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Cryogenic mechanical milling of high density polyethylene

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Abstract: HDPE was analyzed after being submitted to cryogenic mechanical milling (CMM) by X-ray diffraction (WAXS), polarized light microscopy and differential scanning calorimetry (DSC). After CMM, besides the known phase transformation of the orthorhombic PE crystals into the monoclinic modification, slight changes in the melting and crystallization behavior as well as an unexpected increase in crystallinity were observed. The observed results can be explained by assuming a solid/solid phase transition as the responsible mechanism.

Introduction

Mechanical milling is a powerful non-equilibrium processing method for synthesizing a variety of stable and metastable materials [1]. The formation of nano-structured intermetallics as processed by mechanical attrition, used in order to provide changes in their structure and / or microstructure has been reported [2, 3]. It is a solid-state technique involving repeated welding, fracturing of particles, originally developed to produce oxide-dispersion strengthened nickel- and iron-based superalloys for applications in the aerospace industry [4].

If a polymer is mechanically milled, it is expected that the stress applied to the material is released by molecular place changes of the amorphous phase. Effective milling of polymers demands that molecular chain motion is restricted, i.e. the process should take place below the glass transition temperature (T_g) of the material. So, for polymers mechanical milling at very low or cryogenic temperatures is a suitable process to effectively submit the polymer molecules to the mechanical stress imposed, avoiding chain slippage and molecular place changes.

It is reported that some polymers undergo crystalline phase transitions due to mechanical milling whereas other polymers are simply amorphized [5-7]. For high-density polyethylene (HDPE), a crystalline phase change proceeds from the usual orthorhombic structure to the monoclinic one [8] when submitted to cryogenic mechanical milling (CMM). In the case of poly(vinylidene fluoride) (PVDF), it was found that CMM has the potential to transform PVDF from the usual α-phase into the β-phase crystal modification [8, 9]. The thermal stability was found to be high enough to sinter the obtained β-phase containing powders under a specified pressure and at a temperature slightly below the melting temperature to any contrivable bulky shapes.

The orthorhombic to monoclinic phase transformation was already observed in drawn HDPE by other authors (e.g., [10]). A similar change of the crystal structure was studied by Huang [11] under strong shear stress during pan-milling at ambient temperature. As yet different opinions exit on the transformation mechanism involved: diffusionless, i.e. by shear [12] or quasi-melting below the thermodynamic melting temperature followed by recrystallization of the monoclinic phase [13].

Although the influence of mechanical milling on HDPE at cryogenic temperatures was previously studied, a more detailed examination in this field is missing. Therefore, the aim of this work was to study more systematically the influence of CMM to HDPE using WAXS, light microscopy and DSC.

Results and discussion

X-ray analysis of the cryogenic-mechanically milled HDPE confirms that HDPE undergoes a crystalline phase transition, as expected [7]: During milling the orthorhombic phase gradually transforms into the monoclinic modification. As shown in Fig. **1** untreated polyethylene (HDPE OR) shows strong peaks at 2θ-values of 21,6° and 24°, corresponding to the $(110)_{\mathrm{ortho}}$- and $(200)_{\mathrm{ortho}}$-reflections of the orthorhombic crystal modification. After milling for only 10 min one observes significant peak broadening as well as the development of a new peak at 19,6°, which corresponds to the $(110)_{\mathrm{mono}}$-reflection of the monoclinic crystal modification. This new peak reaches its maximum intensity as compared to the $(110)_{\mathrm{ortho}}$-peak after milling for about 70 min. Longer milling leads to further peak broadening for both, but loss of intensity for the monoclinic phase relative to the orthorhombic one. The peak broadening can be attributed either to the reduction of PE lamellae crystal dimensions or to strong crystal lattice deformations. A rough estimate using the Scherrer equation and neglecting lattices stresses gives crystal dimensions for the orthorhombic phase ranging from about 30 nm in the untreated PE to 10 nm after 10 min of milling; the dimensions for the monoclinic crystals are slightly smaller. These numbers agree very well with those observed after pan-milling at ambient temperature [11]. From our x-ray diffraction it is not clear whether the overall crystallinity (total amount of crystals independent of their structure) is changed during the cryogenic milling.

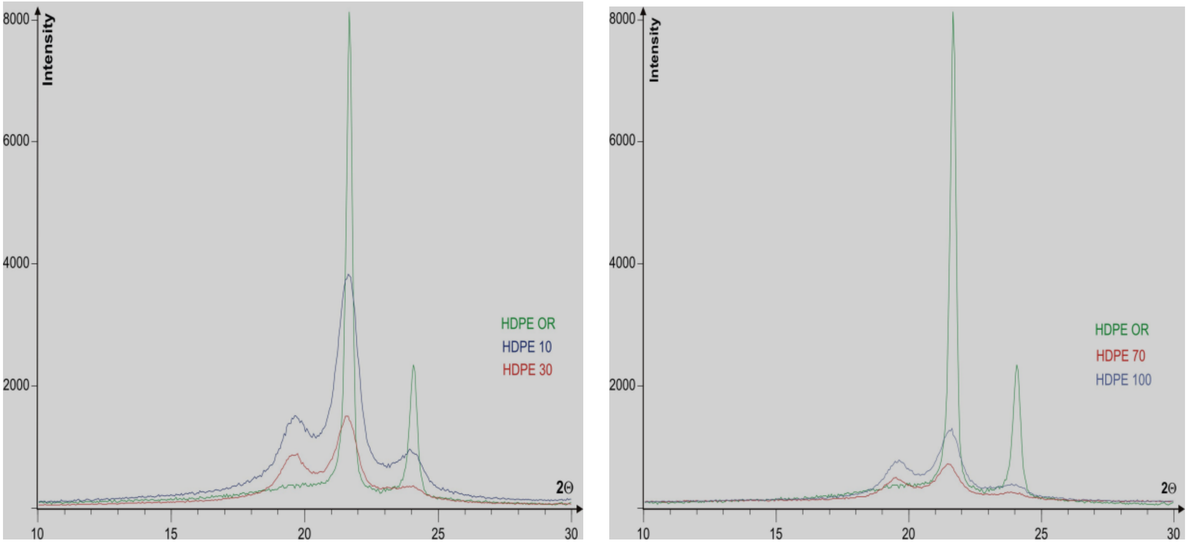

Fig. 1. X-ray diffractograms of untreated HDPE (HDPE OR) and cryo-milled HDPE (the numbers 10, 30, 70 and 100 give the total duration of the cryogenic milling process in minutes).

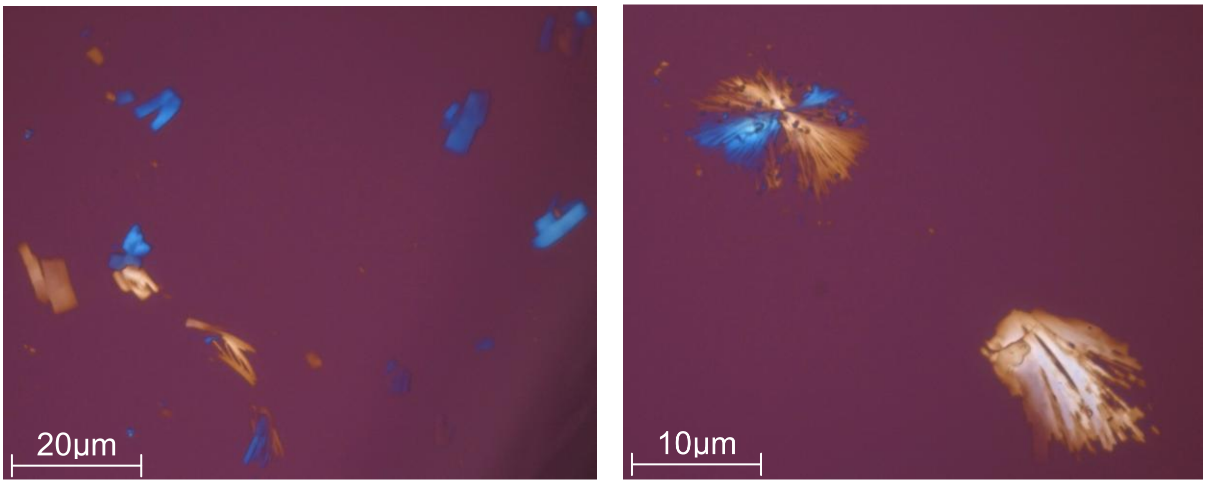

Fig. 2. Cryogenic milled HDPE 30 (polarized light microscopy / suspension of milled powder in optical immersion oil) showing single particles consisting of highly oriented fragments and radially oriented centers of former spherulites.

The characterization of the milled HDPE using polarized light microscopy reveals a decreasing particle size with increasing milling time. After milling for 30 min (see Figure 2) particles show a high degree of uniaxial orientation, except for some few particles which exhibit a radial orientation, similar to that of small spherulites. It looks like these particles are fragments of the former spherulitic morphology of HDPE.

Tab. 1. Thermal data of HDPE specimens determined by DSC.

	1st heating cycle		*Cooling cycle*		*2nd heating cycle*	
	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
HDPE 100	133.4	195.8	120.3	210.9	131.9	223.1
HDPE 70	133.3	172.1	119.8	185.3	132.6	197.1
HDPE 30	132.1	159.0	120.0	192.6	133.1	199.5
HDPE 10	131.5	168.3	119.9	196.4	133.3	198.8
HDPE OR	134.0	149.0	118.7	175.8	136.2	191.1

The thermal data taken from DSC measurements are shown in Table 1. Strangely it is observed that the endothermic enthalpy of fusion (ΔH_m) of the cryo-milled HDPE increases with increasing duration of the milling process. A slight increase in crystallinity of cryo-milled iPP during renewed crystallization was previously observed [14], but it is not of the authors' knowledge that a milled material exhibits higher values of ΔH_m at the first heating scan. Moreover, this tendency is observed not only in the first (

Fig. 3), but also in the second heating cycle (Fig. 5), which indicates irreversible structural changes of PE due to the cryogenic milling. During the first heating cycle this increase in ΔH_m is more pronounced: HDPE 100 shows an increase of more than 30%, HDPE 70 of at least 15%. During the second heating cycle there is still a difference of about 16% observed between HDPE 100 and the original HDPE. Samples which exhibit higher heats of fusion ΔH_m also exhibit higher values for the heat of crystallization ΔH_c.

In addition all cryogenic-mechanically milled specimens are observed to melt during the second heating cycle about 3°C earlier than the unmilled reference. In the case of the 100 min milled PE (HDPE 100) this difference is almost 5 °C. Furthermore, the crystallization of the molten CMM-treated PE starts about 1°C higher as compared to unmilled HDPE.

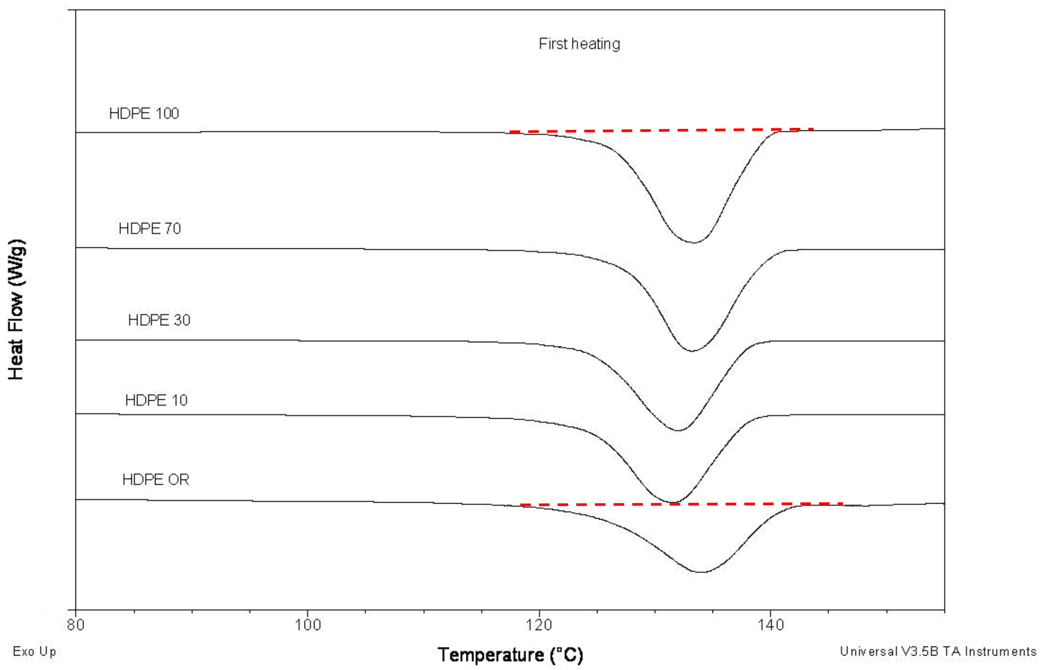

Fig. 3. DSC thermograms of HDPE specimens during the first heating cycle.

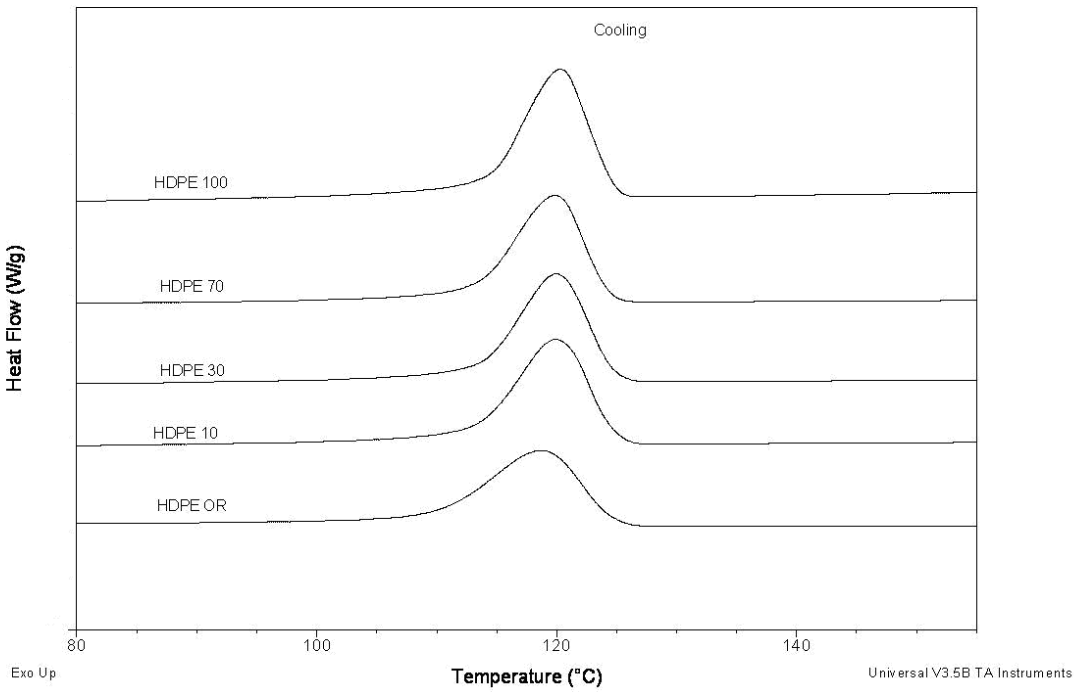

Fig. 4. DSC thermograms of HDPE specimens during the cooling cycle.

The observed increase in ΔH_m during the first heating cycle could be explained either by an increase of the crystallinity of the material or attributed to a higher value of ΔH_m for the monoclinic phase. But as this phenomenon is also seen at the second heating scan, it cannot be due to just a ΔH_m difference between the two crystalline phases, as the orthorhombic phase is restored after renewed crystallization. This unexpected increase of crystallinity could be explained by amorphization and degradation of the HDPE to a lower M_W material. Such a degradation by CMM into a material with lower M_W was already confirmed in iPP [8]. Subsequent recrystallization would take place when the polymer is brought to room temperature, well above its T_g of about -100 °C. On the other hand, as shown in Figure 2, evidence has been found that the particles of the cryo-milled PE are oriented and are probably former parts of the spherulitic HDPE morphology. This indicates that the observed phase transition of the PE crystals is a solid/solid transformation. If there would be an intermediate step of amorphization, the polymer should crystallize due to the strange nucleation conditions (low growth rate and high nucleation rate slightly above T_g) in a morphology with very small crystallites and no single-crystalline-like orientation would be found.

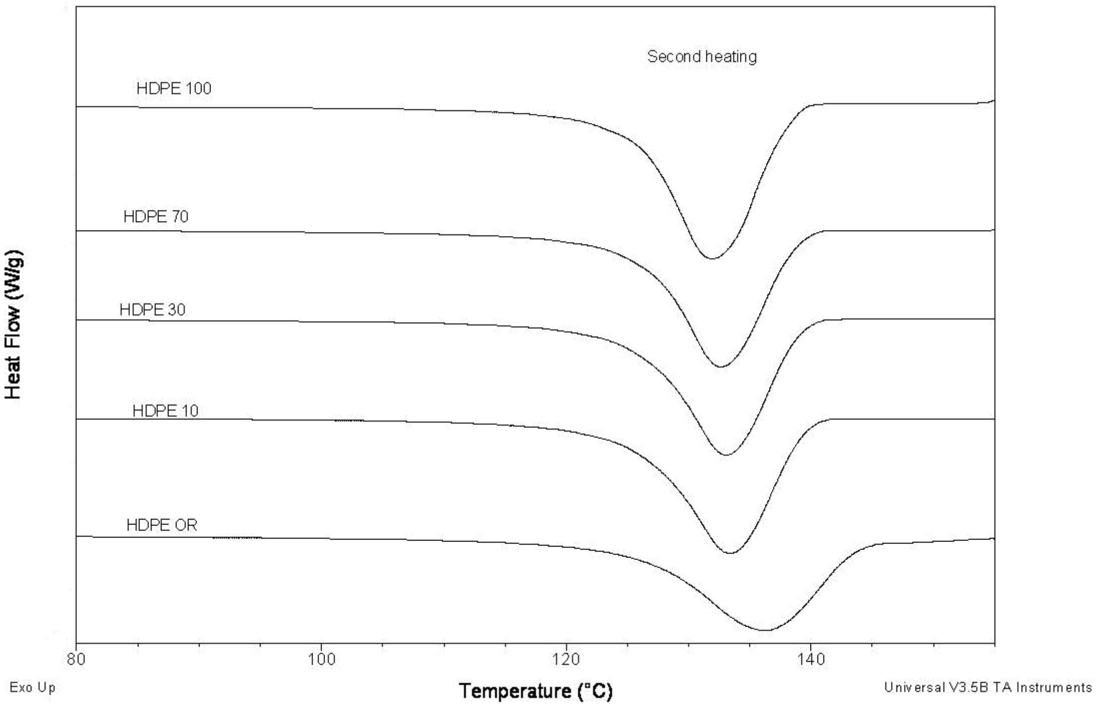

Fig. 5. DSC thermograms of HDPE specimens during the second heating cycle.

Based on the observed effects during cryogenic mechanical milling, in particular the increase in crystallinity as indicated by the significant larger heat of melting, we suggest that the milling process results in a solid/solid phase transition of the PE crystals. Under the assumption that the reaction to the applied mechanical energy on the polymer is related to that one applied by electron beam irradiation, it is presumed that forced by the all-trans conformation of the PE chains, the excessive amount of impact energy may be delocalized out of the crystals into the neighboring amorphous phase. This would lead to chain scission and M_w degradation. Due to this selective decrease of M_w in the amorphous phase, the degree of entanglements decreases so that defect-free polymer segments which were hindered by entanglements are allowed to attain crystallization. Both lamellae thickening of the already existing crystals as well as additional crystallization in form of small micellar crystals in the amorphous phase are conceivable. The latter is quite likely to take place because of the very small size of critical nuclei at such low temperatures. This hypothesis is able to explain the increase in crystallinity as well as the increase of crystallization temperature. It also can be assumed that the increase in crystallinity is limited to the orthogonal phase, thus leading to the observed loss of intensity for the monoclinic phase relative to the orthorhombic one after very long milling times. The slight decrease of the melting temperature, especially observed after shorter milling times, may be explained by fracture of PE-lamellae crystals to smaller dimensions. Such a change in the crystal dimensions is confirmed by the Scherrer analysis as shown above.

Experimental part

The polymer used was HDPE Lupolen 6021 D from Basell Polyolefins. One gram of the polymer was placed in a hardened steel grinding vial (sample capacity max. 4 ml) together with a 32 g steel impactor. Four vials were used simultaneously. The vial assembly was chilled to liquid nitrogen temperature in a SPEX Certiprep 6850 Freezer/Mill coupled with a liquid nitrogen auto-fill system (SPEX 6820). The vials were completely immersed in liquid nitrogen throughout the grinding process. The polymer was pulverized by shuttling the steel impactor back and forth magnetically inside the stationary grinding vial with a frequency of 15 Hz.

Before starting the milling process all samples were allowed to cool down by liquid nitrogen to 77 K and maintained at this temperature for 15 minutes. Between the milling cycles the samples were allowed to re-cool for 2 minutes before starting the next cycle. The milling time in each cycle was 1, 3, 7 or 10 minutes, respectively. The number of cycles was 10; so, the samples were milled for 10, 30, 70 and 100 minutes, respectively. After cryogenic mechanical milling all samples were dried in an oven at 50 °C for 2 hours in order to remove any condensed water; there was no evidence for any significant structural changes during this treatment.

WAXS diffractograms of the mechanically milled HDPE were recorded at ambient temperature using a Philips PW1140/90 goniometer and Ni-filtered CuK_α radiation.

For optical microscopy (Leitz polarized light microscope) suspensions of milled powder in optical immersion oil were used.

DSC was performed on a TA-Instruments DSC-2920. The sample mass used was around 5 mg. The samples were either powder or cut parts of pellets (in the case of the unmilled original polymer). In the last case, care was taken in order to achieve good contact between sample and sample holder.

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