ORIGINAL CONTRIBUTION

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Irreversible structural changes in cryogenic mechanically milled isotactic polypropylene

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Abstract The influence of cryogenic mechanical milling on the structure and the thermal behavior of isotactic polypropylene was investigated by means of wide-angle X-ray scattering, differential scanning calorimetry and transmission electron microscopy. The results presented show that structural changes caused by mechanical milling at cryogenic temperatures are only partly reversible. The decrease in the degree of crystallinity as determined by differential scanning calorimetry with increasing milling time is attributed to a reversible transformation of the initial morphology into a "nanostructured" morphology, consisting of small "fragments" of the original isotactic polypropylene lamellae. During recrystallization from the molten state, there still exists an influence of the previous milling treatment, leading to significantly changed crystallization behavior. The reason for this behavior might be a decrease in the molecular weight or a change in the molecular weight distribution or the formation of long-chain branched polypropylene molecules induced by cryogenic mechanical milling.

Keywords Cryogenic mechanical milling · Polypropylene · Transmission electron microscopy · Nanostructure · Differential scanning calorimetry

Introduction

Recently, interest in the effect of mechanical milling (MM) and mechanical alloying (MA) of polymers has increased considerably. It is supposed that the alteration of physical and/or chemical properties in the solid state by MM and MA offers a valuable, cost-effective and, as in the case of postconsumer plastic waste recycling, a friendly to the environment route to produce tailored functionalized materials from already existing materials [1, 2, 3, 4]. Especially in the field of polymer blends MA has attracted much attention with superior advantages compared to the conventional melt blending techniques [5, 6, 7, 8, 9, 10]. Often phase separation occurs during melt blending, owing to the inherent immiscibility of most polymer systems, resulting in coarse morphologies with, for example,

poor mechanical properties. Therefore, often compatibilizers in form of copolymers are used, but suitable compatibilizers are not always available [11, 12]. The attempt to produce and stabilize homogeneous alloys at a molecular level by MM demands, in the case of multicomponent polymer systems, a dramatic reduction of chain mobility to prevent phase separation and the generation of free radicals by chain scission [13]. The latter could (1) promote chemical coupling of different species, often termed in situ compatibilization [14, 15], (2) chemical cross-linking of a single polymer species or (3) lead to a change of the molecular weight and the molecular weight distribution [16, 17, 18]. The aim of this work is to investigate the effect of cryogenic MM on the structure and the thermal behavior of isotactic polypropylene (iPP) in order to verify the use of these techniques to produce modified iPP as a precursor

material for future applications in polymer blending by cryogenic MM.

Experimental

Materials and sample preparation

A commercial grade of iPP (Novolene 1100H) was kindly supplied by the BASF Ludwigshafen, Germany, in the form of pellets and was used without further purification. Polymer pellets (1g) were placed in a hardened steel grinding vial (sample capacity maximum 4 ml) together with a 32 g steel impactor. The vial assembly and the polymer pellets were chilled to liquid nitrogen temperature in a SPEX Certiprep 6850 freezer/mill coupled with a liquid nitrogen autofill system (SPEX 6820) and pulverized by shuttling the steel impactor back and forth magnetically inside the stationary grinding vial. Since the vial is completely immersed in liquid nitrogen throughout the grinding process, the sample is kept at cryogenic temperatures. Grinding under these conditions results in fine polymer powders, even after milling times as short as 3 min.

The special design of this mill allows us to perform programmed milling experiments on up to four samples simultaneously under exactly the same operating conditions, including milling temperature, milling frequency, R, and milling time, t_m. In this investigation the following milling program was applied for all samples. Before milling, the vials containing the polymer pellets were allowed to cool to liquid nitrogen temperature and were maintained at this temperature for 10 min. Then, milling was started for a different number of milling periods, each 3 min long, and these periods were interrupted by pauses of 2 min for recooling. A milling frequency of 15 Hz was chosen for all milling experiments. In order to detect possible oxidative degradation during milling IR spectrometry was performed on the milled as well as the original materials.

No differences between the IR-spectra of the milled and unmilled samples were detected, indicating the absence of any oxidative degradation originating from cryogenic MM.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) was performed using a DSC-2910 from TA-Instruments coupled with a TA-2000 control system. Temperature calibration was done with Ga, In and Sn with an error of ± 0.5 °C. Each sample was heated from -40 to 220 °C at a heating rate of 10 °C/min. After that, the samples were kept isothermally at 220 °C for 5 min in order to erase the previous thermal history before cooling them to room temperature with a cooling rate of 5 °C/min. To ensure good thermal conductivity, the pulverized polymer samples were put in standard aluminium sample pans and additional aluminium lids were used. For all experiments the sample weight was kept nearly constant at 7 ± 0.2 mg and all DSC-scans were performed under a nitrogen atmosphere in order to prevent oxidation.

Wide-angle X-ray scattering observations

In addition, Wide-angle X-ray scattering (WAXS) patterns of the iPP samples were recorded at ambient temperature using a Philips PW1140/90 goniometer using Ni-filtered Cu Kα radiation to examine whether milling leads to structural changes in iPP. The as-milled polypropylene powders were placed on a sapphire plate fixed in a custom-made metal frame. This assembly ensures a reproducible sample thickness of approximately 300 μm. Films were prepared by compression-molding the pulverized iPP samples; for comparison a sample from the original iPP pellets was prepared to investigate whether milling leads to irreversible structural changes. To ensure exactly the same thermal treatment during the film-preparation, the polymer powders were placed between two glass slides and transferred into a hot press (preheated to 220 °C) and pressed with low pressure (less than 5 MPa). At this temperature the samples were kept for 5 min to erase the previous thermal history before the resultant films were slowly cooled to ambient temperature.

Transmission electron microscopy

Thin films for direct transmission electron microscopy (TEM) observation were obtained by the following procedure. The milled iPP samples and for comparison the original iPP sample were dissolved in boiling o-xylene. The dilute polymerxylene solution (with a concentration of 0.15% w/v) was dropped onto the surface of glycerol at 100 °C. After evaporation of the solvent, the resultant thin polymer films (60–80 nm) were floated onto the surface of water and transferred onto electron microscope copper grids.

Morphological observations were performed using a Philips CM200 transmission electron microscope operated at 200 kV. Bright-field electron micrographs of the thin films were taken by defocusing in order to enhance the contrast between the crystalline and the amorphous phase [19].

Experimental results and discussion

Influence of MM on iPP

Wide-angle X-ray scattering

WAXS data obtained for the original iPP sample (reference) and the cryogenic mechanically milled samples for different milling times, t_m, are presented in Fig. 1. In the reference only the monoclinic α form can be detected; no evidence of any phase transformation due to the cryogenic MM was observed. At the beginning of the
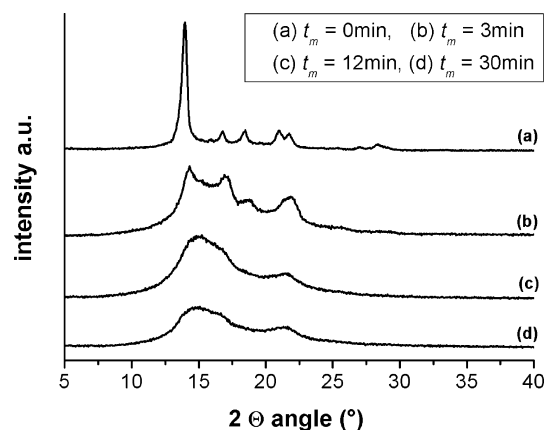

Fig. 1 X-ray diffraction patterns of isotactic polypropylene (*iPP*) samples after cryogenic mechanical milling (*MM*) for different milling times, t_m, including the X-ray plot of the original material (sample a)

milling experiment (sample b) all diffraction peaks undergo a broadening and after $t_m = 12$ min (sample c) no distinguishable diffraction peaks can be observed anymore. Two possible explanations for the absence of any diffraction peaks are reasonable: on the one hand, the initial size of the crystals in the reference sample is markedly reduced during cryogenic MM; on the other hand, prolonged milling leads to a remarkable amorphization of the original semicrystalline iPP. Therefore WAXS is no longer a valuable method capable of revealing an assumed nanostructure in the milled materials.

Differential scanning calorimetry

To investigate whether the thermal behavior of the samples is affected by cryogenic MM, DSC-measurements of samples milled for different milling times were performed with a constant heating rate of 10 °C/min. The influence of t_m at liquid nitrogen temperature on the melting is shown in Fig. 2. For comparison, a plot of the "original" iPP (no milling treatment was applied to sample a) is presented and taken as a reference for fur-
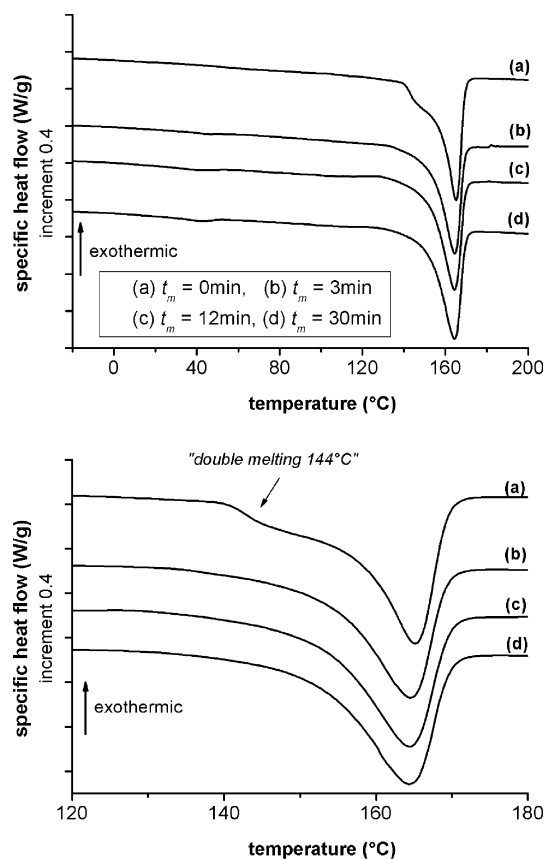
ther discussion. First of all, it is apparent that, although no hints for exothermic transitions or any cold-crystallization can be detected in the DSC traces, all the milled samples exhibit well-defined melting peaks with a maximum, T_m, around 164 °C, independent of the milling program applied. If milling leads to nearly complete amorphization of iPP, as suggested by other authors [20], one would expect either cold-crystallization when the sample is heated above its glass-transition temperature or the absence of any melting peaks if MM promotes cross-linking or degradation. The latter refers to modifications induced by the formation of free radicals during milling and, as a consequence, the configuration of the macromolecules is changed irreversibly.

A close inspection of the melting peaks gave evidence for progressive structural changes in the milled materials with increasing milling time. In accordance with the results from the X-ray experiments, a distinct decrease in the melting enthalpy, ΔH_m, with increasing t_m can be observed and can be attributed to a lower degree of crystallinity in the milled materials. The crystallinity, χ_{cm}, of the sample milled for 30 min decreases by approximately 16% compared to the original material (sample a)[1]. All the thermal data obtained by analyzing the DSC traces are summarized in Table 1. Moreover, the shape of the melting endotherms of the milled samples differs markedly compared to that of the reference sample. Whereas the reference sample exhibits the "double-melting phenomenon", indicated by the occurrence of a shoulder around 144 °C during heating, the milled samples (samples b–d) show only one distinct melting peak. The "double-melting" phenomenon in the α-crystalline form of iPP and its possible relation to structure was widely discussed by several authors [22, 23]. In this investigation mainly the alteration of the melting behavior related to changes in the degree of crystallinity induced by cryogenic MM was taken into account.

However, it might be that during milling the "original" spherulitic morphology consisting of the well known cross-hatched lamellae arrangement in α-iPP [24, 25], usually present under most crystallization conditions and verified by TEM micrographs shown later and our WAXS data of the reference and the melt-crystallized samples (Figs. 1, 3), is transformed into a nanocrystalline morphology where only very short fragments of the original lamellae are present. This also could be a reasonable explanation for the observed changes of the X-ray diffraction patterns shown in Fig. 1. Especially the absence of any crystalline reflection peaks after a

Fig. 2 Differential scanning calorimetry (*DSC*) thermograms of cryogenic MM materials. The heating rate was 10 °C/min

[1] The crystallinity values χ_{cm} and χ_{cc} were determined by integration of the melting or crystallization peak areas and normalizing the resulting enthalpy values ΔH_m or ΔH_c to the specific enthalpy ΔH_m^0. The value ΔH_m^0(iPP) = 209 J/g was taken from the literature [21]

Table 1 Characteristic thermal data and degree of crystallinity values determined by differential scanning calorimetry

Sample	Milling time (min)	Heating cycle			Cooling cycle		
		T_m (°C)	ΔH_m (J/g)	χ_{cm} (%)	T_c (°C)	ΔH_c (J/g)	χ_{cc} (%)
iPP	0	165.16	108.1	52	115.23	95.63	46
iPP_R15_3 min	3	164.46	93.90	45	116.90	94.64	45
iPP_R15_12 min	12	164.46	89.49	43	117.33	99.51	48
iPP_R15_30 min	30	164.39	90.82	43	121.03	101	48

milling time of $t_m = 30$ min (sample d) together with the existence of a melting endotherm in the DSC trace give strong evidence for the previously mentioned transformation into a nanocrystalline morphology.

Reversibility of the observed structural changes

In order to reveal whether milling of iPP under cryogenic conditions leads to irreversible structural changes, additional DSC and WAXS experiments were conducted on melt-crystallized samples (see Experimental section).

Wide-angle X-ray scattering

The X-ray diffraction pattern of the milled samples after melt-crystallization (samples b–d) and for comparison a plot of the reference iPP (sample a) are shown in Fig. 3. Again, only the monoclinic α form of iPP can be observed independent of the previous milling treatment. Regarding the intensity relation of the diffraction peaks located at $2\theta = 13.83°$ (110), 16.9° (040) and 18.34° (130) a significant change can be observed, although the thermal treatment and the thickness of samples a–d were the same. Moreover, the decrease of the (110) reflection with increasing t_m is noticeable. It might be that at least some of the structural changes induced by cryogenic MM are irreversible, owing to the fact that all the
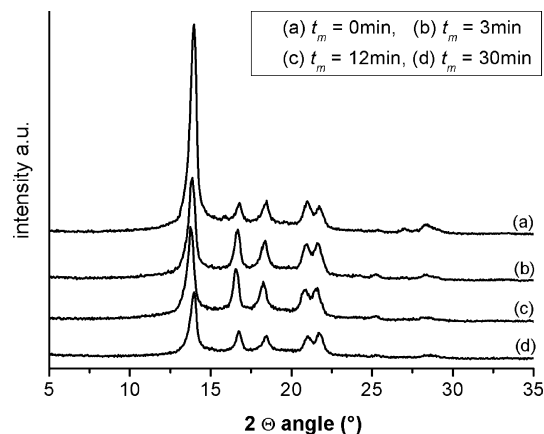
samples were crystallized from the molten state, which usually means the complete erasure of the previous thermal history.

Differential scanning calorimetry

Additional DSC-measurements were performed to clarify whether crystallization of iPP from the molten state is affected by cryogenic MM. The DSC traces obtained by cooling the samples from 220 °C to ambient temperature with a constant cooling rate of 5 °C/min are shown in Fig. 4. Significant changes in the nonisothermal crystallization behavior of iPP with increasing t_m can be observed, namely, the onset of crystallization is shifted to higher temperatures, resulting in an increase of the maximum of the crystallization peak, T_c. Moreover, the calculated degree of crystallinity χ_{cc} of sample d increased slightly by 5% compared to the reference sample (Table 1). These results show clearly that cryogenic MM indeed leads to irreversible structural changes in iPP. The fact that all the milled samples exhibit well-defined crystallization peaks and that increasing t_m leads to slightly higher values of χ_{cc} is clear evidence for the absence of cryogenic MM induced cross-linking of the iPP chains owing to the formation of free radicals. One explanation for the changed crystallization behavior is that iPP undergoes a decrease of its molecular weight or a change of the molecular weight distribution by milling under cryogenic conditions [16, 17]. Crystal nucleation and growth is known to be very sensitive to the
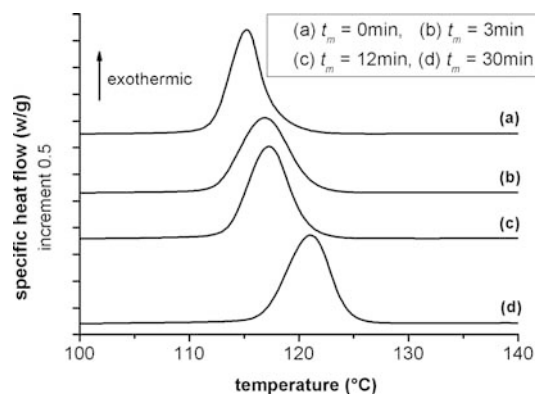

Fig. 3 X-ray diffraction patterns of compression molded iPP samples, after cryogenic MM for different milling times t_m

Fig. 4 DSC cooling curves of iPP samples, after cryogenic MM for different t_m. The cooling rate was 5 C/min

molecular weight and the molecular weight-distribution, but there is still a contrary discussion in the literature about how the overall crystallization rate is affected by changes of the molecular weight [26, 27] and molecular weight-distribution [28].

Another explanation for the higher degree of crystallinity χ_{cc} and the increase of recrystallization temperatures with increasing t_m (Table 1) could be the formation of long-chain branches owing to cryogenic MM. Rätzsch et al. [16] published an excellent review article on the modification of iPP initiated by radical reactions in the solid state. They report that long-chain branched polypropylene products, prepared by electron-beam radiation or chemical modification of iPP, can be used as nucleation agents for linear polypropylene in low concentrations.

Transmission electron microscopy

TEM micrographs were taken from the milled and the original polymers to exclude cross-contamination during milling (e.g. metal particles originating from the grinding vial or the impactor) which might lead to additional heterogeneous nucleation. TEM micrographs of solution cast iPP films crystallized at 100 °C are shown in Fig. 5. In both cases the micromorphology of the samples consists of a cross-hatched arrangement of iPP lamellae in an iPP spherulite, often cited in the literature [24, 29, 30]. No significant differences can be observed between the sample milled for 30 min (Fig. 5b) and the original sample (Fig. 5a). Moreover, no metallic contamination due to the milling treatment could be found. However, comparing the microstructures of both samples more carefully, one might speculate, that the milled sample (Fig. 5b) develops a slightly higher degree of crystallinity as seen by a higher cross-hatched density, although both samples were prepared under identical crystallization conditions. Such an observation is in good agreement with the calculated crystallinity values (Table 1) obtained by DSC.

Conclusions

Our results reveal a strong influence of cryogenic MM on the structure and the thermal behavior of iPP. With increasing milling time (up to $t_m = 12$ min) all diffraction peaks of the monoclinic α form of iPP undergo distinct broadening. No distinguishable diffraction peaks could be observed after longer milling times. The melting behavior investigated by DSC for different milling times gives evidence for progressive structural changes in the milled materials with increasing milling time. A distinct decrease in the melting enthalpy with increasing t_m can be observed and can be attributed to a lower degree of crystallinity in the milled polymers.
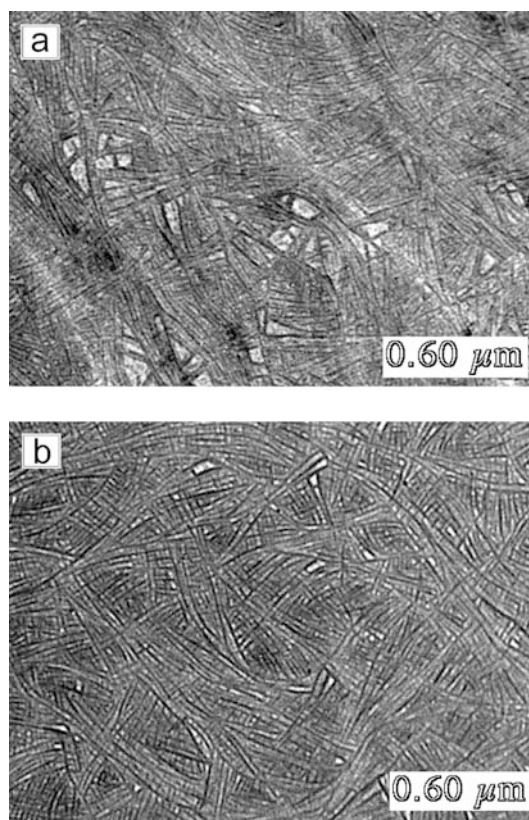

Fig. 5a, b Bright-field electron micrograph of **a** an original iPP sample cast on glycerol surface at 100 °C and **b** an iPP sample after cryogenic MM for 30 min, prepared under the same conditions as sample a

We assume that the "original" spherulitic morphology consisting of a cross-hatched lamellae arrangement in α-iPP is transformed during milling into a nanocrystalline morphology with only very short fragments of the original lamellae.

It was shown that milling of iPP under cryogenic conditions leads to irreversible structural changes. To our knowledge, it is the first time it has been reported that even during recrystallization of cryogenic mechanically milled samples from the molten state there is still an influence of the milling treatment on the crystallization. Regarding the intensity relation of the diffraction peaks, a significant change could be detected, in particular, a decrease of the (110) reflection with increasing t_m. The onset of crystallization is shifted to higher temperatures, resulting in an increase of the maximum of the crystallization peak (T_c) accompanied by a slight increase in the degree of crystallinity.

Therefore, structural changes induced by cryogenic MM are only partially irreversible. It might be that iPP undergoes a decrease of its molecular weight or a change of the molecular weight distribution by milling under cryogenic conditions. Also the formation of long-chain

branched polypropylene molecules is considered to be responsible for the changed crystallization behavior. However, the mechanisms by which cryogenic MM alters the molecular structure of the materials are still unclear and should be clarified by further microstructural investigations. Additional work on other homo-polymers and polymer blends will be published in a forthcoming paper.

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