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A STUDY OF MILLING OF PURE POLYMERS AND A STRUCTURAL TRANSFORMATION OF POLYETHYLENE

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Abstract

We investigated possible physical and chemical changes in inert polymers by means of mechanical milling. No chemical changes were observed. However, in polystyrene we found two glass temperatures after milling, in contrast to one glass temperature in the original material. Under certain conditions crystalline polyethylene transformed almost completely from the orthorhombic to the monoclinic structure.

Introduction

High-energy ball milling has been used widely during the past decade for mechanical alloying (MA) of metallic systems, i.e. starting from a mixture of elemental powders and for mechanical milling (MM) of metallic systems, i.e. starting from pre-alloyed intermetallic compounds [1,2]. MA leads to alloying on an atomic level in many cases and even it turned out to be possible to alloy immiscible metallic binaries. In intermetallic compounds MM induces atomic disorder in the early stage of milling and eventually a phase transformation may follow. Pure metals do not show a phase transformation, but become nanocrystalline (see, e.g. [1]).

In contrast to the many studies on metallic systems, ball-milling experiments on polymers seem to be scarce [3,4]. In these scarce studies, on the one hand degradation of polymers by ball milling as a result of chain scission was reported [4], on the other hand mechanical milling of ABS (Acrylonitrile-Butadiene-Styrene) rather resulted in a small increase in the weight-average molecular mass than in a decrease [3]. In the same study [3] the alloying of normally incompatible polymer mixtures by MA was claimed. The possibility of producing amorphous powders of polymer mixtures by MA was reported by [5].

It was the aim of the present study to investigate possible chemical and physical changes by mechanical milling in a number of simple polymers.

Experimental procedures

For the milling of inert polymers two types of mills were used. The first mill is an improved design of a home-built vibratory mill, consisting of a stainless steel vial with an inner diameter of 6.5 cm and one hardened steel ball, with a diameter of 6 cm, as described in [6]. The second mill consists of two stainless-steel vials, with an inner height of 4 cm and an inner diameter of 4 cm, which are mounted on the disk of the planetary machine (Fritsch Pulvereisette 7). A vertical stainless-steel cylindrical-shaped rod with a height of 3 cm and a diameter of 3.2 cm was used in each mill as a milling tool. In order to guarantee the balance of the equipment both vials should contain the same quantity of material. While working, the disk is rotating clockwise, and the mills are rotating anti-clockwise. Then, the cylinder inside the mill moves always along the inner wall and performs the milling action. Typically 2 grams of polymer were loaded in each vial. The

milling is carried out in an air atmosphere, and after a certain period (maximum 15 minutes) the milling is interrupted for cooling down of the rotator and for ensuring that the temperature of the mills does never exceed 50 °C.
The analysis of the milling-products was performed by X-ray diffraction, mass spectrometry, Gel Permeation Chromatography (GPC) and Differential Scanning Calorimetry (DSC).
X-ray diffraction patterns were taken at room temperature by means of a position-sensitive Enraf Nonius PDS 120 diffractometer using Cu Kα radiation. The measuring range is from $2\theta=10°$ to 130°. Mass spectrometry was performed at the Institute for Mass Spectrometry of the University of Amsterdam by a Field Desorption Mass Spectrometer (FDMS) [7], and at the FOM institute for Atomic and Molecular Physics (AMOLF) by Matrix-Assisted Laser Desorption and Ionisation on an external ion source Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (MALDI-FTICR-MS) [8]. GPC was carried out at Shell Research in Amsterdam (KSLA). DSC scans were taken on a Perkin-Elmer DSC-7 in an argon gas atmosphere.

Results and Discussion

Milling of amorphous polymers

Several pure polymers were milled, mainly by using the planetary mill. As mentioned before, bond breaking (scission) and polymerisation could occur by milling (see for example [4]): chemical bonds could be broken and free radical ends could even form a new bond. This - in turn - would give a significant change in molecular masses. These are defined as follows [9], where n_i is the number of molecules with mass M_i:

number-average molecular mass $\overline{M}_n = \Sigma\, n_i\, M_i / \Sigma\, n_i$

weight-average molecular mass $\overline{M}_w = \Sigma\, n_i\, M_i^2 / \Sigma\, n_i\, M_i$

z-average molecular mass $\overline{M}_z = \Sigma\, n_i\, M_i^3 / \Sigma\, n_i\, M_i^2$

These quantities define the shape of the molecular mass distribution. We investigated polystyrene (chemical formula $[-CH\ C_6H_5\ CH_2-]_n$) with $M_w \cong 2500$, a standard purchased from Aldrich, and polystyrene (PS 87) from Shell Research with $M_w \cong 6150$, by FDMS and GPC respectively. Polyethylene glycol ($HO-[C_2H_4O]_n-H$), PEG 1000 from Serva (Heidelberg, Germany) with $M_w \cong 1000$, and PEG 4000 with $M_w \cong 4000$ from Fluka Chemical (Buchs, Switzerland) were analysed by MALDI-FTICR-MS. From field-desorption mass spectrometry performed on PS 2500 no significant change was found. This is clear from Table 1, where the values for the three characteristic masses are presented which were calculated from the mass spectra.

milling time	M_n	M_w	M_z
0 minutes	2338	2562	2765
15 minutes	2466	2671	2859
30 minutes	2463	2723	2943
45 minutes	2329	2567	2768
60 minutes	2461	2697	2888

Table 1: The molecular masses M_j of PS 2500 as a function of milling time as measured by mass spectrometry.

The same conclusion was drawn for PS 87 using GPC for the assessment of the molecular masses (Table 2). Any bond breaking or polymerisation would undoubtly have broadened the (narrow) mass distribution, and would thus have given an experimentally significant change in the values of the various molecular masses. Fig. 1, showing the molecular mass distribution before and after

milling PS 87 clearly shows that no such broadening occurs. Neither was any change found by MALDI-FTICR-MS on polyethylene glycol performed at AMOLF.

Milling time	M_n	M_w	M_z
0 hour	5756	6155	6511
1 hour	5727	6161	6606

Table 2: The molecular masses M_j of PS 87 as a function of milling time as measured by GPC.

Of course the mechanical properties of polymers are different from those of intermetallic compounds. The elastic character of the polymers investigated may make it more difficult to store energy in these materials by milling than in brittle intermetallic compounds. Moreover, the atomic defects that are induced in intermetallics have typically energies of 100-200 kJ/mole of defects [2], whereas the C-C bond in the polymers represents an energy of 328 kJ/mole [9]. This could also be the reason why it is difficult to break the C-C bond by milling. It is concluded that, by our milling tools, no bond breaking takes place. Thus no chemical changes were induced by milling of PS and PEG. X-ray diffraction showed that upon milling the materials remained fully amorphous. However, changes were observed in most of the milled samples of PS 87 by heating them in the DSC. Remarkably, two glass temperatures were observed after milling, one close to the original glass temperature of about 80° C and a second one at about 30° C higher temperature. After heating the samples to 200° C and an arrest at this temperature for a few minutes, the original glass temperature was recovered. Apparently physical changes of a so-far unknown nature are induced in the amorphous polymer by milling.

Milling of crystalline polyethylene, a structural phase transformation

High-density polyethylene (HDPE), chemical formula $[-CH_2\ CH_2-]_n$, is partially crystalline and is known in different crystal structures among which the normal orthorhombic one, and monoclinic [11]. The content of monoclinic in as-prepared material is normally small (about 5–10 %) as compared to the orthorhombic component, and is usually explained in terms of a somewhat different packing of the folded polymer chains in a strained lattice array [12,13].

HDPE beads with an average diameter of 4 mm and with $M_w \cong 2–3 \times 10^5$ (Lupolen 5021 D, ex. Basf) were milled in the vibratory mill. During milling the beads were broken into flakes. Fig. 2 shows the X-ray diffraction pattern of pure and ball-milled HDPE beads. Besides a number of weak peaks, the orthorhombic structure (O) of the original material (labelled 0h) is characterised by a very strong (110) peak and a strong (200) peak. Careful examination shows a very weak intensity of the monoclinic $(\bar{1}10)$ peak (M). Apparently, the as-prepared polymer contains a trace of the latter phase as was found and analysed in [12,13]. As milling proceeds, the intensity of the orthorhombic (200) peak decreases and this peak almost disappears for milling periods longer than 165 hrs. The main (110) peak broadens, probably due to strain and possibly crystallite refinement, as is found in metallic systems. On the other hand a peak, left to the main peak, appears. This $(\bar{1}10)$ peak of the monoclinic phase is, together with a (110) peak in the same position as the (110) peak of the orthorhombic structure, characteristic of the monoclinic structure [12,13]. From Fig. 2 it can be concluded that after 165 hrs of milling, by far most crystalline material is monoclinic, and it may even be implied that the material has nearly completely transformed to the monoclinic structure. This is, to our best knowledge, the first time that an (almost) complete structural phase transformation was driven by mechanical milling in a pure polymer. The explanation of the

transformation could be sought in shear, induced by the milling process. It should be noted that, due to the irregular shape of

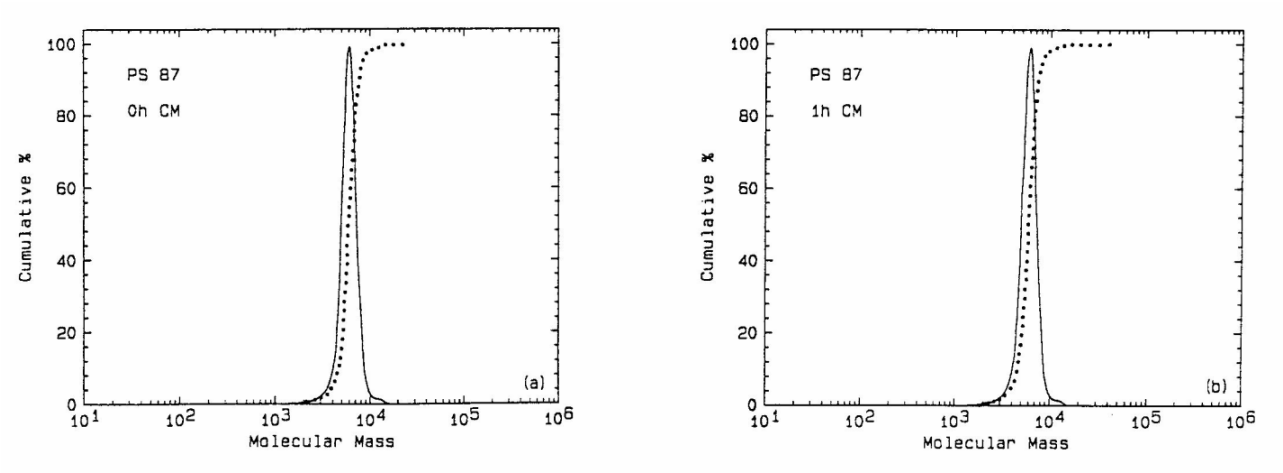

Fig. 1 The molecular mass distribution of (a) as-prepared and (b) 1 hour milled PS 87 samples as measured by GPC.

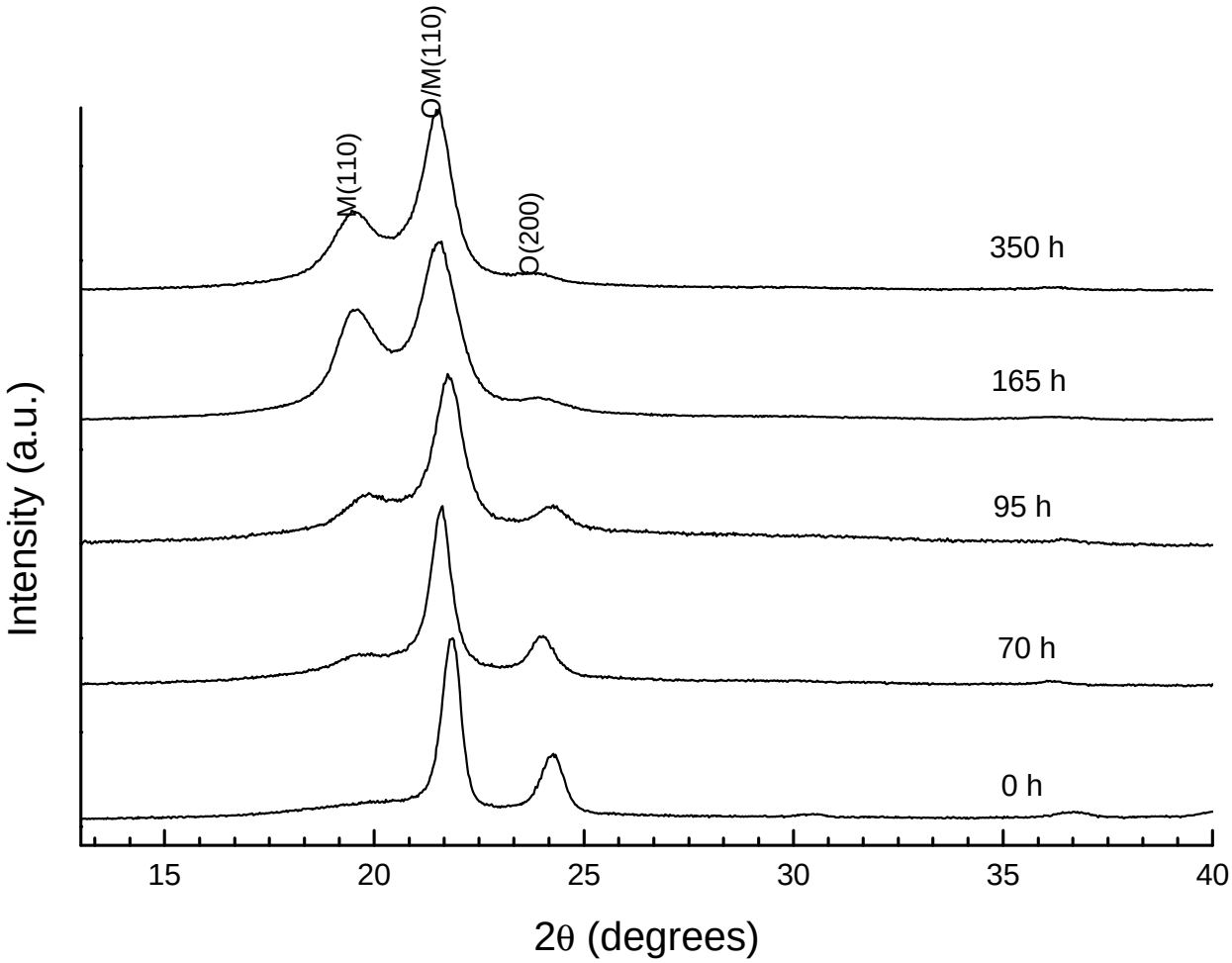

Fig. 2 X-ray diffraction patterns of HDPE Lupolen 5021 D after various periods of milling.

the flake-like samples, reproducible positioning of the samples in the X-ray diffractometer gives problems. Therefore, no conclusions should be drawn from small deviations in the peak positions.
In order to examine possible influences of chain length and sample shape, we milled ultra-high molecular weight HDPE powder and beads (Hostalen GUR 412, ex. Hoechst) with $M_w \cong 4–6 \times 10^6$ and low molecular weight HDPE beads (Stamylec 2H280, ex. DSM) with $M_w \cong 6 \times 10^4$ in the vibratory mill as well as in the planetary mill. In Table 3 we compare the end product forms and extent of transformation of these materials with HDPE Lupolen, which was also milled in both mills. It turns out that the only almost full transformation occurs for beads of Lupolen, milled in the vibratory mill and forming flakes.

Material	M_w	**starting form**	**type of mill**	**end product form**	**extent of transform.**
Hostalen GUR 412	$4–6 \times 10^6$	bead (home made)	vibratory	bead	–
			planetary	powder	+/–
		powder	vibratory	powder	+/–
			planetary	powder	+/–
Lupolen 5021 D	$2–3 \times 10^5$	bead	vibratory	flakes	+
			planetary	powder	+/–
Stamylec 2H280	6×10^4	bead	vibratory	powder	+/–
			planetary	powder	+/–

Table 3: A comparison between the end products and extent of transformation of various materials under different milling conditions.

It can be seen that as soon as any material formed powders, the transformation was only partial, which leads us to the conclusion that the flake-like form is essential for a complete transformation and that molecular weight has scarcely any influence. For all materials the final state was much faster established in the planetary mill than in the vibratory mill. Hence the planetary mill is apparently more powerful than the vibratory mill. For the planetary mill the time required to form powder out of beads is longer for a higher M_w: about 2.5 hr for HDPE Stamylec, 6 hr for HDPE Lupolen and 20 hr for HDPE Hostalen. This can be understood from the influence of chain length on the force with which one molecule is bond and with some imagination it could be suggested that the milling time is linear to the root of the molecular mass M_w. No detectable changes occurred in DSC in any of the samples and after melting, the material became orthorhombic again.

Conclusions

Bond breaking (scission) and/or polymerisation by milling different pure polymers were not found neither using a planetary nor a vibratory mill. Milling beads of crystalline high-density polyethylene with high molecular weight drove an almost complete phase transformation from the orthorhombic to the monoclinic structure. The orthorhombic phase was restored after melting. The degree of transformation appeared to depend on the shape of the end-product. When flakes were obtained, the transformation was most complete.

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