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Fractionated crystallization in blends of functionalized poly(tetrafluoroethylene) and polyamide

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SUMMARY: Blends of poly(tetrafluoroethylene)/polyamide (PTFE/PA) were prepared to combine the good processing properties of PA with the excellent sliding properties of PTFE. For the compatibilizing of the immiscible components the chemical reaction of functional groups of modified PTFE (micro powder produced by electron irradiation in air) and polar PA during a reactive extrusion process was used. The parameter influencing the efficiency of the *in-situ* reaction between both components were varied.

The crystallization and melting behaviour of the different blends was investigated by DSC. In dependence on the degree of compatibilization the phenomenon of fractionated crystallization of the dispersed PTFE component was observed. In this way a qualitative characterization of the dispersity of PTFE in dependence on the functionality of the components and the processing conditions is possible, and therefore an estimation of the efficiency of the *in-situ* reaction.

Introduction

The effect of fractionated crystallization is a special crystallization process which can be observed in blends of immiscible polymers under certain conditions[1-3]. In dependence on the size of the semicrystalline disperse blend component a higher supercooling ΔT_c for the crystallization can be observed in comparison to the bulk phase. Sometimes, the crystallization can take place stepwise at different supercoolings.

Normally, the crystallization will start by heterogeneous nucleation[4]. The crystallization temperature is determined by the interfacial tension between liquid and solid phase influenced by the kind of heterogeneous nuclei. The crystallization will be initiated at these nuclei which are energetically favourable, and so by the lowest supercooling $\Delta T_{c,1}$ typically for the pure polymer. With decreasing particle size the number of the dispersed regions increases. If the number of the dispered regions in the blend is higher than the number of these heterogeneous nuclei, the crystallization at $\Delta T_{c,1}$ is almost suppressed.

In case that no other heterogeneous nuclei exist, the crystallization cannot be started until the homogeneous nucleation occurs at a high supercooling $\Delta T_{c,hom}$[5].

$$\Delta T_{c,hom} = T_m^\circ - T_{c,hom} = 0.2\ T_m^\circ \qquad (1)$$

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T_m° is the melt/crystal equilibrium temperature, and $T_{c,hom}$ is the onset temperature of homogeneously nucleated crystallization.

It is remarkable that the melting behaviour observed in blends with a fractionated crystallization is almost unchanged[3]. That could mean that the crystallite type and size are not strongly changed by the different crystallization steps taken place at different temperatures.
The compatibilization of immiscible blends is necessary to obtain materials with optimum mechanical properties[5]. The improved compatibility results in a decrease of the interfacial tension between both blend components. The averaged particle size near the equilibrium state during the melt mixing is given by the relation[7]:

$$R_d = [(12/\pi)\, P_d\, v_d\, \sigma] \,/\, [\eta_m\, \gamma - (4/\pi)\, P_d\, v_d\, E_b] \qquad (2)$$

P_d is the probability that a collision will result in a coalescence, v_d is the volume fraction of the dispersed phase, η_m is the matrix viscosity, σ is the interfacial tension between matrix and dispersed phase, γ is the shear rate, and E_b is the macroscopic bulk breaking energy.

The Eq. (2) shows the direct correlation between dispersed particle size and interfacial tension determined by the degree of compatibilization. In this way, the appearance of fractionated crystallization can be used for an estimation of the degree of compatibilization and therefore for the efficiency of the *in-situ* interfacial reaction during processing.
In the present work blends of PA and PTFE were prepared by a reactive extrusion process. During processing a reaction can take place between the amino and amide groups of PA and the carboxyl groups of a micro powder PTFE which was produced by electron irradiation in air[8,9].

$$\begin{aligned} &R\text{-}[PA_1]\text{-}CO\text{-}NH\text{-}[PA_2] \;+\; PTFE\text{-}COOH \rightarrow \\ &R\text{-}[PA_1]\text{-}COOH \;+\; PTFE\text{-}CO\text{-}NH\text{-}[PA_2] \end{aligned} \qquad (3)$$

R is $-NH_2$ and/or $-NH-COCH_3$, and $PA_{1,2}$ are polyamide chain segments.
The chemical coupling of the components should result in an enhanced compatibility connected with a fine disperse morphology. DSC investigations were done to analyse the thermal behaviour of the blends with regard to the appearance of fractionated crystallization.

Experimental

Materials

The polyamides were PA6 mainly COOH-terminated (PA6), PA12 mainly COOH-terminated (PA12a) and PA12 mainly NH_2-terminated (PA12b). As Poly(tetrafluoroethylene) micro powder the commercial radiation degraded emulsion polymerizate PTFE-MP 1100 (Du Pont) was used. Special micro powders were produced from the emulsion polymerizate PTFE-TF 2025 (Dyneon) by electron irradiation in air. The radiation dose was varied as below: 500 kGy, 1000 kGy, and 2000 kGy. In general, the blend composition of PTFE/PA was 50/50 w/w. For the blend of PTFE-E (MP1100) with PA12a the composition was varied: 30/70, 50/50, and 70/30 w/w. The characteristic temperatures of the crystallization and melting of the initial polymers determined by DSC are summarized in Table 1.

Table 1: Characteristic temperatures of the blend components

sample	cooling		2nd heating
	$T_{c,m}$ (°C)	$T_{c,o}$ (°C)	T_m (°C)
PA6	172.8	181.8	221.2
PA12a	141.7	148.0	179.2
PA12b	137.7	148.6	180.5
PTFE-MP1100	312.0	315.7	324.0
PTFE-TF 2025 - virgin	312.2	318.0	324.4
PTFE-TF 2025 - 500 kGy	307.8	312.2	324.3
PTFE-TF 2025 - 1000 kGy	304.6	309.3	320.2
PTFE-TF 2025 - 2000 kGy	298.5	302.9	312.4

Preparation

For the preparation of the granules the blend components were mixed in the twin screw extruder ZSK 30 with the screw configuration A (high shear rate). The mass temperatures during extrusion were 255°C for the pure PA12 samples and 260°C for the blends PTFE/PA12. The pure PA6 was processed at a mass temperature of 270°C and the blends PTFE/PA6 at 285°C. Additionally, the blend of PTFE-TF 2025 (1000 kGy) and PA6 was extruded using the screw configuration B with a lower shear rate than A.

The tensile specimen were produced from the granules by injection moulding (Battenfeld BA 500) at mass temperatures similar to the extrusion.

DSC measurements

The thermal behaviour was investigated on a Perkin-Elmer DSC 7 with Pyris-software 3.51. The samples of (8±2) mg were measured in the temperature range from -30°C to 360°C at scan rates of +/- 20 K/min. The calibration of the device was done at 10 K/min with In and

Pb. The thermal lag amounts to only 0.2 K per 10 K/min change in the rate and was not corrected. For the comparison of the results the heat flow was given in W/g_{PTFE}. That means that the measured values were related in each case to the respective PTFE content.

Results

The blends PTFE/PA show three transitions which are demonstrated in Fig. 1. The crystal-crystal transition of PTFE from the triclinic to the hexagonal/pseudohexagonal modification occurs in the temperature range of 0°C to 30°C[10]. In the range from 150°C to 220°C the crystallization and melting of PA takes place. The endo- and exothermic effects above 250°C were caused by the solid-liquid transition of the PTFE phase.

The further considerations are focused on the crystallization behaviour of the PTFE component in the blend, since the correlation between crystallization and morphology is determined by the disperse PTFE phase.

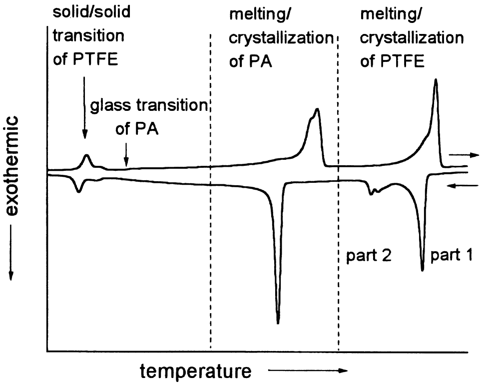

Fig. 1: Transitions in PTFE/PA blends

Influence of the blend composition on the crystallization behaviour of the PTFE phase

The changes in crystallization behaviour of PTFE in PTFE-MP1100/PA12a blends illustrated in Fig. 2 are remarkable. For PTFE contents ≤ 70 wt% (≈ ≤ 33 vol%) a second crystallization step (part 2) at about 265°C appears, additionally to the crystallization occuring at 312°C typically for the bulk behaviour (part 1). The value of the volume concentration shows that PTFE in these blends is the disperse phase. The part 2 represents PTFE particles finely dispersed and crystallized at the supercooling which is about 50 K higher than for the bulk state. The crystallization heat $\Delta H_{part\ 2}$ related to the PTFE content increases with decreasing

PTFE content. It should be mentioned that the melting behaviour is not remarkable influenced by the different crystallization behaviour. This is typically for the thermal behaviour in blends with fractionated crystallization[3]. The experimental values of the crystallization heat determined in the blends agree with the calculated values based on the transition heat of the pure polymers and their content in the blend. There is no effect of a mutual influence of the blend partners.

For the discussion of the correlation between fractionated crystallization and dispersity $\Delta H_{part\ 1}$ is plotted in Fig. 3 versus the PTFE volume content in the blend. Additionally, the total crystallization heat $\Sigma\Delta H = \Delta H_{part\ 1} + \Delta H_{part\ 2}$ is shown which is almost unchanged. $\Delta H_{part\ 1}$ increases linearly up to 30 vol% PTFE. The linear behaviour corresponds to the expected behaviour given in Eq. (2).

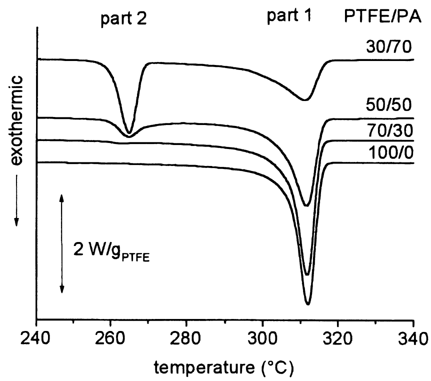

Fig. 2: Fractionated crystallization in blends of PTFE-MP 1100 with PA12a in dependence on composition

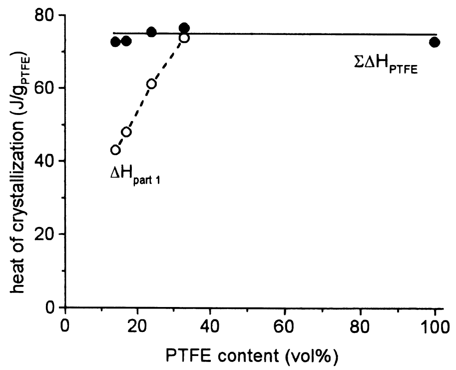

Fig. 3: Crystallization heat in dependence on PTFE-MP 1100 content
—●— $\Sigma\Delta H_{PTFE}$, —O—$\Delta H_{part\ 1}$

Influence of functionality of the PA component on crystallization behaviour of the PTFE phase

The influence of functionality of the PA on the thermal behaviour was investigated in PTFE/PA blends with a composition of 50/50 w/w. In Fig. 4 the cooling scan of the blend with PA12a which is mainly COOH-terminated is compared to the scan of the blend with PA12b which is mainly NH_2-terminated. The effect of the fractionated crystallization is strongly increased by using the PA12b. Only a small part of about 15% of PTFE particles crystallizes at 312°C. The most PTFE particles crystallize at 265°C (part 2). That means that a high degree of compatibilization was achieved by the *in-situ* reaction between the functionalized PTFE micro powder and the NH_2-terminated PA12b. Additionally, the blend of PTFE-MP 1100 with PA6 was investigated. Both the PA12a and the PA6 were mainly COOH-terminated. The behaviour of the PTFE-MP 1100/PA6 blend is similar to that with PA12a in relation to the PTFE crystallization. The results mean that in blends with COOH-terminated polyamide the PTFE show a reduced tendency of fractionated crystallization compared to blends with NH_2-terminated polyamide. Apparently, the interfacial reaction or amidization reaction of NH_2-groups of PA with the COOH-groups of PTFE is prefered.

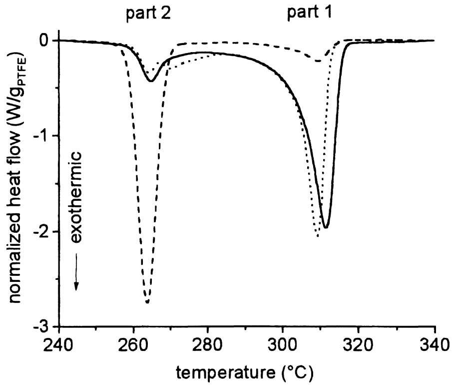

Fig. 4: Influence of functionality of PA on the fractionated crystallization in 50/50 w/w blends with PTFE-MP 1100
—— PA12a, - - - PA12b, ········ PA6

Influence of the irradiation of PTFE on the crystallization behaviour of the PTFE phase

It is known that irradiation of PTFE results in an enhanced functionality, a decrease in molecular weight and a decrease in particle size[11]. The averaged particle size decreases from 210 μm for the virgin PTFE-TF 2025 to 5 μm for PTFE irradiated with 500 kGy, and to 3 μm with ≥ 1000 kGy. An enhanced compatibilization in the blends with PA should result in an increased part 2 of PTFE particles crystallized at higher supercooling. The melting and crystallization behaviour of pure PTFE irradiated at various radiation doses is shown in Fig. 5a. The characteristic temperatures decrease due to the reduced molecular weight. In Fig. 5b the crystallization behaviour of the radiated PTFE phase in the reactive blends 50/50 (w/w) is shown. The samples used were tensile specimens. The initial state with unradiated PTFE-TF 2025 is not given because such blend cannot be produced.

The second crystallization step characteristically for the fractionated crystallization appears in the temperature range at about 270°C. Both the crystallization temperature of part 1 and part 2 decreases with increasing radiation dose. It is remarkable that the second crystallization step (part 2) is splitted into two overlapped steps. This is apparently typical for the PA6 used because that tendency can already be observed for PTFE-MP1100/PA6 = 50/50 (w/w) measured on granules (see Fig. 4). Whether or not other types of active heterogeneous nuclei exist in this PA 6 responsible for the observed behaviour is not clear at present. Further investigations are in progress. The difference of the supercooling necessary for the crystallization of the part 1 and 2 is almost independent of the radiation dose. For the first step in part 2 a value of about 36 K was determined. In Fig. 6 the crystallization heat $\Delta H_{part\ 1}$ of PTFE particles with bulk behaviour related to the whole crystallization heat of PTFE is shown in dependence on the radiation dose. The decrease confirms the expected behaviour because the particle size decreases directly by the radiation as well as indirectly by the enhanced compatibilization. At a dose of 2000 kGy the crystallization in this temperature range is almost suppressed.

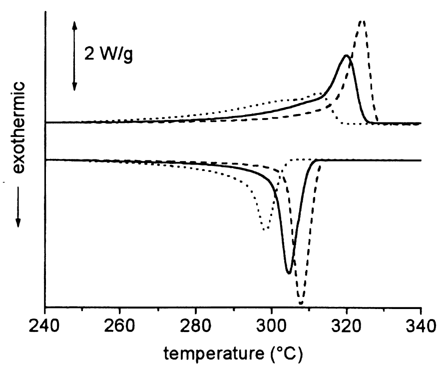

Fig. 5a: Melting and crystallization behaviour of pure PTFE-TF 2025 in dependence on radiation dose
– – – 500 kGy, —— 1000 kGy,
········· 2000 kGy

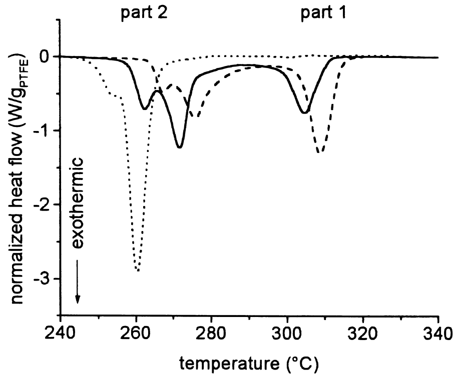

Fig. 5b: Crystallization behaviour of radiated PTFE in blends with PA6 in dependence on radiation dose
– – – 500 kGy, —— 1000 kGy,
········· 2000 kGy

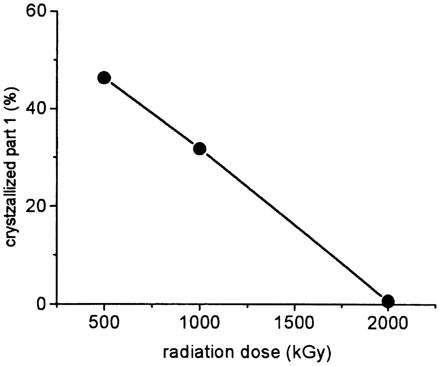

Fig. 6: Decrease of bulk crystallization (part 1) in dependence on radiation dose

Influence of the shear rate during the extrusion on the crystallization behaviour of PTFE phase

Independent of the compatibilization by the interfacial reaction the shear rate should influence the size and distribution of the dispersed phase (see Eq. (2)). Therefore, the blend PTFE-TF 2025 (1000 kGy)/PA6 = 50/50 (w/w) was additionally extruded with the screw configuration B instead of A, and thus at a lower shear rate. The influence of the various shear rate during the extrusion was investigated on tensile specimens (see Fig. 7) injection moulded under the same conditions. A decrease of the degree of fractionated crystallization was found indicating the influence of the shear rate which is preserved during the injection moulding followed.

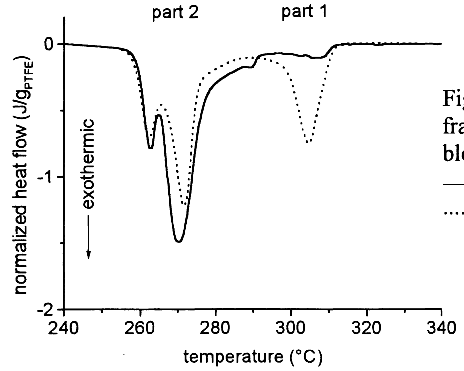

Fig.7: Influence of shear rate on the fractionated crystallization in the 50/50 (w/w) blend of PTFE-TF 2025 (1000 kGy) with PA6
—— screw configuration A (high shear rate)
········ screw configuration B (low shear rate)

Conclusions

It is known that the particle size of the dispersed blend component is dependent on the shear rate during processing and the volume content of the dispersed blend component (Eq. (2)). The investigations of the influence of the parameters mentioned above on the degree of fractionated crystallization in PTFE/PA blends show that in these blends an unambiguous correlation exists between the degree of fractionated crystallization and the number of dispersed PTFE particles with a size lower than a critical value.

In this way, the degree of the fractionated crystallization is a helpful tool for the estimation of the efficiency of the *in-situ* reaction causing the compatibilization of the blend components. It was found that the degree of the fractionated crystallization increases by using NH_2-terminated PA instead of COOH-terminated PA and by using PTFE with increased functionality as a result of increased radiation dose.

Summarizing, the DSC analysis of compatibilized blends with a semicrystalline, dispersed component can be used to characterize qualitatively the blend morphology state. Particularly, changes to a finely dispersed blend morphology in dependence on the compatibilization during reactive extrusion of functionalized polymers could be shown. This method is a simple way for a first characterization, and sometimes the only way of characterization, when difficulties exist for the preparation of images.

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