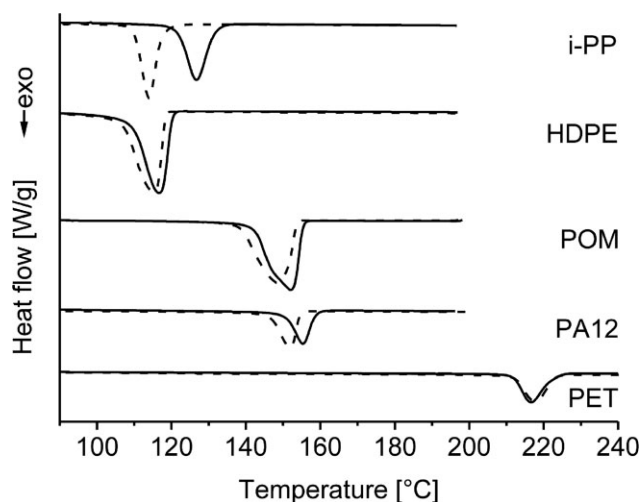


Figure 4 DSC cooling thermograms recorded for the different melt-compounded polymers, neat (---) and blends containing 1% w/w fibrillated PTFE (-).

of fibrillated PTFE. The highly efficient nucleating ability of the PTFE fibrils is clearly demonstrated by the difference in number, size, and shape of the crystalline entities, most notably for i-PP (α -polymorph, as determined by wide-angle X-ray diffraction²⁵) and POM [Fig. 3(a,c), respectively]. Oriented crystallization onto the PTFE fibrils was most conspicuous in HDPE, PA12, and PET [Fig. 3(b,d,e)].

Thermal analysis (DSC) was conducted to gain a more quantitative insight of nucleation of the various bulk polymers induced by the fibrillated PTFE (cf. Fig. 4). The crystallization peak temperatures derived from these thermograms are presented in Table II. Generally these data are in concert with those obtained in the previous experiments with friction-deposited PTFE layers, i.e., the presence of PTFE invariably raised the T_c of the bulk polymers. It should be noted, however, that the crystallization temperatures

of the neat polymers were found to alter slightly after compounding for all polymers. For PET this change was rather significant—the peak crystallization temperature increased from 205.6°C for as-received PET to as high as 217.5°C for the same material compounded at 200 rpm. This is in accord with the results of previous studies of melt-compounded PET,^{26–28} and is thought to be mainly due to macromolecular orientation induced by the shear forces during compounding, as evidenced also in our compounded material in the form of row nucleation. As a result, the presence of fibrillated PTFE in blends with PET was overshadowed by this effect, unlike in the previous set of experiments involving friction-deposited PTFE and noncompounded PET.

Kinetic constants and half times of crystallization of the bulk polymers, neat and in the presence of fibrillated PTFE, were derived from a series of isothermal crystallization experiments, employing Avrami's equation^{29,30}:

$$X(t)/X(\infty) = 1 - \exp(-k_n t^n), \quad (1)$$

where $X(t)$ is the crystallinity at time t , n the Avrami constant, and k_n the kinetic constant.

Assuming that only heterogeneous and instantaneous nucleation occurred, the kinetic constant is proportional to the number of nuclei, N , according to³¹:

$$N = \frac{3k_n}{4v^3\pi}, \quad (2)$$

where v is the radial crystal growth rates, which were determined by optical microscopy studies during isothermal crystallization, conducted at the same temperature as in the DSC experiments.

The results of the above analysis for the various polymers are presented in Table II. As is evident, the presence of 1% w/w fibrillated PTFE not only

TABLE II
Crystallization Peak Temperatures, T_c , of Melt-Compounded Bulk Polymers, Neat and in the Presence of Fibrillated PTFE, Recorded by DSC, and Data Derived from Avrami Analysis of Isothermal Crystallization of the Same Polymers at the Temperatures Indicated

	T_c (°C) nonisothermal cryst.	T_c (°C) isothermal cryst.	Avrami constant (n)	Kinetic constant (k_n)	Number of nuclei/mm ³ (N)	Cryst. half-time, $t_{1/2}$ (min)
i-PP	113.8	138	3.4	3.0×10^{-6}	6×10^2	85.8
i-PP + PTFE 0.001% w/w	121.0		2.8	1.2×10^{-4}	2×10^4	13.5
i-PP + PTFE 1% w/w	126.6		2.0	6.6×10^{-2}	1×10^7	3.2
HDPE	115.2	125	3.5	7.5×10^{-7}		50.8
HDPE + PTFE 0.001% w/w	115.6		3.4	1.6×10^{-6}		43.8
HDPE + PTFE 1% w/w	117.0		2.0	5.5×10^{-3}		11.5
POM	148.4	160	3.0	1.8×10^{-5}	7×10^2	34.5
POM + PTFE 1% w/w	152.1		2.8	1.8×10^{-3}	7×10^4	8.3
PA12	151.8	165	3.9	2.8×10^{-4}		7.4
PA12 + PTFE 1% w/w	155.3		2.9	2.3×10^{-2}		3.2
PET	217.5	235	4.9	9.8×10^{-8}		24.8
PET + PTFE 1% w/w	216.5		2.8	6.2×10^{-4}		12.2

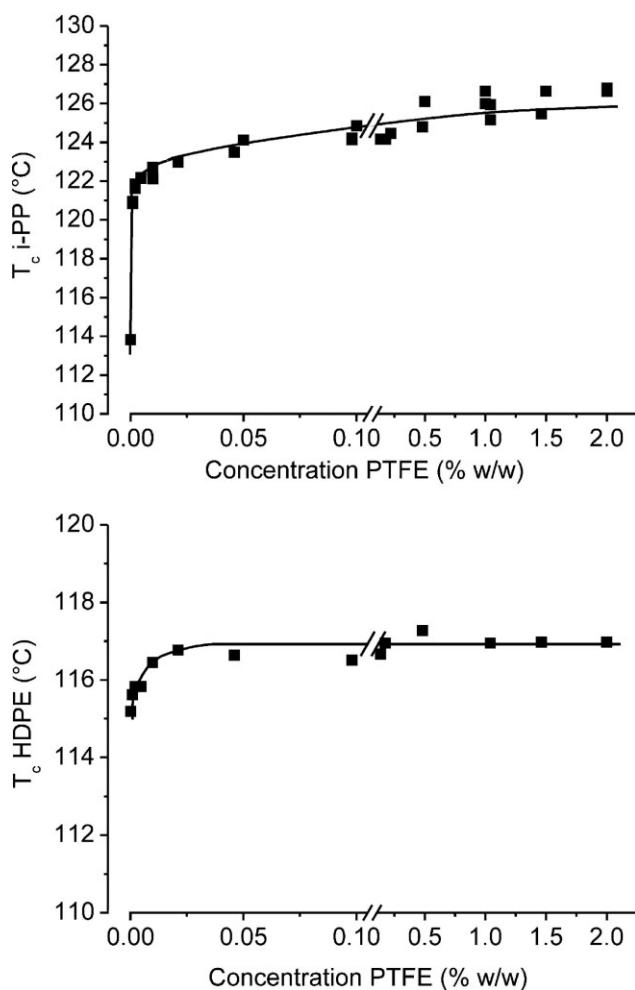


Figure 5 Peak crystallization temperature, T_c of i-PP (top) and HDPE (bottom) versus fibrillated PTFE content. Samples compounded for 10 min at 200 rpm at 230 and 200°C, respectively. The drawn lines are a guide to the eye only.

increased the crystallization temperature for the bulk polymers, but also significantly reduced the half-time of crystallization, $t_{1/2}$ —most notably for i-PP, for which this value at isothermal crystallization at 138°C decreased from 85.9 to 3.2 min only, in concert with a previous report.¹⁷ Even for HDPE, which did not feature an important increase in crystallization temperature with the addition of PTFE, $t_{1/2}$ significantly decreased from 50.8 to 11.5 min.

In more detailed studies, changes in peak crystallization temperatures of i-PP and HDPE were investigated as a function of the PTFE content in the range of 0–2% w/w (see Fig. 5). Most remarkably, it was found that even at the lowest concentration employed, i.e., 0.001% w/w PTFE, noticeable nucleation of polypropylene was observed, as manifested in an increase of the T_c from 113 to 121°C. This should be contrasted with, for instance, the commonly employed nucleating and clarifying agent bis(3,4-dimethylbenzylidene)sorbitol (DMDBS) that

is required to be present in concentrations exceeding 0.1% w/w, i.e., 100-fold, to be effective.³² Increasing the PTFE content above 0.5% w/w did not further augment the crystallization temperature significantly. As a matter of fact, the T_c of i-PP commenced to level off already at 0.05–0.1% w/w PTFE.

Finally, the importance of fibrillation of the added PTFE due to compounding was confirmed by thermal analysis of dry-powder-mixed samples of i-PP and 1% w/w of PTFE. The samples were simply melt-compression molded into films, which featured mostly undeformed PTFE particles and few fibrillar entities. The peak crystallization temperature of i-PP, as measured by DSC, in these specimens was ~115°C.

Optical properties

As shown earlier, efficient nucleation by fibrillated PTFE caused a reduction in spherulite size of most of the bulk polymers investigated (cf. Fig. 3). Because the latter generally results in reduced scattering of light,^{32–36} we also explored the potential of fibrillated PTFE to enhance optical properties—i.e., to act as a “clarifying” agent—for iPP and HDPE.

The clarity of i-PP and HDPE containing 1% w/w of PTFE is plotted against the compounding speed in Figure 6, clearly revealing that this optical characteristic of these polymers was enhanced with increasing speed, evidently due to the increased “degree” of fibrillation of the added PTFE (cf. Fig. 2). In more elaborate studies, haze and clarity of injection-molded i-PP samples were examined as a function of PTFE content (Fig. 7). A maximum in clarity and a minimum in haze were detected at a PTFE content of about 0.05% w/w. This value coincides with the PTFE concentration at which the crystallization temperature of i-PP commenced to level

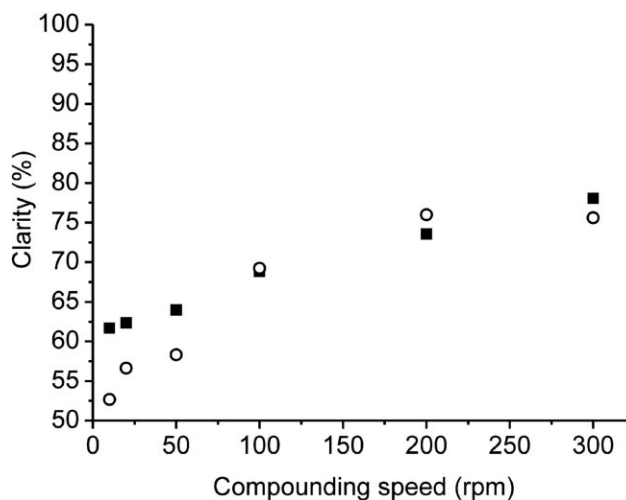


Figure 6 Clarity of i-PP (■) and HDPE (○) comprising 1% w/w PTFE versus compounding speed (time 10 min).

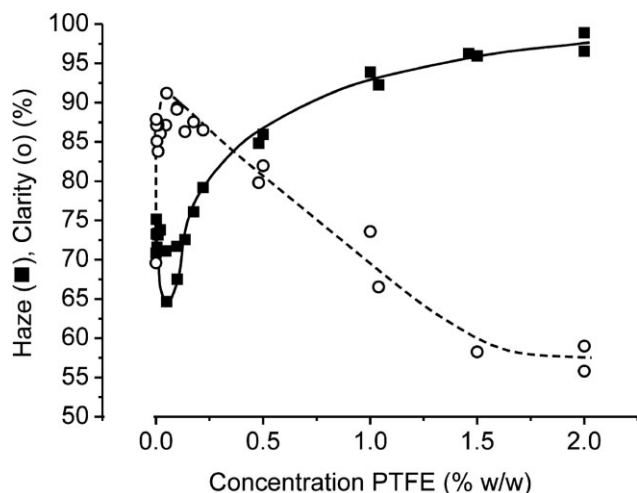


Figure 7 Haze (■) and clarity (○) of i-PP/PTFE blends, compounded at 230°C for 10 min at 200 rpm. The drawn curves are a guide to the eye only.

off, and, thus, represents an optimum between nucleation efficiency and the amount of PTFE present. The above—admittedly very modest—reduction in haze and increase in clarity evidently is not as conspicuous as observed for small-molecular organic clarifying agents employed for i-PP (typically, haze and clarity values of ~15% and ~98%, respectively, can be obtained).^{12,32} One obvious reason is that the difference in refractive index of PTFE and i-PP is significant (approx. $\Delta n = 0.16$ ³⁷), causing unfavorable scattering of light. Furthermore, the dispersion of PTFE is, even after extensive fibrillation, not as optimal as that achieved with the clarifying agents that are soluble in the polypropylene melt. Nonetheless, the observed enhancement in optical properties of i-PP is remarkable and may be of use.

CONCLUSIONS

The ability of PTFE to efficiently nucleate five important bulk polymers was demonstrated in model crystallization experiments of these materials onto friction-deposited PTFE layers, as well as under technologically more relevant conditions, in which virgin PTFE particles were deformed into fine, nanoscopic fibrils by compounding with the molten matrix materials. In addition, fibrillated PTFE was shown to (modestly) enhance the clarity of i-PP and HDPE, despite the large mismatch in their refractive indices.

The authors are grateful to Prof. H.-W. Schmidt and Sandra Ganzleben (Universität Bayreuth, Germany) and Dr. Kirill Feldman (ETH Zurich) for stimulating discussions and experimental assistance. The authors also thank Dr. Theo

Schroots (E.I. du Pont de Nemours and Company, Inc.) for the generous supply of PTFE dispersion and his interest in this work.

References

- Wittmann, J.-C.; Smith, P. *Nature* 1991, 352, 414.
- Fenwick, D.; Smith, P.; Wittmann, J.-C. *J Mater Sci* 1996, 31, 128.
- Hayes, N. W.; Beamson, G.; Clark, D. T.; Clarke, D. T.; Law, D. S. L. *Polymer* 1996, 37, 523.
- Yan, S.; Petermann, J. *J Polym Sci Part B: Polym Phys* 2000, 38, 80.
- Damman, P.; Fischer, C.; Kruger, J. K. *J Chem Phys* 2001, 114, 8196.
- Tosaka, M.; Tsuji, M.; Ogawa, T.; Kitano, H.; Nakano, K.; Kohjiya, S.; Danev, R.; Nagayama, K. *Polymer* 2006, 47, 951.
- Friend, R. *Nature* 1991, 352, 377.
- Last, A. G. M. *J Polym Sci* 1959, 39, 543.
- Kargin, V. A.; Sogolova, T. I.; Rapoport, N. Y. A.; Kurbanova, I. I. *J Polym Sci Part C: Polym Symp* 1967, 16, 1609.
- Binsbergen, F. L. *Polymer* 1970, 11, 253.
- Hoffmann, K.; Huber, G.; Mader, D. *Macromol Symp* 2001, 176, 83.
- Kristiansen, P. M.; Gress, A.; Smith, P.; Hanft, D.; Schmidt, H.-W. *Polymer* 2006, 47, 249.
- Ebnesajjad, S. *Non-Melt Processible Fluoroplastics*; Plastics Design Library: Norwich, NY, 2000.
- Gore, W. L.U.S. Pat. 3,315,020 (1967).
- Gore, W. L.U.S. Pat. 3,953,566 (1976).
- Gore, W. L.U.S. Pat. 3,962,153 (1976).
- Van Der Meer, D. W.; Milazzo, D.; Sanguineti, A.; Vancso, G. *J Polym Eng Sci* 2005, 45, 458.
- Xu, W. B.; He, P. S. *J Appl Polym Sci* 2001, 80, 304.
- Qian, J. S.; He, P. S. *J Mater Sci* 2003, 38, 2299.
- Liang, G. D.; Xu, J. T.; Xu, W. B. *J Appl Polym Sci* 2004, 91, 3054.
- Hu, Y. L.; Ye, L. *Polym Eng Sci* 2005, 45, 1174.
- Shu, Y.; Ye, L.; Zhao, X. W. *Polym Plast Technol Eng* 2006, 45, 963.
- Olley, R. H.; Bassett, D. C. *Polymer* 1982, 23, 1707.
- ASTM. ASTM Standard D 1003. Standard test method for haze and luminous transmittance of transparent plastics; ASTM: West Conshohocken, PA, 1961.
- Jones, A. T.; Aizlewood, J. M.; Beckett, D. R. *Makromol Chem* 1964, 75, 134.
- Khanna, Y. P.; Kumar, R.; Reimschuessel, A. C. *Polym Eng Sci* 1988, 28, 1612.
- Kim, S. P.; Kim, S. C. *Polym Eng Sci* 1993, 33, 83.
- Chisholm, B. J.; Zimmer, J. G. *J Appl Polym Sci* 2000, 76, 1296.
- Avrami, M. *J Chem Phys* 1939, 7, 1103.
- Avrami, M. *J Chem Phys* 1941, 9, 177.
- Wunderlich, B. *Macromolecular Physics*; Academic Press: New York, 1976.
- Kristiansen, M.; Werner, M.; Tervoort, T.; Smith, P.; Blumenhofer, M.; Schmidt, H.-W. *Macromolecules* 2003, 36, 5150.
- Beck, H. N.; Ledbette, H. D. *J Appl Polym Sci* 1965, 9, 2131.
- Pritchard, R. *SPE Trans* 1964, 4, 66.
- Jabarin, S. A. *Polym Eng Sci* 1982, 22, 815.
- Garg, S.; Stein, R. ANTEC 1988, 1021.
- Seferis, J. c. In *Polymer Handbook*; Brandrup, J.; Immergut, E. H.; Grulke, E. A., Eds.; Wiley: New York, 1999; Chapter 6, p. 571.